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IMS Applications Analysis

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IMS Applications Analysis

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Abstract

This report examines the market potential of a miniature, hand-held Ion Mobility Spectrometer. Military and civilian markets are discussed, as well as applications in a variety of diverse fields. The strengths and weaknesses of competing technologies are discussed. An extensive Ion Mobility Spectrometry (IMS) bibliography is included. The conclusions drawn from this study are: (1) There are a number of competing technologies that are capable of detecting explosives, drugs, biological, or chemical agents. The IMS system currently represents the best available compromise regarding sensitivity, specificity, and portability. (2) The military market is not as large as the commercial market, but the military services are more likely to invest R&D funds in the system. (3) Military applications should be addressed before commercial applications are addressed. (4) There is potentially a large commercial market for rugged, hand-held Ion Mobility Spectrometer systems. Commercial users typically do not invest R&D funds in this type of equipment; rather, they wait for off-the-shelf availability.

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Contents

| | |
|---|----|
| INTRODUCTION | 7 |
| BACKGROUND | 8 |
| APPLICATIONS AND MARKET POTENTIAL | 8 |
| DEMONSTRATED APPLICATIONS..... | 9 |
| <i>Potential Use of IMS in Trace Chemical Detection or Classification of Landmines.</i> | 9 |
| LANDBASED UXO DETECTION – MILITARY APPLICATIONS..... | 12 |
| UNDERWATER MINE AND UXO DETECTION – MILITARY APPLICATIONS | 13 |
| CHEMICAL AND BIOLOGICAL AGENT DETECTOR..... | 13 |
| COMMERCIAL APPLICATIONS | 15 |
| UNDERWATER AND LANDBASED MINE AND UXO DETECTION – COMMERCIAL APPLICATIONS | 15 |
| FORENSICS..... | 15 |
| DRUG INTERDICTION | 16 |
| SECURITY APPLICATIONS | 17 |
| DEMILITARIZATION | 17 |
| ENVIRONMENTAL ANALYSIS | 18 |
| AGRICULTURAL APPLICATIONS..... | 18 |
| INSTRUMENT DETECTORS..... | 18 |
| COMPETING TECHNOLOGIES..... | 19 |
| BIOSENSORS - DOGS AND OTHER TRAINED ANIMALS | 19 |
| SPECTROSCOPIC TECHNIQUES | 20 |
| IR SPECTROSCOPY, FTIR | 20 |
| LASER MEASUREMENTS | 21 |
| ACOUSTIC SENSORS | 22 |
| IONIZATION DEVICES | 23 |
| ELECTRON CAPTURE DETECTORS..... | 23 |
| THERMAL NEUTRON ANALYSIS (TNA) | 24 |
| FIELD ION SPECTROMETRY | 24 |
| MASS SPECTROMETRY | 26 |
| ENZYMIC REACTIONS | 27 |
| CHEMILUMINESCENCE..... | 29 |
| USE OF AUTOMATED SIGNAL PROCESSING IN IMS..... | 30 |
| IMS INSTRUMENT IMPROVEMENTS | 31 |
| RESPONSE TIME..... | 35 |
| AFFORDABILITY | 36 |
| EASE OF MAINTENANCE | 36 |
| SUMMARY AND CONCLUSIONS | 37 |
| REFERENCES CITED | 38 |
| APPENDICES..... | 41 |
| DISTRIBUTION..... | 43 |

Table

| | |
|---|----|
| <i>Table 1. Advantages / Disadvantages of Animals.....</i> | 20 |
| <i>Table 2. Advantages / Disadvantages of Infrared Spectroscopy</i> | 21 |
| <i>Table 3. Advantages of Laser Measurements</i> | 21 |
| <i>Table 4. Advantages of Acoustic Sensors (SAW)</i> | 23 |
| <i>Table 5. Advantages of Electron Capture Detectors</i> | 24 |
| <i>Table 6. Advantages of Thermal Neutron Analysis.....</i> | 24 |
| <i>Table 7. Advantages of Field Ion Spectroscopy.....</i> | 26 |
| <i>Table 8. Advantages of Mass Spectroscopy.....</i> | 27 |
| <i>Table 9. Advantages / Disadvantages of Enzymatic Reactions.....</i> | 29 |
| <i>Table 10. Advantages / Disadvantages of Chemilumisence.....</i> | 30 |

IMS Applications Analysis

Introduction

In order to help the reader understand the potential role of a handheld, rugged, portable Ion Mobility Spectrometer (IMS) sensor system, this report covers three aspects: (1) To provide a very brief explanation of how an IMS operates, (2) To examine possible applications for a miniaturized, hand-held Ion Mobility Spectrometer (IMS), and (3) To examine competing technologies.

This report is not technically a marketing report in that the number of units that could be sold for a particular market, or the cost/marketability tradeoffs was not determined. Rather, areas were identified that would advantageously utilize IMS technology. Consideration of each of these areas will identify those where more detailed marketing surveys should be initiated. Costs have not been analyzed in detail; rather, one should recognize that an instrument designed to protect a battleship could be sold for significantly more than one designed for atmospheric monitoring. However, very few people need to protect ships whereas many people are interested in the environment.

In order to be able to evaluate the market potential of a portable IMS system, one must also examine the competing technologies. Therefore, several other techniques will be examined and their potential as competing technologies will be evaluated.

The final conclusion is that a rugged, handheld IMS system has significant potential for sales in a number of diverse fields.

The military sector would utilize the system both underwater (explosives detection) and on land (explosives, chemical agents, and biological agents). The military market imposes the most stringent performance and durability requirements. In addition, their primary target, explosives, is one of the more difficult applications. Military organizations are the most likely to contribute development funds to obtain the desired product(s).

Commercial (civilian) applications represent a much larger potential market than the military. The commercial sector, which would primarily target drugs, environmental work, law enforcement, agricultural compounds, and detectors for instruments, often presents easier targets.

There is, of course, a great deal of overlap between the military and commercial applications. The initial requests for continued R&D funding should be directed toward the military, but that the potential for use in the commercial sector should not be ignored.

Background

A conventional IMS operates at atmospheric pressure, and consists of a method for ionizing the target molecules. The ionized molecules are then injected into a "drift tube" which contains a uniform axial electric field. The ions move down the tube under the influence of this electric field. Their velocities ($v=\mu E$) are determined by their mobility μ and the electric field E . Mobility depends on an ion's size and mass, and represents the ease with which it moves through the tube under the influence of the electric field. Different molecules have different mobilities. Thus, a pulse of ions injected into the drift tube will separate by mobility as the ions travel down the tube, with the largest mobility ions arriving at the end of the tube first. At this end of the tube, the ions are detected with a Faraday cup or electrode that collects the charge from the ions, resulting in a small current pulse. The resolution of the IMS or the ability to distinguish ions of different mobilities is given by:

$$R = \frac{\mu}{\Delta \mu} = \frac{\Delta t}{t} \quad (1)$$

where Δt is the width of the ion pulse and t ($=L/\mu E$) is the time it takes the ions to transit a drift tube of length L . Thus for a given electric field shorter drift tubes result in a loss in resolution. Increasing the field gradient can restore the resolution.

Applications and Market Potential

Sandia National Laboratories has been involved in IMS research since the early 1970s. The primary application has been in the explosives detection arena. Some basic ion chemistry research has been completed, as well as instrument design and fabrication. Sandia National Laboratories has been contacted by agencies interested in landmine and UXO detection, forensics, security, demilitarization, drug interdiction, chemical and biological agent monitoring, and agricultural applications. The current Sandia National Laboratories / Lockheed Martin project is focussed on underwater applications. However, the technology being developed under this program, i.e., a rugged, hand-held, IMS with an application-specific concentrator on the front-end, can easily be applied to many other problems. Indeed, the market potential for non-explosive applications is perhaps greater than the potential market for explosive detectors. Each of the potential markets will be briefly discussed in following sections of this brief. Each application would utilize essentially the same IMS; in most cases, a different concentrator / front end would be used to collect the specific samples. Additional applications could possibly be identified through a more thorough market analysis.

IMS has also been used as a detector for a wide variety of separation technologies, as a research instrument for ion chemistry studies, for chemometric studies, and other miscellaneous applications. A comprehensive bibliography attached as Appendices I through X provide additional sources of information.

As this paper is read, it needs to be emphasized that the current explosive applications are focussed on confirmation of the presence of an explosive and not on the detection of that explosive item. Once an item is detected, either through the use of electronic sensors or visual sighting, chemical sensing can confirm whether that item contains explosives. As the technology develops with increased speed, sensitivity and selectivity, it may be possible to use the chemical sensor as the primary means of detecting a hidden object, and indeed, this is the long-range goal. Nonetheless, the words "confirm" and "detect" are often used interchangeably in this paper depending on the application. For example, we will "confirm" the presence of an explosive by "detecting" the explosive signature released by a target.

Demonstrated Applications

Sandia National Laboratories has demonstrated that an IMS system can be used to rapidly screen environmental samples for the presence of explosive compounds by thermally desorbing soils into the IMS carrier gas. The range of explosive concentrations, soil types, and environmental conditions under which this thermal desorption is effective has not yet been thoroughly characterized. It has also been demonstrated that the IMS is capable of being used to detect the presence of explosives in the marine environment. This capability has been demonstrated in several field tests, including work at San Clemente Island, CA, Panama City, FL, and Halifax, Nova Scotia. IMS has been used to survey artillery shells, mortar rounds, and cluster grenades to determine which were inert and which were live. Details of these demonstrations can be found in Appendix XI.

Potential Use of IMS in Trace Chemical Detection or Classification of Landmines

The detection of trace concentrations of explosive compounds such as TNT in the local water currents downstream from an underwater UXO item is possible with only moderate preconcentration of the analyte when using IMS as the detector. This success can be attributed in part to the sensitivity of the detection technique, and in part to the homogeneous fluid medium that is sampled.

The problem of trace chemical detection of buried landmines is much more difficult. In the case of the marine environment, water acts as a solvent and transport medium for TNT or other relevant trace compounds. Water is a relatively poor solvent for TNT, which has an equilibrium saturation solubility of approximately 100 $\mu\text{g}/\text{mL}$ at 25 °C [1]. However, water is much better than air as a solvent for TNT, as evidenced by the Henry's

law constant, H_c , for TNT of $(5.9 \times 10^{-7}) \left(\frac{\text{mole}}{\text{liter} \times \text{atm}} \right)$ at 25°C [2]. Assuming that a

starting point in this discussion is that the operational requirements for a trace chemical landmine detector would be dictated by the potential user community to be similar to the operational deployment of the U.S. Army's only currently fielded landmine detector, the AN/PSS12 electrometer. For the present, we will set aside performance comparisons of the technologies in terms of probability of detection (P_d) vs. false alarm rates (FAR), and concentrate only on user preferences for operational acquisition of data with the sensor systems. Under such an assumption, the operation of a trace chemical sensor as a *mine detector* rather than an *anomaly classifier* requires rapid cycle times (on the order of a few seconds) for the collection, preconcentration, and analysis of environmental samples. Potential DoD users of trace chemical sensors, including DARPA, have insisted on such rapid analysis cycle times in order to make the search rate (area sampled/time) comparable to the search rates of electromagnetic anomaly detectors, or, for that matter, of free-running mine search dogs. This rapid sampling constraint has driven attempts at trace chemical detection toward the use of vapor sampling, since drawing air into a sensor device is mechanically faster and simpler than sampling of solids or liquids. For this reason, estimation of nitroaromatic vapor concentration above buried landmines or UXO objects has been the subject of considerable study in recent years.

