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Chemical Sensing System for Classification of Mine-Like Objects by Explosives Detection

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ABSTRACT

Sandia National Laboratories has conducted research in chemical sensing and analysis of explosives for many years. Recently, that experience has been directed towards detecting mines and unexploded ordnance (UXO) by sensing the low-level explosive signatures associated with these objects. Our focus has been on the classification of UXO in shallow water and anti-personnel/anti tank mines on land. The objective of this work is to develop a field portable chemical sensing system which can be used to examine mine-like objects (MLO) to determine whether there are explosive molecules associated with the MLO. Two sampling subsystems have been designed, one for water collection and one for soil/vapor sampling. The water sampler utilizes a flow-through chemical adsorbent canister to extract and concentrate the explosive molecules. Explosive molecules are thermally desorbed from the concentrator and trapped in a focusing stage for rapid desorption into an ion-mobility spectrometer (IMS). We will describe a prototype system which consists of a sampler, concentrator-focuser, and detector. The soil sampler employs a light-weight probe for extracting and concentrating explosive vapor from the soil in the vicinity of an MLO. The chemical sensing system is capable of sub-part-per-billion detection of TNT and related explosive munition compounds. We will present the results of field and laboratory tests on buried landmines which demonstrate our ability to detect the explosive signatures associated with these objects.

Keywords: landmines, mine detection, unexploded ordnance (UXO), ion mobility spectrometer (IMS)

1. INTRODUCTION

Through programs sponsored by the Department of Energy and the Department of Defense Office of Munitions, we are developing a miniaturized, portable detection system that can be used to investigate objects submerged in shallow water, or buried on land, to determine whether there are explosive molecules associated with the objects. Our approach is to adapt and incorporate off-the-shelf technology to the extent possible. Only a few basic detection instruments are available to be used in a chemical sensor system, whether the search is for objects in water or on land. We evaluated the available technology for application to this sensing system and determined the most practical instrument to be the ion mobility spectrometer (IMS). The IMS has the best balance of sensitivity and specificity available today. By specificity we mean that the IMS is capable of determining the identities of several explosive molecules in the same sample and isolating their signals. Using an IMS, it is possible to estimate the 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 can regard as "signal strength," to adapt a common electronic terminology. We have an ongoing, internal research project directed at estimating this signal strength through the development of a mathematical model supported by laboratory and field experiments. Additional contributions to this effort, related to underwater UXO clearance and environmental restoration, have been provided by the Office of Naval Research. The work accomplished

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under these programs has allowed us to estimate the concentrations of molecules to be expected in real field conditions. These 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]. A reasonable target concentration for a chemical sensor 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 which may be readily adapted to portable use. Therefore, it will be necessary to artificially increase the signal concentration before submitting the explosive analyte to the detection instrument.

2. WATER SAMPLING SYSTEM

The process of detecting explosive signatures in water includes three basic steps. The first step involves sampling the water near a suspected target. The second step involves separating and concentrating the explosive molecules from the water and finally, the third step involves transferring the explosive analyte to a detector for processing. A schematic of the system in development at Sandia is shown in Figure 1.