For both underwater and buried UXO objects, the trace chemical signature is due to a combination of sources. These include surface contamination of the object due to handling and storage, leakage at unsealed points in the casing such as fuze wells, and permeation through the casing in the case of plastic land mines. Because of grossly similar design and construction of mines and other UXO items, the source terms can be assumed to be comparable in the underwater and buried (land) cases. However, the transport of the signature compounds from the source to a detector is much more complex for the buried object. The chemical can be present in the aqueous, vapor, or solid phases. Mass transport will occur in the aqueous and vapor phases. The distribution or partitioning of the chemical signature among these three phases depends strongly on local environmental conditions. For the nitroaromatic compounds of interest, model studies and laboratory measurements indicate that the partitioning strongly favors the adsorbed or solid. In particular, measurements of the soil-vapor partition coefficient for 2,4-DNT indicate that the partition coefficient (K_d) can vary by five orders of magnitude, from 10^5 to 10^{10} mL/g, depending on the amount of moisture in the soil [3]. Values of K_d were reported as $\{(\text{micrograms DNT/g soil}) / (\text{micrograms DNT/mL air})\}$ for soil DNT concentrations on the order of 1 $\mu\text{g/g}$, and soil water contents varying over the range of 1 – 10 % (mass H_2O /mass soil). Thus for the case of DNT, we can expect that the concentration in the vapor phase will be 5-10 orders of magnitude lower than the concentration in the adsorbed phase. TNT is significantly less volatile than 2,4-DNT, so for the case of TNT the partitioning would be expected to be even worse with respect to sensing vapor concentrations above a buried object.

The amount of TNT and 2,4-DNT in the soil at numerous locations around defused landmines buried at a DARPA research minefield at Ft. Leonard Wood, MO has been reported by Jenkins and coworkers [4]. They measured the concentrations of TNT and 2,4-DNT in the soil around and above buried mines at intervals two, four, and eight months after mine emplacement. Former Yugoslavian mines of four types (TMA5 and

TMM1 antitank, and PMA-1A and PMA-2 antipersonnel) were used in that study. The observed concentrations of 2,4,6-TNT and 2,4-DNT in surface soils above TMA5 mines were in the low $\mu\text{g}/\text{kg}$ range, and were very heterogeneously distributed. Explosive concentrations in the surface soil above the PMA-1A mines were only irregularly detectable. Nitroaromatic surface concentrations were generally below detection limits ($<1 \mu\text{g explosive}/\text{kg soil}$) near the TMM1 and PMA-2 mines.

Even for the largest concentrations measured in the field study of Jenkins et al., the detected concentrations of the nitroaromatic signature compounds ($\mu\text{g}/\text{kg}$) were approximately three orders of magnitude lower than the laboratory DNT concentrations (ug/g) used in the K_d' determinations of Phelan and Barnett. Assume that the K_d' values measured in the ppm soil concentration range are applicable to the ppb range seen in the field measurements. Under this assumption, for the "best case" of the TMA5 antitank mine, the maximum expected vapor concentration of 2,4-DNT above a buried landmine can be estimated to be in the range of $10^{-14} - 10^{-19} \text{ g DNT/mL air}$. The value within this range will depend strongly on the soil moisture content and temperature. Due to the lower volatility of 2,4,6-TNT as compared to 2,4-DNT, the TNT concentration in the vapor phase would be expected to be even lower.

It is instructive to compare these estimated vapor concentrations for DNT or TNT above a buried landmine to the detection limits for IMS instruments. The noise-limited detection limit for TNT measured under this project for the PCP111 IMS was reported at the December, 1999 program review as $<27 \text{ pg}$, while the value for the ERG (miniaturized) IMS was reported as $<197 \text{ pg}$. IMS Detection limits as low as $\sim 1.0 \text{ pg}$ for TNT have been previously reported by other authors [5]. The detection limits for 2,4-DNT were not measured in that study, but are assumed to be comparable. Assume that the "best case" upper limit for the DNT vapor concentration of 10^{-14} g/mL , *and a uniform concentration of analyte in the volume sampled*. Under such conditions, a 100 mL air sample would have to be preconcentrated in order to provide a signature detectable by an IMS with a 1 pg detection limit. Given the observed heterogeneity of nitroaromatic concentration in field samples, it is unlikely that such a 100 mL air sample could be successfully collected with a uniform concentration of the signature compound. Further, the local concentration in the vapor phase could be 5 orders of magnitude lower based on the variation in K_d' values reported by Phelan and Barnett, presuming a soil concentration of $1 \mu\text{g}/\text{kg}$. Considerably lower soil concentrations may be present near buried landmines, depending on the mine type, soil type, and environmental conditions. To summarize, if buried landmines are to be detected using a *trace vapor sensor* with a cycle time of a few seconds per analysis, a detection sensitivity *at least* 6-7 orders of magnitude better than that typically reported for IMS instruments would be required in order to access the estimated range of signature concentration.

There are several possible alternatives to try to close the gap between current IMS detection capability and the estimated vapor phase concentrations of nitroaromatic signature compounds. An obvious approach is to improve the sensitivity of the instrument, where possible. A recent patent [6] has claimed that the sensitivity of IMS instrumentation can be improved by a factor of 100 by use of an efficient, two-stage

chemical ionization mechanism. The effectiveness of this approach for the specific case of nitroaromatic analysis has not yet been tested. Even if successful, this improvement by itself would leave the IMS sensitivity many orders of magnitude short of the required performance estimate. Possible improvements to IMS detection sensitivity will be discussed in a separate section of this report. It is important to stress that while several possible methods of improving the sensitivity could be pursued, the effectiveness of these methods is difficult to predict. Significant research and development efforts will therefore be required in order to determine the effectiveness of these IMS improvements.

Another possibility is to improve the sampling of nitroaromatic signature compounds in the environment around the buried landmine or other UXO. Based on the results discussed above, the greatest single improvement would be to sample contaminated soil directly, rather than sampling the vapor above the mine. This would remove the 5-10 orders of magnitude depletion of the signal due to soil-vapor partitioning. However, sampling soil, and then removing the signature compounds from the soil for presentation to a trace chemical detector, is mechanically much more complicated than air sampling. Thus, soil sampling places constraints on the operation of the detection system, especially with regard to the time required per sampling and analysis cycle. The time required for solvent elution and preconcentration of signature compounds from a soil sample will probably preclude the use of trace chemical sensing as a stand-alone search and detection method for buried mines or UXO. However, this technology could be much more promising as a *confirmation* or *discrimination* sensor, to reduce the high clutter rate of physical detection methods such as electromagnetic induction.

Finally, we note that the discussion of this section has concentrated on the considerable difficulty caused by signature transport in the case of *buried* landmines or UXO. The use of IMS as an effective means of discriminating between inert and explosive UXO items has been demonstrated, when those items are unearthed and available for contact or vapor sampling. This topic is discussed in the following section and in Appendix XI.

Landbased UXO Detection – Military Applications

As explained above, the detection (or confirmation of the presence of) a landmine is not believed to be an appropriate application of IMS technology at this time. The primary difficulty is getting the sample from the source (soil) into the instrument. Given the concentrations present in the near-surface layers of the soil, the development of significantly better concentrators would be required. Pending this development, IMS has the potential to provide the required sensitivity and specificity. Current military applications for landbased UXO detection systems based on the IMS is believed to be limited to those applications demonstrated in our laboratory and in the field at the Massachusetts Military Reservation (MMR). Specifically, unearthed rounds could be rapidly screened to determine which were live and which were inert. The inert rounds can often be distinguished from live rounds for the presence of trace amounts of explosives permeating through joints and seals. This technique has been applied to 105 mm artillery shells, 61 mm and 80 mm mortar rounds, and M77 cluster grenades with a reasonable

degree of success. Additional work is required to develop a database of the types of rounds that can be screened using this methodology, and false positive / false negative rates must be determined. Surface contamination of buried shells that have been recovered has not proven to be a source of interference, but again, additional testing is required to ascertain the accuracy of this screening technique.

Underwater Mine and UXO Detection – Military Applications

From a military standpoint, underwater explosives detection can be divided into two basic application areas – tactical and occupational. Tactical applications, i.e. breaching operations, require fast detection and analysis, simple operation, and rugged equipment for use under very adverse conditions. Often, detection accuracy is less important than speed.

Occupational applications will likely have reduced speed requirements, but detection accuracy becomes much more important. Some tactical operations, such as clandestinely screening an area prior to an operation may fall into the occupational classification in that a longer screening time is available, and accuracy becomes more important than speed. As an example, an area could be clandestinely screened by deploying a series of sensors in a grid pattern in a suspect area. Recovery of the sensors (or the data could be telemetered to a base station) could help ascertain whether an area contained explosive devices. Large areas of beachfront/shoreline could be monitored by analyzing ripcurrents.

The military market will be relatively small until there is a change in the overall tactical thinking by the military. After acceptance and proofing of the new technology, new doctrines will have to be formulated and implemented. Proofing the technology to the satisfaction of the military is anticipated to be a rather sizeable, relatively expensive effort. Should the technology prove to be satisfactory, and the concept of the “organic navy” implemented, the size of the market will increase significantly. Military users will likely be willing to pay a higher price for the equipment than commercial users, but the performance requirements will likely be significantly higher as well.

Chemical and Biological Agent Detector

The military currently has a need for small chemical and biological agent detectors. The currently used chemical agent detector is the Graseby CAM (Chemical Agent Monitor). This IMS-based device was designed to verify that military equipment was satisfactorily decontaminated after a chemical attack. It was not designed to be used as an “early warning” system, but has been used in that capacity. In this mode, it produces a relatively high rate of false alarms. The ability of an IMS system to detect chemical agents has been well-demonstrated. Instrument modification, however, is required to meet the upcoming military goal of an organic army. The military has expressed a desire for a true early warning system for chemical and/or biological agent attacks. Two types of instruments are desired. First, a portable device that can be deployed in advance of the troops via airborne or landbased autonomous vehicles is needed. This system would be

programmable for a variety of threat agents, and would be as versatile as possible so that it could be used for a wide variety of applications. It is envisioned that each platoon would be issued one of these perimeter monitoring systems.

The second type of chemical and/or biological detection system would be a miniaturized version (pocket calculator sized) that would be issued to each soldier as a personal monitor. These devices would not need to be as versatile as the system described above, but would need to be relatively cheap as well as rugged and dependable. These individual monitors may only need to monitor one or two specific compounds, but should be field-programmable. Analytical and computational requirements are thus minimized. If each soldier were issued a detector, the accuracy requirements may be able to be relaxed. For example, if 99+ percent accuracy (low false negative/false positive rate) were required, the cost per unit would likely be quite high. If, however, each soldier was issued a sensor, the accuracy requirements could be relaxed without reducing the overall effectiveness of the warning system. For example, assume that 20 soldiers were wearing sensors that yielded an accuracy of only 95%. Individually, this rate may not be acceptable, but if, say, 15 of the sensors began alarming whereas five did not, one would believe that the response of the alarming sensors was accurate. Conversely, an alarm by only a few sensors would probably be ignored. In this case, the effectiveness of the collective group is greater than the effectiveness of each individual sensor. A rigorous statistical analysis of the collective response of several sensors, based on carefully measured probability of detection and false alarm rates for individual units, would be needed in order to minimize the risk of sensor employment in this manner.

One application of a chemical or biological agent detector that has drawn attention is a device to help seal buildings, subways, or other areas to prevent the spread of agents in case of a terrorist attack. In this scenario, IMS based sensors would be placed in air ducts to continually monitor the air quality. If a chemical agent were to be released in a room, the sensor would detect the agent and immediately trigger an airbag or deploy foam to seal the duct, thereby isolating the chemical agent and preventing its spread throughout the facility.

The current state of the art in IMS based sensors which approach the desired performance for a handheld chemical agent sensor has been developed by Graseby. The device has been reported in the literature for several years. This device, which is approximately the size of a large pocket calculator, utilizes a corona discharge source to ionize molecules of interest. Internal batteries, that provide power for small pumps, high voltages, and signal processing, reportedly last for nine hours. Recent unconfirmed reports indicate that Graseby has completed a limited, 50-unit production run for the British military. Unfortunately, Graseby has not made these units available for examination or purchase by universities or other laboratories, so independent data regarding sensitivity, false alarm rate, battery lifetimes, durability, and so forth, is not available.

The development of a biological sensor is one of the primary needs of today's military services as well as agencies concerned with terrorist attacks. Several calls for proposals to develop such a sensor have been released. Previous work to develop a biological agent

monitor has focussed on capturing and pyrolyzing (rapidly heating the organisms to create smaller fragments) the biologicals. The resulting fragments are then separated by using a mass spectrometer; the organisms are identified by comparing the resulting "fingerprint" to a fingerprint library. Equipment requirements have precluded using this technique in the field; only laboratory demonstrations have been completed. Sandia National Laboratories and New Mexico State University have demonstrated that intact biological agents can be ionized using an electrospray source, and will survive passage through an IMS. A change in the reactant ion concentration has been noted, indicating that other charged species are present, and small signals have been noted at long (ca.70 – 90 milliseconds) drift times. The ability to identify biological species by their drift times is being investigated, with the ultimate goal of developing instruments capable of analyzing biological agents as funding permits.

Commercial Applications

Commercial applications of IMS are believed to have a larger market potential than the military applications. These commercial applications include not only the UXO work discussed in this section, but also the forensic sciences, law enforcement, drug, and other applications discussed below.

Underwater and Landbased Mine and UXO Detection – Commercial Applications

Humanitarian demining and environmental cleanup has been receiving a considerable amount of attention in recent years. Politically, there is a lot of pressure to reclaim former firing ranges for civilian use, and much attention is being applied to increase the rate of clearance in humanitarian demining.

Commercial companies are spearheading both the reclamation of firing ranges and humanitarian demining. Military organizations typically contract with commercial firms to provide post-operational cleanup. The restrictions imposed by the instrumentation and methodology are the same for commercial users as for many of the military occupational applications.

Forensics

There are several forensics applications for handheld explosives and narcotics detectors. Rapid, on-site, post-blast analyses can be achieved with a handheld IMS system. By acquiring this on-site data, the investigators can better tailor their sample collection activities to maximize the probability of solving the crime. The ability to rapidly map concentrations of post-blast residues over an area could provide clues as to the blast origin, the type of explosive used, and perhaps the quantity of explosive used. Traces of the same compound(s) on a suspect can help indict them.

Drug Interdiction

Law enforcement agencies, the Border Patrol, and the Coast Guard have identified a need for a handheld detector that could be used to analyze for explosives and narcotics. Drug detection is generally considered a much easier problem to address than explosives due to the higher volatility of the drugs and drug precursors. Sensitivity for drugs is about an order of magnitude less than for explosives, but the higher vapor pressure at lower temperatures compensates for the difference in sensitivity.

Ideally, a system that could track gradients would be employed; the ability to track gradients in near-real time has not yet been demonstrated. However, a non-tracking sensor could still be utilized to detect trace amounts of narcotics on suspects or in vehicles. Suspicious packages could be screened, as could school lockers, bus stations, and the like.

The National Institute of Justice has asked Sandia National Laboratories for a hand-held sensor that could be used to sample the air being discharged by air conditioners in hotel rooms. The presence of traces of narcotics in the air is considered to be sufficient evidence that a search warrant or raid on the room is justified.

Personnel could potentially be screened for drug use without urinalysis testing, which is a relatively expensive procedure. It has been demonstrated in a prison (by Barringer, an IMS manufacturing company) that analysis of a skin swipe by IMS can be used to detect drug residues. Such residues will reportedly be found if the person has been using drugs within the past several days. Enough non-metabolized drug is excreted by the body that reliable detection is achieved.

Solubility of drugs (or extractables) in water is generally fairly high. Sandia National Laboratories has been asked by the Spanish government if it were feasible to develop an IMS based sniffer that could be used to detect drugs in the ocean. The scenario presented is that drug dealers, when being pursued, often throw packages of drug overboard. Most of these packages are equipped with self-inflating buoys and signal devices so that at a later time, the dealers can return and recover the floating packages. Without recovering the drugs as evidence, prosecution is normally unsuccessful, so the suspected dealers are released. If a system capable of detecting drug residues emanating from these packages were available, it could be used to sample water near the tossed package. Signals obtained from the sensor would then be used to help narrow the search area so that the drugs could be recovered.

Conversations with law enforcement agencies, including the FBI, CIA, State Department and local personnel indicate that they can foresee a low-cost (< \$5000) unit as standard equipment in most patrol cars. Given that the drug problem is likely to increase, this potential market is continually growing

Security Applications

The maturest application of IMS technology applied to explosives detection is in the area of personnel screening. There are currently two types of systems deployed; those that utilize swipe sampling and walk-through systems. The swipe system is typical of those sold by Barringer and IonScan. A paper pad is used to wipe the surface of the object being tested, be it luggage, vehicles, or personnel. Alternately, a small vacuum (similar to a "Dust Buster") is used to draw air through a filter pad. The pad is then placed on a platen that is subsequently heated to desorb any explosives present. The IMS then analyzes the resulting vapor stream. The IMS can be tuned to analyze for drug residue in the same manner.

The walk-through systems are just now beginning to be deployed; systems have been tested, and commercial production is expected to begin in 2000 or 2001. The prototype IMS portal system was developed at Sandia National Laboratories and licensed to Barringer for commercial production. In walk-through systems, which are designed to rapidly screen personnel, laminar airflow is used to sweep across the person. Explosive vapors or particulates are entrained in the air, which flows through a concentrator. The airflow is stopped, and the concentrator is heated to desorb any explosives that were collected.

A small, portable system would be useful to more rapidly screen personnel, luggage, and less accessible items. Swipe sampling is time-consuming, and often inefficient, as the detector may not be located near the sampling site. A hand-held system would provide more rapid analysis and simplify logistics.

Many scenarios that would utilize this technology could be proposed. As well as finding utility in airport screening, this system could be used to provide enhanced security in embassies, schools, and prisons. A unit mounted on a robotic vehicle could be used for interrogating a suspicious package without placing personnel in harm's way, and provide bomb squad members with additional information prior to neutralizing a potential bomb. These proposed applications would be of interest to law enforcement agencies.

Demilitarization

Safety issues associated with demilitarization facilities are becoming more important in light of recent accidents involving materials that have been released into the public sector. Although most demilitarization lines are very effective, occasionally a live round is released, or a unit is not totally cleaned out. Sandia National Laboratories facilities in Albuquerque and in Livermore, CA are currently funded to perform a pilot study to determine the background levels of explosives in a demilitarization facility, and investigate means of surveying the materials prior to being released. IMS has been identified as the primary analytical tool for this purpose. If the current pilot project is successful, additional work to develop a sensor system for demilitarization applications is anticipated.

Environmental Analysis

Environmental monitoring is an area where budget often overrides the technical requirements, especially when screening for the presence of explosives. In these instances, large fields are typically required to be screened. If explosives are anticipated to be found, all samples taken from that field are required to be treated as being potentially explosive. This significantly increases the collection, handling, shipping, and analysis costs associated with screening the area. Sandia National Laboratories has demonstrated that Ion Mobility Spectroscopy can be used to screen soils for the presence of explosives. The results compare very favorably to those obtained by HPLC analysis, which is the EPA-approved method for explosives analysis. A summary of this work can be found in Sandia National Laboratories Report SAND97-2215. The work described in this report used a laboratory -based IMS, with samples being transported to our laboratory. The LasVegas office of the EPA reviewed this work and agreed to consider it as an EPA-approved field screening method for explosives. Unfortunately, the funding required to generate an EPA-approved data package was not granted, so EPA approval was not formally requested.

The development of a handheld, portable system would make this type of analysis feasible in the field, greatly reducing the cost of field screening. In addition to explosives screening, this type of system would be suitable for screening soils or soil gases for the presence of halogenated compounds.

Agricultural Applications

In many cases, agricultural applications are very similar to atmospheric monitoring applications; air or water must be monitored for various compounds. To date, there have been a limited number of demonstrations wherein pheromone concentrations in apple orchards have been monitored. Pheromones are released in orchards to attract various pollinating insects; these pheromones are extremely expensive, and excessive doping not only reduces the farmer's profit, it increases the cost of produce for the consumer. Dr. Herb Hill (Washington State University) has used one of his laboratory IMS instruments to monitor the pheromone concentration in an orchard, and used the resulting signal to control the amount of pheromone being released. Similar systems can be set up for pesticide monitoring. Other potential agricultural applications include waste runoff monitoring, and monitoring the ripeness of fruit and vegetables.

Instrument Detectors

As can be seen in the attached bibliography, numerous researchers have used IMS systems as detectors on gas chromatographs, supercritical fluid chromatography systems, and even on liquid chromatographs. None, however, has produced a commercial product. As environmental regulations continue to be more restrictive, analytical labs are seeking more efficient ways to screen samples. Whereas most chromatography instruments

provide a signal that tells the analyst how much of a compound is present, no structural information is obtained without using a mass spectrometer or infrared system, and co-eluting peaks can provide incorrect analytical results. In contrast, an IMS provides a fingerprint for each eluting GC peak. This multi-dimensional data decreases the likelihood of misidentification and increases the reliability of the analysis. We believe that a significant market for such a detector based on a small, rugged IMS system exists.

Competing Technologies

The array of current technologies discussed below could be useful for applications that could utilize an IMS. These technologies should be considered to be competitors from a marketing standpoint.

Biosensors - Dogs and Other Trained Animals

Canines have been used extensively for the detection of non-toxic substances such as explosives and narcotics, and in tracking humans. The estimated expenses associated with training, upkeep, transportation, and handling of trained detection dogs has been estimated at upwards of \$100,000 per year per animal [7]. Gerbils have been trained as detectors, but their relatively short lifetimes have relegated their use to experiments designed to determine how an olfactory system works rather than being used as routine explosive or narcotics detectors.

Advantages associated with using various animals include their ability to traverse a wide variety of terrain, ability to incorporate intelligence in the search, and the ability to follow a gradient or plume to its source. In addition, animals are used on a regular basis by many agencies for a variety of purposes. Thus, there is a large user base and wide acceptance of animals by law enforcement personnel and military agencies. Much of the performance data concerning animals is anecdotal – hard data regarding sensitivity, accuracy, and performance is extremely limited. Quantitative data on the performance of canines in detecting landmines is currently limited to the report of Nolan and Gravitt [8]. Auburn University is performing research to determine the detection limits of dogs exposed to various compounds [9].

Disadvantages associated with animals include relatively short working times before resting is required, high costs, the inability of a handler to know whether or not the animal is working well (sickness, boredom, and distractions can impair their performance), and lack of knowledge as to the detection limits or interferences that can produce false positives or false negatives. Deployment is often an issue. For example, although canines are commonly used for drug detection, the Coast Guard has found that the dogs become disoriented in the holds of ships and are not usable.

Animals are generally not used to detect substances that, when present, can kill or injure either the animal or the handler. A historical exception was the use of canaries to determine low O₂ levels and high CO or CO₂ levels in mineshafts, but modern detection equipment has essentially eliminated animals from this role, with a few exceptions.

Table 1. Advantages / Disadvantages of Animals

| Advantages of Animals | Disadvantages of animals |
|---|---|
| • Excellent specificity and sensitivity | • Relatively short working times |
| • Very mobile – can traverse wide variety of terrains independently | • Performance level varies with health of animal. Performance level at any given time is unknown. |
| • Can track gradients | • Unknown animal / handler interactions |
| • Used by various agencies to track a variety of chemical signatures | • Deployment sometimes difficult. |
| • Skills honed over thousands of years | • High maintenance costs |
| Overall: Great for some applications, but area of deployment often limited. | |

Spectroscopic Techniques

IR spectroscopy, FTIR

Infrared (IR) and Fourier Transform Infrared Spectroscopy (FTIR) have long been used to detect and identify organic compounds. IR systems exhibit excellent specificity for a wide range of compounds. Sensitivity, however, is relatively poor. Part per thousand or greater detection limits are common. In order to detect lower concentrations of gaseous compounds, long path length gas cells are used. These cells range in length from approximately three inches to several feet and utilize internal mirrors to increase the effective path length and thus the amount of IR absorbance.

IR systems for remote monitoring are commercially available. These systems utilize a source at one location and place the detector (or a reflecting sphere) at a second location. The distance between the source and detector is used as a long path length cell. Systems of this type are used to monitor stack emissions from factories and power plants. Since the signal over the entire path length is monitored, interferences are common, and point sources are difficult to detect. For surreptitious work, these remote IR systems may not be suitable as the IR beams are easily detected. Current systems typically weigh around 40 kg and consume significant electrical power.

Table 2. Advantages / Disadvantages of Infrared Spectroscopy

| Advantages of Infrared spectroscopy | Disadvantages of Infrared spectroscopy |
|--|--|
| • Excellent specificity for many analytes | • Poor sensitivity. Often ppm to percent levels required |
| • Structural information obtained / library searching allows identification of unknown analytes | • Systems relatively large. Miniaturization limited due to spectrometer limitations. |
| • Remote monitoring systems available. Can be mounted on aerial platforms. | • Power consumption relatively high. Hundreds of watts typical |
| Overall: Limited sensitivity may limit the applications, but IR can provide sample integration over a long path rather than point analysis. Miniaturization prospects are limited. | |

Laser measurements

Laser systems can be used to monitor the emission of organic compounds. One such system is used by the customs department to search for clandestine drug laboratories. A laser system is typically mounted in a helicopter, which is flown near treetop level. As the laser beam scans across the area, organic compounds can be excited. As they relax, many of the organics will fluoresce or emit some other signature. A separate fluorescence detector measures this signal, and can classify the emitted organics into classes, such as hydrocarbons, aromatics, ketones, and so forth. Sensitivity is excellent, with some fluorescent techniques yielding part-per-trillion detection limits, but specificity is fairly poor since many species can produce similar, if not identical, fluorescent signatures.

Table 3. Advantages / Disadvantages of Laser Measurements

| Advantages of laser measurements | Disadvantages of laser measurements |
|--|--|
| • Aerial mounted systems available | • Aerial systems obtain signal of integrated path; this is sometimes an advantage. |
| • One of most sensitive techniques for some analytes | • Poor specificity. Useful for limited range of analytes; target analyte must fluoresce. |
| • Could be miniaturized if laser diode of proper wavelengths were available. | • Development of laser diodes of proper wavelength unlikely. |
| • Integrated sampling can be done. | Power consumption high |
| Overall: Likelihood of miniaturization is poor. Interferences may interfere with target compounds. | |

Acoustic Sensors

Over the last 30 years, much work has gone into the development of a variety of acoustic devices as chemical and biological sensors. The devices differ primarily in the particular acoustic wave or mode excited. Thickness shear mode (TSM) devices and surface acoustic wave (SAW) devices are the most developed of the acoustic sensors. TSM devices are frequently called quartz crystal microbalances (QCM's) due to their earliest and still dominant embodiment. QCM's were first used for detection of organic vapors in 1964. Less developed acoustic sensors include flexural plate wave (FPW) and acoustic plate wave (APW) devices, whose chemical sensing capabilities have only recently been characterized. For the purposes of this trade-off study, we can consider the whole class of acoustic sensors together because they all rely on the same basic mechanisms to achieve sensitivity and selectivity for chemical and biological agents. A thorough review of this field is given in Ballentine, et al. [9].

Adequate sensitivity and selectivity for the detection and measurement of a given analyte requires a chemical or biochemical interface referred to as the "coating." The coating may be a solid absorbent, a chemical reagent, or a sorptive liquid or polymer that is bound to the sensor surface. The coating captures and immobilizes a small quantity of some chemical species from the environment. Physical and/or chemical changes induced in the coating by the absorbed species, in turn, perturb the operation of the acoustic wave sensor. Some of the intrinsic film properties used in sensing are area mass density, stiffness, viscoelasticity, viscosity, electrical conductivity, and permittivity. Extrinsic variables (like ambient pressure and temperature) can also affect sensor response, and must be accounted for when determining the chemical response. The wide selection of sensing mechanisms has both advantages (versatility) and disadvantages (interference or masking due to multiple mechanisms). Mass loading (or unloading) is the most commonly used and easily interpreted detection mechanism, and is accessible to all of the different acoustic modes. The minimum detectable mass using the different acoustic modes depends upon the mass sensitivity of the particular mode and the noise characteristics of the complete sensor system. For the compounds of interest in this report, SAW's have demonstrated the lowest minimum detectable levels so far among the acoustic sensors. Preconcentration and separation are required to push the sensitivity and selectivity of a SAW-based system into the required range. The preconcentrated vapors are injected into a GC column where temporal separation occurs. The vapors are condensed onto the SAW sensor as they exit the column. An array of sensors with appropriate coatings enables further discrimination between the compounds exiting the GC column. These SAW-based systems are fairly rugged and can be made reasonably small. Disadvantages include high frequency electronics (at least a few hundred MHz), and restriction to gas-phase applications. FPW devices may be able to overcome these shortcomings, but are not yet as well developed.

Table 4. Advantages / Disadvantages of Acoustic Sensors (SAW)

| Advantages of acoustic sensors (SAW) | Disadvantages of acoustic sensors (SAW) |
|--|---|
| <ul style="list-style-type: none">• Bare (uncoated) SAW devices very sensitive | <ul style="list-style-type: none">• Coated SAW sensitivity typically ppb |
| <ul style="list-style-type: none">• Much research being performed by many organizations. | <ul style="list-style-type: none">• No inherent specificity. Specificity obtained from surface coatings. Arrays needed to obtain specificity. |
| <ul style="list-style-type: none">• Size can be very small; devices rugged | <ul style="list-style-type: none">• Coatings not yet very specific. Exhibit slow responses and hysteresis effects |
| <ul style="list-style-type: none">• Variants available: (quartz crystal microbalances, flexural plate wave devices, and acoustic plate wave devices). | <ul style="list-style-type: none">• High frequency electronics required. |
| <ul style="list-style-type: none">• Power consumption very low. | |
| Overall: SAW technology is a viable candidate for many applications, but additional work is needed to develop application-specific coatings. The response time / hysteresis effects need to be improved. | |

Ionization devices

A range of sensors containing various ionization sources are perhaps the most common, and the most useful for chemical detection of explosives, drugs, chemical agents, and many other compounds. Several of these are discussed below.

Electron capture detectors

Electron capture detectors have been used for many years to detect halogenated compounds, pesticides, and explosives in gas chromatographic analyses.

Scintrex produces a small, hand-held explosives detector (EVD-8000) based on multi-column gas chromatography with electron capture detection. This unit weighs approximately 48 pounds, and can be operated for up to four hours on internal batteries and carrier gas supply. In use, only a sample collection wand is carried by the operator, with the bulk of the instrument residing on a bench. A similar system, the model NDS-2000, is a self-contained unit capable of detecting narcotics, and weighs only 12.5 pounds. Battery lifetime is limited to less than 8 hours. This device has not seen widespread usage, and field performance data are not generally available.

A device marketed by Thermetrics Detection (Woburn, MA) also uses a fast GC/ECD system and claims a detection limit of 10 to 20 picograms of TNT [11].

Table 5. Advantages / Disadvantages of Electron Capture Detectors

| Advantages of electron capture detectors | Disadvantages of electron capture detectors |
|--|--|
| <ul style="list-style-type: none">Very sensitive for electronegative compounds. Doesn't respond to others. | <ul style="list-style-type: none">No inherent specificity. Specificity depends on gas chromatographic separations. |
| <ul style="list-style-type: none">Long use history | <ul style="list-style-type: none">Requires high voltages |
| <ul style="list-style-type: none">Used in portable explosive detectors (Scintrex) | <ul style="list-style-type: none">Uses 10 mC ^{63}Ni for source; regulatory issues |
| Overall: Can be used in portable systems. May not respond to all analytes of interest (especially those producing primarily positive ions). Miniaturization is possible. | |

Thermal Neutron Analysis (TNA)

Thermal neutron systems are large, very costly, complex instruments. They have been designed for the detection of bulk (bomb quantities) of explosives, and are not portable or suitable for field use. Besides their size, TNA systems suffer from a lack of specificity. Typically, they are used to examine the C:H:N ratios of objects. Since most explosives have a high percentage of nitrogen, they are easily detected. Common interferents include Melamine and similar plastics containing high nitrogen contents. Trace detection is not possible using these instruments.

NASA is developing small thermal neutron sources that are designed to determine the presence of H_2O on planets. Low power devices have been proposed that will use naturally occurring neutrons as the source, but these do not exist as of today.

Table 6. Advantages / Disadvantages of Thermal Neutron Analysis

| Advantages of Thermal Neutron Analysis | Disadvantages of Thermal Neutron Analysis |
|---|---|
| <ul style="list-style-type: none">Used for bulk explosive detection | <ul style="list-style-type: none">Very large, costly, complex systems |
| | <ul style="list-style-type: none">Poor specificity |
| | <ul style="list-style-type: none">Very poor sensitivity. Typically requires grams of analyte. |
| | <ul style="list-style-type: none">Power consumption is high |
| Overall: Not considered a competitor for the handheld IMS system. | |

Field Ion Spectrometry

The Field Ion Spectrometer (FIS) was originally developed in Russia. The Mine Safety Appliances Company (MSA) has set up a joint venture with the Siberian Branch of the

Russian Academy of Sciences to develop and market the system. FIS was first introduced publicly at the Pittsburgh Conference in 1996.

FIS is a trace analytical technique with a great deal of similarity to IMS. In fact, FIS was initially known as Transverse Field Compensation Ion Mobility Spectroscopy (TFCIMS). The device is now considered to be different than IMS because of its mode of operation. Like IMS, molecules entering the instrument are ionized using a radioactive source or an UV lamp. Whereas in an IMS the molecules enter a drift region, in FIS the ions pass between two parallel plates (one at ground potential, the other at high voltage) that have a strong oscillating asymmetric field applied across them. Since the mobilities of the ions formed are nonlinear at high electric fields, they begin to oscillate and drift sideways towards one of the electrodes. They drift because they are attracted more and moved further during the positive AC field cycles than they are repelled during the negative ones. A compensating DC field counterbalances the drift, so that selected ions can be filtered and allowed to reach the detector.

One other difference between IMS and FIS is the ion injection technique. In IMS, a shutter is used to pulse ions into the drift region; typically, the shutter is open only 10 to 15% of the time, effectively reducing the sensitivity. In contrast, the FIS does not use a shutter, and nearly 100% of the ions are injected into the drift field, thus theoretically increasing the sensitivity. According to MSA's advertisements, by utilizing 100% of the ions, sensitivity for TNT is about 80 ppt. In contrast, MSA claims that the older IMS systems were less sensitive by a factor of approximately 100.

Recent work with chemical agent simulants in our laboratory yielded a minimum detection limit of approximately 0.5 picograms DMMP, with the linear range extending up to approximately 0.3 nanograms DMMP when using the PCP IMS. MSA quotes a minimum detection limit of one picogram for this compound; no linear range is given. We have not been able obtain data verifying the FIS sensitivity claims.

Coupled with the sensitivity issue, the selectivity of the technique is of concern. By injecting packets of ions in the conventional IMS, ions can be separated by determining their mobilities. Even very similar molecules, such as the isomers of dinitrotoluene (1,3-DNT and 2,4-DNT) can be separated with baseline resolution. By injecting ions continuously, as is done in the FIS, selectivity is achieved by changing the transverse and compensating voltages to allow only one ion to pass. In current instrument designs, these voltages are not swept or coupled, so only one species can be detected at a time. To detect a second species, the voltages must be adjusted. No information regarding the amount of time required to achieve the switch and allow the instrument to stabilize could be found.

The following conclusions regarding FIS are based on our experiences, conversations with MSA representatives and other workers in the field of IMS who have had the opportunity to examine the FIS. After building several prototypes and obtaining some data, MSA announced a limited (10 unit) production in 1996. Sandia National Laboratories placed an advance order for one of the units, but after 12 months, the unit

was not ready to ship and the order was canceled. Another inquiry in October 1997 indicated that no units were available for purchase at that time, but a MSA representative has reported that by March, 1998, several units had been purchased and were being used. Current cost is approximately \$30,000. All units require 120V AC power, but MSA has stated that a battery-powered unit could be built if user demand justified the development costs.

MSA continues to be optimistic that the FIS will be a valuable technique for trace gas analysis and is continuing development. We agree that FIS shows a great deal of potential for specific applications, but feel that until additional units are sold, and a user base is established, development of applications and improvements to the instruments will be slow in coming.

Table 7. Advantages / Disadvantages of Field Ion Spectrometry

| Advantages of Field Ion Spectroscopy | Disadvantages of Field Ion Spectroscopy |
|---|---|
| • Extremely sensitive (sub pg.) | • High voltage required |
| • Can detect either positive or negative ions | • Uses 10 mC ^{63}Ni for source; regulatory issues |
| • Non-radioactive sources can be used as they are developed | • Requires 110V power; no battery powered unit exists |
| • Ions difficult to separate with IMS can be separated by adjusting the transverse field voltage | • Small user base |
| • Lower cost than IMS (\$30,0000 vs \$63,000) | • No field usage reported |
| Overall: Similar operation to conventional IMS; no clear advantages over IMS. Small user acceptance or demand makes miniaturization efforts unlikely. | |

Mass Spectrometry

Mass spectroscopy has traditionally been used as a laboratory technique to identify and quantify organic compounds. These instruments typically have been difficult to use, high maintenance systems that require considerable operator training and laboratory support facilities.

Recently, however, several manufacturers have developed portable GC/MS systems that can be operated in the field using battery power. These systems typically weigh on the order of 80 pounds, and have short battery lifetimes. Essentially, these systems are not suitable for long-term unmanned operation.

One such instrument, designed and marketed by Bruker, is the Chemical Biological Mass Spectrometer. This unit has been ruggedized to U.S. Army MIL standards. The unit weighs 65 kg and has detection limits of 0.04 mg/m³ GD, 0.02 mg/m³ VX, 0.07 mg/m³

HD, and 1.4 mg/m³ L. The detection of biological agents, which are pyrolyzed prior to analysis, is 100ng of spores.

Small, truly portable mass spectrometers have been developed at the Jet Propulsion Laboratory (JPL) by Ara Chutjian. These mass spectrometers, which were developed for monitoring the atmospheres in spacecraft, utilize quadrupoles that are only one inch long, and yet provide unit resolution and scan masses up to 300 Daltons. Chutjian and coworkers have used electron attachment ionization techniques and mass spectrometry to detect trace explosives signatures from undersea UXO items [12]. Analysis of explosives in seawater by ion trap mass spectrometry in conjunction with solid phase microextraction (SPME) sampling has also been reported by Barshick and Griest [13].

Table 8. Advantages / Disadvantages of Mass Spectrometry

| Advantages of Mass Spectrometry | Disadvantages of Mass Spectrometry |
|---|---|
| • “Universal” detector for organic compounds | • Can be difficult to operate; user training required |
| • Structural information easily obtained | • Required high vacuum system |
| • Large user base | • Relatively high maintenance requirements |
| • Can be automated for unattended operation | |
| • Miniaturized systems being developed by Jet Propulsion Laboratory | |
| • Unknown analytes can be identified through library searching or spectral interpretation. Large libraries are available and can be customized for specific analytes. | |
| • One field unit, the Bruker Chemical Biological Mass Spectrometer is being used. 65 kg | Unlikely to miniaturize the Bruker type system. |
| Overall: Mass spectrometry is the best technique available to identify unknown analytes. Vacuum system requirements typically make power consumption high. | |

Enzymatic Reactions

Systems based on enzymatic and immunoresponses have received a great deal of attention in the past 5 to 10 years. These systems take a number of forms, from flow immunoassay sensors being developed by the Naval Research Laboratory (NRL) [14,15] to various coated surfaces being developed by numerous researchers [16]. Several means have been developed to detect the binding of analyte to antibody, including modified

atomic force microscopy [17]. Solution-based assays have demonstrated the ability to detect ~1000 analyte molecules in a ~10 microliter aqueous sample [18].

The NRL flow immunoassay systems utilizes antibodies coupled to fluorescent dyes. The coupled moiety is bound to a stationary substrate. When the analyte of interest enters the flow path, it displaces the bound antibody/dye. As the dye passes a fluorescent detector, a signal that is proportional to the amount of analyte that was injected onto the column is produced. In its current form, the system is less than a cubic foot in size, and the columns are a couple of inches long. Each column is capable of several hundred analyses. Sensitivity and reproducibility is excellent. Samples must be in solution before being injected into this system. One problem that is specific to this system is that if an injection is made that contains a fluorescent signature, the response from the analyte can be masked.

Various coated surfaces are also being investigated in a number of laboratories. One scheme involves coating the ends of fibers in a fiber optic array with various enzymes or antibodies. As the end of the fiber is exposed to an analyte, the various enzymes will exhibit behaviors such as color changes. By developing a catalog of responses, "fingerprints" of different species can be developed. Other similar arrays have been developed, differing only in their configuration and the software used to process the signals; the basic idea behind the various systems remains the same.

The strengths of the enzymatic reactions, and especially the immunoassay systems are their extremely high specificity. The antibodies are extremely specific in their response, and hence the false positive rate is very low. This specificity is a disadvantage if one needs to determine the presence of other compounds in the environment, as no response will be obtained. Specific antibodies for many analytes can be easily developed. A major concern with many of these biologically based systems is their stability and robustness. Shelf life is generally limited to a few months (there are a few exceptions), and they degrade rapidly with slightly elevated temperatures.

The enzymatic and immunoresponse based systems have the potential to be miniaturized and will most likely have very low power requirements. Additional work to stabilize the enzymes and antibodies will have to be undertaken, and work to efficiently coat fiber ends is needed. Automated systems are currently not available.

Table 9. Advantages / Disadvantages of Enzymatic Reactions

| Advantages of enzymatic reactions | Disadvantages of enzymatic reactions |
|--|---|
| <ul style="list-style-type: none">Possibly most specific detection system available | <ul style="list-style-type: none">Enzymatic systems are not robust. Tend to degrade rapidly with increasing temperatures. |
| <ul style="list-style-type: none">Often very sensitive. Rely on dyes or fluorescence to obtain signal. | <ul style="list-style-type: none">Systems have short shelf life, especially under uncontrolled conditions. |
| | <ul style="list-style-type: none">No automated systems available; samples analyzed individually. |
| | <ul style="list-style-type: none">Specific antibody must be developed for each compound of interest |
| | <ul style="list-style-type: none">Will not detect presence of unknown analytes. |
| Overall: Enzymatic reactions are the most specific available. They can be very sensitive, but the systems are not robust. Microsensors specific to a limited number of analytes could be developed. Unknown analytes can not be identified. Assuming that the system can be made more robust, this is a viable candidate for several applications if the user can accept detection of a limited number of compounds. | |

Chemiluminescence

Chemiluminescence detectors are extremely sensitive detectors for compounds containing nitrogen. Typically used in conjunction with a GC, the GC output is pyrolyzed and the nitrogen-containing compounds converted to nitric oxide. The nitric oxide then enters a reaction chamber viewed by a photomultiplier tube. The photomultiplier is equipped with a filter that allows only infrared wavelengths to pass. In the reaction chamber, the nitric oxides are reacted with ozone to form an excited state of NO₂. As the excited NO₂ relaxes, infrared light is emitted and detected by the photomultiplier. This detector, when coupled to a fast GC, is capable of detecting picogram levels of analyte.

Based on laboratory studies, this type of GC / chemiluminescent detector system could be developed into a portable battery powered unit for field usage, but a system of this type has not been demonstrated.

Table 10. Advantages / Disadvantages of Chemiluminescence

| Advantages of chemiluminescence detectors | Disadvantages of chemiluminescence detectors |
|---|---|
| <ul style="list-style-type: none">• Extremely sensitive | <ul style="list-style-type: none">• Ancillary reaction chambers required. |
| <ul style="list-style-type: none">• Very specific for detection of NO₂ | <ul style="list-style-type: none">• Will not detect analytes of interest to this program. |
| <p>Overall: Very limited range of analytes; not suitable for field work..</p> | |

Use of Automated Signal Processing in IMS

The use of advanced signal processing is an area of increasing interest to many IMS users. The software that currently exists for IMS operation is typically limited to control of the instrument, including heating, aperture gating, signal acquisition, and minimal processing. The signal processing is typically rudimentary, often being limited to display of the waveform and perhaps an indication of the signal strength. The more sophisticated programs allow a user to monitor the signal amplitude within one or more ion drift time windows, a method that can be used to identify a known compound. This section is included in order to direct attention to the fact that potential gains in IMS performance may be available through intelligent post-processing of the data, but that application of such methods to IMS data remains largely unexplored at present.

Oftentimes, the IMS is used under controlled conditions, where interferences can be controlled, and the background is relatively clean. Examples of this controlled environment include laboratory settings and samples collected in forensic work, and during explosive screening. In contrast, field applications of IMS such as those investigated for this project often force one to work in uncontrolled conditions with unknown interferences. Fortunately, in many cases, the IMS is still usable. Our laboratory has analyzed several hundred soil samples collected from sites throughout the country, unexploded ordnance, over one hundred marine samples, and thousands of air samples in airports. With very few exceptions, we have not found interferences that prevent the use of the IMS or degrade its performance for the detection of explosives.

Under conditions where interferences are significant, peak deconvolution programs have been used in chromatographic applications to enhance the accuracy of peak integration and in identifying compounds. However, such peak deconvolution methods have not been extensively utilized to date in the interpretation of IMS data. While peak deconvolution and other fitting methods are potentially useful, we note that such methods do not often yield mathematically unique results for a given data set. Therefore, the assignment of specific peaks to an unresolved spectrum typically must rely on *a priori* assumptions about the sample subjected to analysis, on information independent of the IMS measurements, or both.

One shortcoming of IMS technology, as well as of most chromatographic analyses, is the inability to identify unknown compounds. Researchers using chromatographic methods have historically identified unknown compounds in a mixture by matching the retention time of the unknown to the retention time of known standards that have been run previously using the same set of conditions. The use of more than one column and matching retention times using two or more different stationary phases significantly increases the probability of a correct identification of the unknown.

An analogous method of identifying unknowns using IMS has been used by commercial manufacturers to identify specific drugs or explosive compounds. Identification is achieved by calculating the reduced mobility of an unknown peak found in the IMS plasmagram and matching its mobility with the reduced mobilities of previously run standards. In most cases, the number of standards contained in these libraries are very limited; often a dozen or less. Users of the instruments can add compounds they are interested in to the manufacturer-supplied libraries, thus customizing the instrument to better suit their purpose.

A more robust method of identifying unknown compounds, utilizing neural nets, is under investigation in Professor Gary Eiceman's laboratory at New Mexico State University. Work in this lab has demonstrated that neural net software can be "trained" to recognize IMS spectral features, and to assign identities based on these spectral features. The neural nets are trained using a variety of compounds, and unknowns are identified by comparing the spectral features embedded in the unknown spectrum to those contained in the neural net. Typically, the compounds which can be identified are the same as those used to train the net, and all spectra must be acquired under rigorously controlled conditions.

One problem with application of this approach is that IMS spectra, particularly in field applications, have been typically acquired using relatively uncontrolled conditions. Temperatures and gas flow rates are controlled to <1% variation, but other parameters, such as the humidity of the carrier and drift gases, and the pressure in the instrument has not been controlled. Dr. Eiceman has recently demonstrated that by carefully controlling all of the parameters, including the humidity, temperatures, pressures, and flows, neural networks can be used to extract spectral information out of IMS data.

IMS Instrument Improvements

In addition to the work currently being done on the Sandia / ERG IMS, there are a number of other modifications that could be made to enhance the performance of the system being developed under the Lockheed Martin Shared Vision Program. These include:

1. *Reduction in size.* Researchers at several laboratories are attempting to reduce the size of the IMS without sacrificing sensitivity or losing too much resolution. These efforts are utilizing modeling programs, improvements in data processing, and materials research to obtain the desired results. Improved fieldability with longer battery lifetimes will enhance user acceptability.
2. *Laminar flow designs.* Most IMS systems, being of segmented design, do not have smooth internal surfaces. Flow calculations have indicated that as the drift gas flows along the tube, turbulence is introduced in the drift tube. It is generally believed that this turbulence contributes to spreading of the ion packet, which decreases both the sensitivity and the resolution. To date, instruments utilizing drift tubes designed to minimize turbulence have not been constructed or demonstrated.
3. *Potted / Cast drift tubes.* The segmented drift tubes currently available perform adequately, but several shortcomings are evident. First, the cell is not sealed, and if operated at pressures slightly below ambient, leakage of atmospheric gases through the walls of the drift tube can occur. As these atmospheric gases enter, contaminants and moisture can be drawn into the IMS, causing interferent peaks and cluster ions to appear in the plasmagram. Secondly, a segmented drift tube design is inherently less durable than a monolithic design. Finally, the number of closely fitting parts increases the manufacturing and assembly costs, and makes maintenance more difficult. Attempts to construct a monolithic IMS cell have been limited to ceramic tubes coated with a semiconducting film on the inner surface [19,20]. These instruments were designed to optimize the electric fields in the drift regions rather than prevent leakage. Difficulties in producing a uniform semiconducting film prevented further development of these devices. Improved engineering materials, such as the S-glass developed at Sandia National Laboratories, raise the possibility of economically producing a pseudo-monolithic IMS. The S-glass binds very tightly to stainless steel, and its coefficient of thermal expansion matches that of the stainless steel, allowing temperature fluctuations to occur without inducing cracking of the glass. Segmented conducting rings could be placed in a mold, and cast in place with S-glass. This assembly could then be machined and honed to produce a hermetically sealed drift tube with very smooth internal surfaces. Manufacturing costs should be quite low, and the unit would be expected to be very rugged.
4. *Power consumption.* Power consumption is of concern only when it is necessary to depend on battery power to operate an instrument. Commercial instruments, in general, have not been optimized to minimize their power consumption. Consequently, battery powered units have limited lifetimes. For example, the Graseby PLASTEC can operate for only 85 minutes on its internal battery, while the Barringer Model 350 has an 8-hour lifetime. Unfortunately, the battery pack for the Barringer instrument weighs nearly 300 pounds. The main source of power consumption is the heaters. Units that are operated above ambient temperature consume considerably more power than ambient T systems. Obvious ways to increase battery lifetimes are to reduce the operating temperature, but this cannot always be done because of the analytical requirements. Alternately, more effective

insulation could be used to minimize the heat loss. Finally, reducing the size of the IMS can reduce the power consumption.

5. *Improved Sensitivity.* It is sometimes stated that at sufficiently high sensitivity, every molecule that exists could be detected in every sample; resolving the molecules would then require nearly infinite resolution. Although this is an extreme statement, it points out the inter-relation between sensitivity and selectivity. As the sensitivity is increased, a larger number of compounds can often be detected, making improved resolution and/or signal processing capabilities mandatory.

The sensitivity of a conventional IMS could possibly be improved by implementing some of the changes suggested in this paper, such as producing a system that minimizes internal turbulence. One could improve the efficiency of ionization by utilizing more of the ions that are produced. When IMS systems were first developed, they were built using existing hardware. The ionization source, which was adapted from the electron capture detector, is a plated cylinder. Due to its configuration, only 50% of the total beta particles are available to ionize the analyte. Addition of a repeller to the source region could improve the efficiency of ion extraction. Computer programs that predict the ion trajectories in various fields can now be used to optimize the design of the IMS. These programs have not been applied to current IMS systems, but improved performance is likely to result with their application. One could also focus on developing a means to collect more analyte and deliver it to the detector in a more efficient manner.

6. *Non-radioactive sources – Corona Discharge.* Corona discharge sources are the most likely candidates to replace radioactive sources. There are several different corona discharge designs. The most commonly used design is the line - to - plane discharge. This design, is used in laser printers to both transfer a charge to the drum, and to then transfer the toner from the drum to the paper. It has proven to be very robust, and can operate for extended times before replacement of the corona discharge wire is required. A modification of this design, the line - to - tube, has been briefly examined by Dr. Cash Olsen, (Electronic Research Group, Mesilla, NM) and has been shown to be suited for use with an IMS. A prototype ion source was built using a short (ca. 1.5 inch) length of copper tubing. A length of wire running down the axis of the tube completed the circuit. Efficiency of the source has not been demonstrated relative to that obtained using ^{63}Ni . A more efficient corona discharge source is a point - to - plane design. In this case, a potential is developed between the sharp point of a needle and a plane. An intense corona can be developed near the tip of the needle, but erosion of the needle occurs. This results in short operating times, often on the order of minutes to hours. Graseby has reportedly developed a corona discharge source that can operate for long times, but attempts to purchase an instrument containing this source, or to obtain documents verifying its existence and performance have been unsuccessful. Dr. Gary Eiceman (New Mexico State University) has built a point - to - plane corona discharge source, and has been operating it in his laboratory for several months. Addition of a feedback circuit to control the current and minimize erosion could lead to the development of corona discharge sources that operate for significant periods of time before maintenance is required.

7. *Non-radioactive sources – Photo-ionization.* Photo-ionization is a method for producing ions that is used in commercially available detectors, called simply Photo-Ionization Detectors (PID). The light sources used are hollow cathode discharge lamps with MgF_2 windows. These devices use about 200 mW when operating and produce large fluxes of photons at 10.2 -11.0 eV. This is enough energy to ionize many, but not all, organic compounds. This selectivity could be an advantage or disadvantage, depending on the application. Another advantage of photo-ionization sources over radioactive ion sources is that they produce no reaction ions that can interfere with the detection of the desired species. The available lamps are not large but no effort has been undertaken to micro-fabricate them. Operating voltages are quite large, with several kilovolts required to ignite the lamps, and half a kilovolt required during steady state operation. Ion production is much larger than that of typical radioactive sources due to the high photon flux relative to the radioactive source flux. However, photoionization sources are limited by the same dimensional limits as radioactive ionizers. A reduction in the ionizer volume will reduce the number of ions produced.
8. *Microvolcanoes.* Microfabricated field emission and field-ionization sources have been pioneered primarily by SRI International in Menlo Park, CA. A good recent description of this technology with a rather complete list of references to earlier developments is given in reference 21. Although most of the testing of these devices has been done in (at least) a modest vacuum, they should still operate with sufficient efficiency at atmospheric pressure to make them attractive as low-power, non-radioactive IMS sources. The variation of these devices most applicable to ion mobility spectrometry is the microvolcano. The appearance of the structure gives rise to its name. A hollow metallic cone with an open top (the volcano) is fabricated so that its rim is precisely centered in a slightly larger circular opening of a metallic ground plane. Bias is applied between the volcano and the ground plane. Gas is forced into the high-field region by flowing through the throat of the volcano. The small separation of the volcano rim from the edge of the ground plane makes the microvolcano particularly applicable to IMS. These devices operate on the left-hand side of the Paschen curve shown in Fig. K1 of the above reference, which shows the breakdown potential for a variety of gases as a function of the product of ambient pressure and electrode separation. As the electrode separation shrinks for a given pressure, the breakdown potential initially slowly decreases, goes through a minimum, and then increases dramatically. The increase at small separation arises from the fact that there are not enough electrons around the tip to support an avalanche breakdown (spark). At atmospheric pressure in air, submicron gaps can support voltages of hundreds, to perhaps a thousand volts. These fields are adequate to gently strip electrons from gas molecules in the high field region, leaving M^+ ions for analysis by the IMS unit. To produce negative ions, the microvolcano can be reverse biased to just below the field-emission threshold. Electronegative gas molecules may then be able to capture a loosely held electron from the volcano rim to form an M^- ion. Both of these methods should produce ions with very little excess energy, and thus reduce the probability of fragmentation. All else being equal, this should produce a much simpler ion mobility spectrum than a Ni-63 source. The

microvolcano can also be operated as a field-emission source to generate electrons. In this mode, it should behave much like the commonly used Ni-63 beta emitter source.

9. *Laser Ionization.* Laser ionization has been briefly investigated as an ionization source for IMS. In 1988, at the University of Michigan, a power density of 10^7 W/cm² at 266 nm was used to ionize both explosives and other compounds. Generally, M⁺ or MH⁺ peaks were detected; no fragmentation was observed. CO₂ lasers are used to both desorb and ionize compounds in the Nicolet Fourier Transform Mass Spectrometer. Diode lasers, which are typically low power, have not been used for IMS applications primarily due to their small size, and hence low efficiency in the relatively large volume of a conventional IMS source. Miniaturization of the IMS would provide a smaller ionization region and thus more efficient utilization of diode laser ionization. Additional work is required to match the laser output to the ionization energy of the target compounds.

Response Time

Instrumental response time is not necessarily the most important factor in determining an instrument's usefulness for a particular application. For the explosives analysis applications of primary interest here, IMS essentially provides an instantaneous response. Integrating 50 to 75 scans (to improve the signal to noise ratio), with each scan consisting of several hundred data points, requires less than one second. If an analyte's concentration is such that the instrument has sufficient sensitivity to detect the compound, one can obtain response times less than one second. At higher concentrations, the number of scans that are integrated can be reduced, or the IMS can be set to monitor a peak in real time, thus reducing the response time even further.

Rather than instrumental response time, a more valid measure of operational usefulness is the "cycle time". The cycle time includes not only the instrumental response time, but the sample collection, sample transfer, and data processing time. In most cases, the instrumental response time is not the limiting parameter. Sample collection is often the most time consuming step in the process, especially when the analyte concentration is low. In this case, a concentrator or collector of some type must be employed. Often, an air stream is passed over a filter or other collection medium. As the analyte contacts the collection medium, which is often tailored to selectively trap specific compounds, the analyte is preferentially adsorbed and retained, while many potential interferents pass by. After sufficient time has passed, the collection medium is heated to thermally desorb the analyte into the detector.

In some cases, as with ultratrace analysis, this collection phase can require seconds, minutes, weeks, or even months of collection. Our laboratory has utilized collection times of up to 45 minutes when analyzing marine samples containing less than 0.005 part-per-trillion of analyte. By utilizing long collection times, one obtains an integrated sample. The analyst is unable to determine whether the final detector response is due to a long-term, low level concentration of the analyte within the medium sampled, or to one higher concentration "burp".

Affordability

Affordability of an instrument is always a relative parameter, and what is affordable in one situation is not necessarily affordable in another. For example, cost is almost ignored for space applications due to the importance of the analysis and the inaccessibility of the instrument for repairs. In this case reliability, and perhaps power consumption, are the overriding factors. In contrast, many applications demand the use of numerous, low cost sensors that are not critical, and that could be considered to be disposable. In most cases, the affordability lies somewhere between these two extremes.

Commercial IMS systems from PCP and Barringer cost between \$60,000 and \$80,000. These provide quite a bit of flexibility in that the operator may choose to analyze either positive or negative ions, control scan times and temperatures, and perhaps program different compounds into a library. In contrast, single purpose instruments, such as those designed to be handheld explosive detectors or narcotics detectors, can be obtained for around \$20,000. These lower priced instruments are not nearly as versatile as the more expensive units.

A significant drop in price is expected when micromachined IMS systems are available on a chip. Although not available at present, the frequency domain IMS under development at Sandia has the potential to be mass-produced like many electronic components. When this occurs, the IMS has the potential to be cheap enough to be considered disposable. It is likely that these systems will be designed to perform a specific analysis rather than as a "do it all" IMS system.

Ease of Maintenance

Maintenance is typically considered as a normal part of instrument ownership. The amount of maintenance often depends on both the sensitivity and complexity of the instrument. As an instrument becomes more complex, the amount of time needed to tune and repair that instrument usually increases. As the required sensitivity increases, the need for careful calibration and other required maintenance often increases as well. The instrument must be kept cleaner, and tuning becomes more critical.

The use of smaller, dedicated microfabricated instruments often minimizes maintenance since fewer parts are required, tolerances are often better, and the devices are often more rugged. The cost of a smaller instrument is often lower as well, making it feasible to deploy multiple "sacrificial" units. When one system no longer meets the required performance criteria, a second or third unit can be automatically switched online while the poorly performing instrument can be eliminated without compromising the mission. This regime has not yet been reached with IMS instrumentation, but microfabricated designs currently under development may enable such use.

Summary and Conclusions

Based on prior experience in sensor development, discussions with current and potential customers, attendance at various demilitarization, counterterrorism, and law enforcement conferences, and information gathered through library searches, it appears that a rugged, handheld IMS system has significant potential for sales in a number of diverse fields.

The military sector could utilize IMS-based detection systems both underwater (explosives detection) and on land (explosives, chemical agents, and biological agents). These applications impose the most stringent performance and durability requirements. The military market is likely to be smaller than the commercial market, but the military applications will allow higher-cost systems to be marketed. Military organizations are the most likely to contribute development funds to obtain the desired product(s).

Commercial (civilian) applications represent a much larger potential market than the military. The commercial sector would primarily target drugs, environmental work, law enforcement, agricultural compounds, and detectors for laboratory instruments. In addition, much of the military environmental work and base cleanup efforts will be contracted by commercial firms. Commercial firms are unlikely to contribute R&D funds to develop the technology. Rather, they will wait until the technology (instrumentation) is developed, proof-of-concept work is completed, and the unit is available as a commercial off-the-shelf item.

There are a number of competing technologies that are capable of detecting explosives, drugs, biological, or chemical agents. These can be generally categorized as either laboratory techniques or field screening techniques. Few methods have been applied to date for underwater sensing of explosives. The IMS system currently represents the best available compromise regarding sensitivity, specificity, and portability for underwater sensing of explosives. A number of researchers are developing miniature sensors for various applications, but none currently have as broad a range of potential applications as the IMS. Other sensor technologies should be monitored, but currently, IMS is a leading candidate for field sensing of explosives, chemical agents, and drugs on land, and is the most mature technology that has been evaluated for potential autonomous use underwater.

It is recommended that the military be approached to obtain development funds for the IMS technology, and that the initial applications be focussed on addressing the military's requirements. After instrument development matures sufficiently, commercial applications should become the focal point as this market will ultimately become the primary user of the technology. Determination of "sufficient maturity" for commercial interest will be difficult to quantify, and may only be accomplished by repeated periodic efforts to attract commercial partners for applications of the technology.

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APPENDICES

The following bibliographic appendices are sorted according to various applications. In many cases, the reference could be placed in to more than one category. To eliminate redundancy, the most logical category was chosen. There are no duplicates listed. Within each category, the references are sorted chronologically, with the most recent publications listed last. The bibliography covers the period 1937 through December 1997. The most recent search was performed in February 1998.

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Environmental applications and process control

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Appendix J.

Demonstrated IMS Explosive Detection Capabilities

EXPLOSIVE DETECTION IN THE MARINE ENVIRONMENT AND ON LAND USING ION MOBILITY SPECTROSCOPY

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 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 unexploded ordnance (UXO) in shallow water, unearthened 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

1 Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000

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 is available by contacting the authors.

Keywords: landmines, mine detection, unexploded ordnance (UXO), mine-like-object (MLO), ion mobility spectrometer (IMS)

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. Unfortunately, this technique 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 naturally occurring items, such as rocks, and munitions. The success of these systems varies and 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. 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 that the analyses may be reduced by microprocessor to simple yes/no results. 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. 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. 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 demonstrations at San Clemente 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

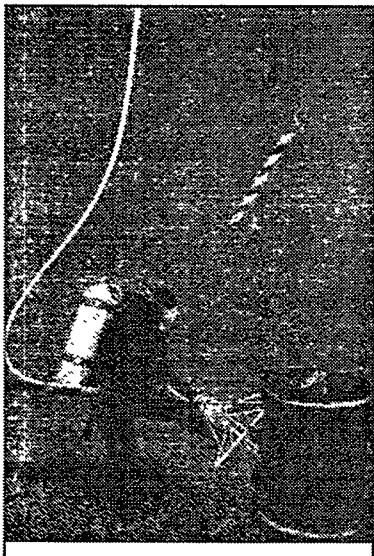


Figure 1. Diver using hand-held sampling wand.

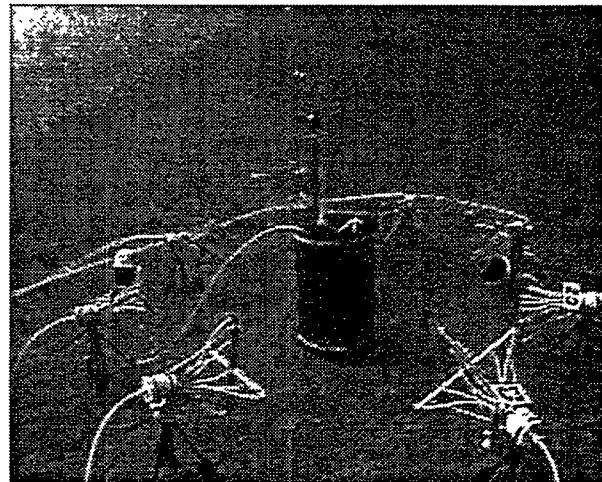


Figure 3. Sampling manifold setup.

through the wand for collection and analysis on the surface (Fig 2), or from a stationary sampling manifold (Fig.3).

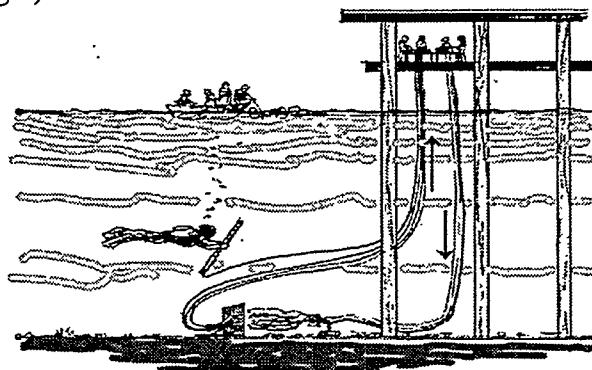


Figure 2. Field test setup at San Clemente Island.

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.
- In clear water, explosive signatures could be obtained at distances greater than four feet from the target.
- Explosive signatures are released from targets for long time periods.
- Explosives can be removed from the marine environment with good efficiency and without interferences from marine organisms.
- 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 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.

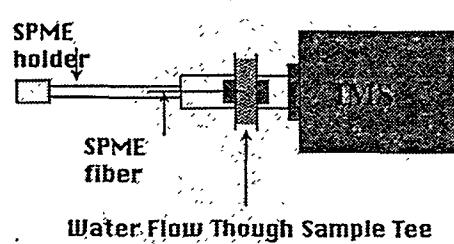


Fig. 4.. SPME / IMS concentrator / sampler schematic

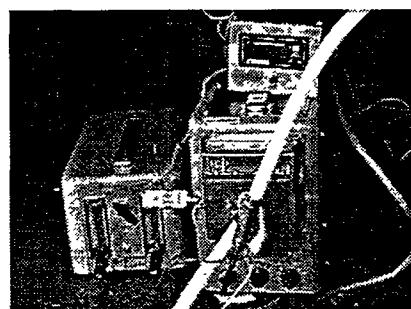


Fig. 5. SPME / IMS system in fieldable configuration.

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.

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. Efficiency 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.

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 was less sensitive to vibration than our research-grade IMS would be suitable for on-board 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. Figure 7 shows a diver collecting a sample near a 5-inch 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

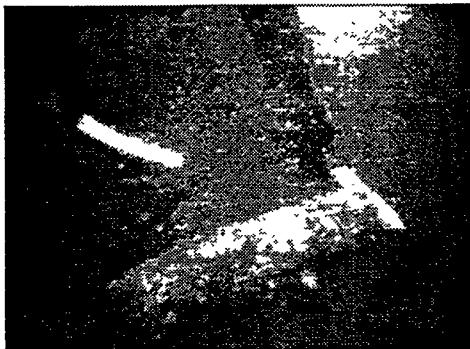


Figure 7. Sampling 5-inch shell with pump and hose to surface. Knife illustrates scale.

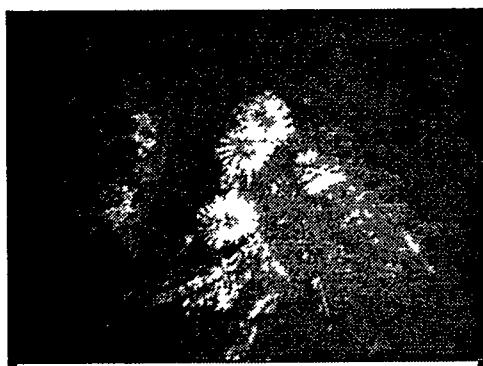


Fig. 8. 4-inch partially buried shell showing typical marine growth and amount of target exposed to the environment.

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.
- 27 sediment samples were analyzed. 26 samples (96%) produced detectable explosives signals.
- Compounds that could be attributed to 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.

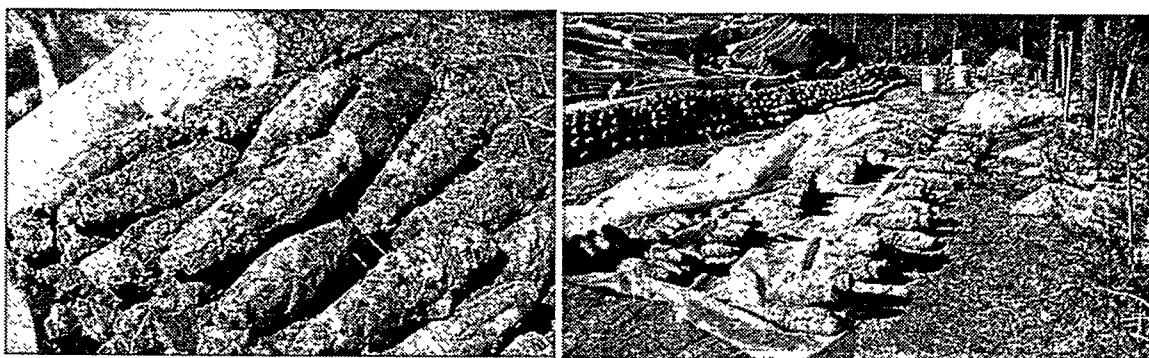


Fig. 9 Condition of mortar shells and partial view of sampling site.

The shells were analyzed by drawing air (100 ml/min) through a $\frac{1}{4}$ 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.

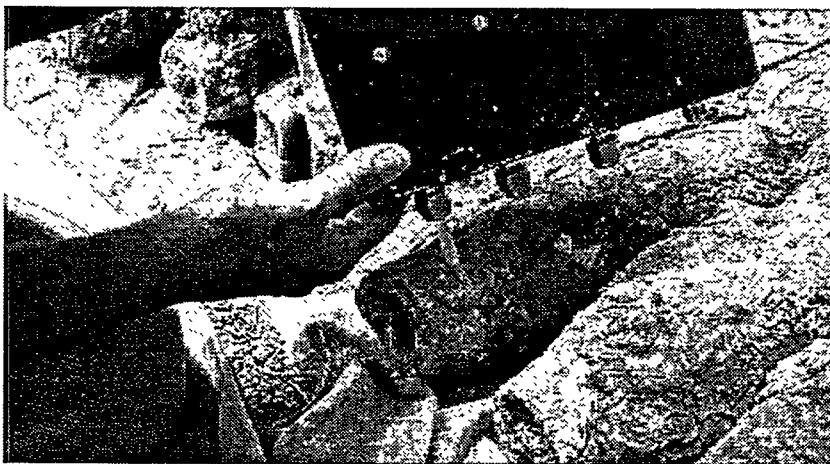


Fig. 10. Sampling pump being used to sample along seam.

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.

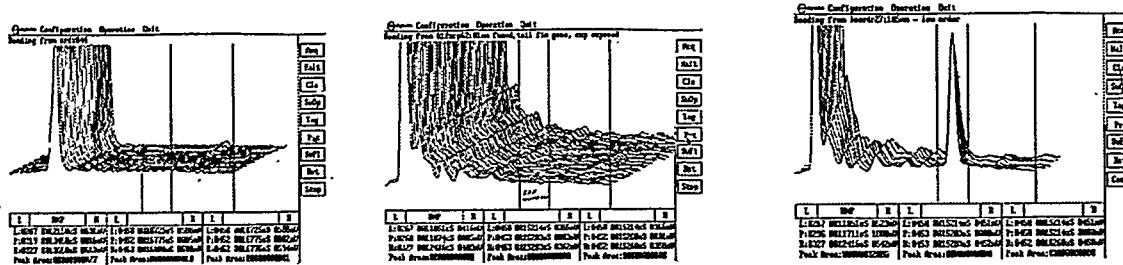


Fig. 11 Background signal, signal from inert round, RDX from live round.

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. 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 pump described above. Six rounds produced a signal indicating a TNT fill, and four produced signals 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.
- 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.

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 contamination³. Following completion of the swipe tests, the unfuzed mines were buried at the test site.

| <u>Identity</u> | <u>Casing Material</u> | <u>TNT (ng/cm²)</u> | <u>2,4-DNT (ng/cm²)</u> | <u>RDX (ng/cm²)</u> |
|-----------------|------------------------|--------------------------------|------------------------------------|--------------------------------|
| 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 |

Table 1. Surface contamination of TM62-P antitank mines

The transport of chemical signatures through soil is affected by a number of environmental factors. 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 surface⁴. 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.

| Soil surface | TNT (ug/g) / DNT (ug/g) | | | | |
|------------------------------------|-------------------------|------|------|------|------------|
| | 2.03 / <0.01 | | | | |
| 3" spacing between sampling points | 0.06 / 0.06 | | | | |
| | 0.06 / 0.47 | | | | |
| | 0.10 / 1.50 | | | | |
| TM-62P Mine | | 0.02 | 0.07 | 0.02 | TNT (ug/g) |
| | | 0.02 | 0.15 | 0.01 | DNT (ug/g) |
| | 0.16 / 2.70 | | | | |
| | 0.08 / 0.20 | | | | |

↔ Note: 1 ug/g = 10^{-6} g/g = ppm
3"

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.

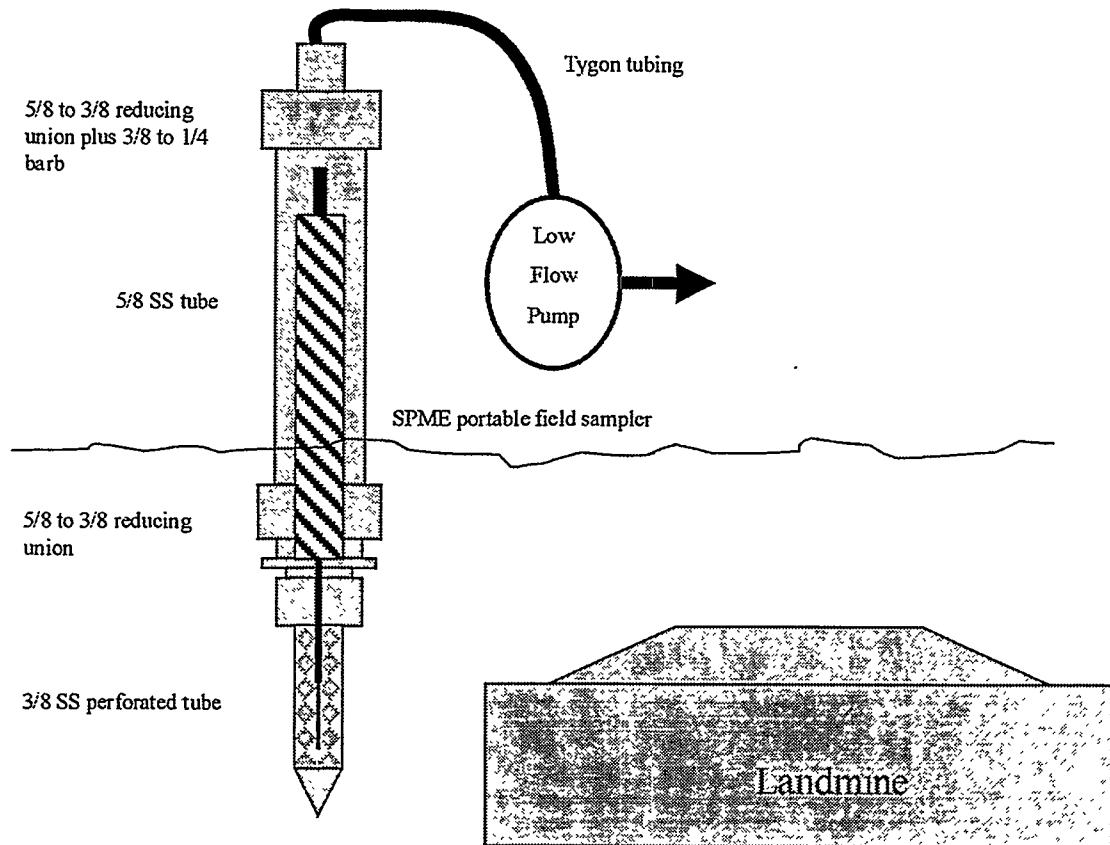


Fig. 13. SPME / lawn dart for landmine / UXO sampling

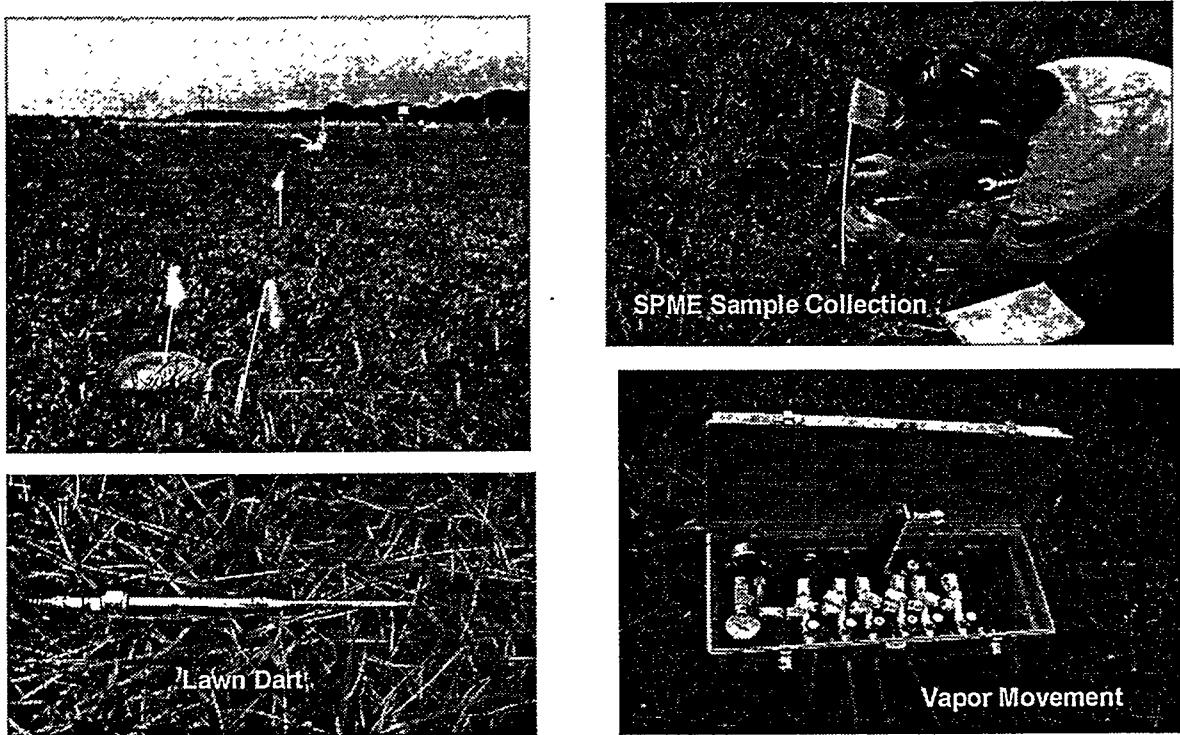


Figure 14. Lawn dart, SPME deployment, multi-station pumping system.

Laboratory and field experiments have shown that wetting soil in the vicinity of a buried mine will increase the amount of vapor present such that the possibility of detection is enhanced. The addition of water creates a "microenvironment" in which the explosive molecules are extracted from the soil particles and preferentially re-adsorbed to the chemically selective SPME fiber.

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.

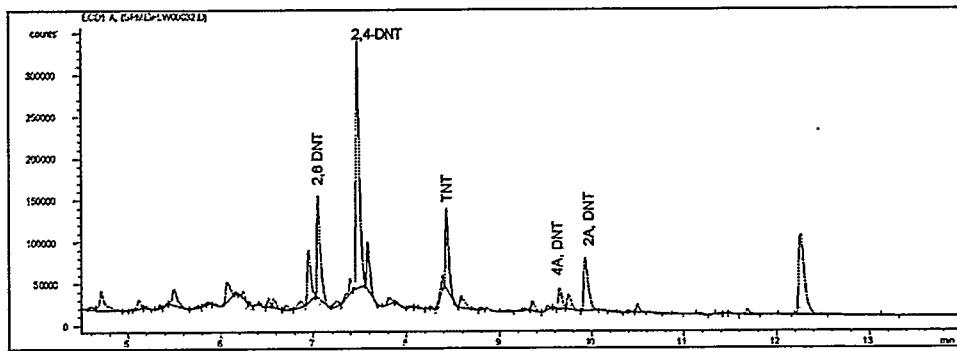


Fig. 15 Soil gas analysis of buried mine. Sampled using SPME / lawn dart; analyzed by GC/ECD

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.

ACKNOWLEDGEMENTS

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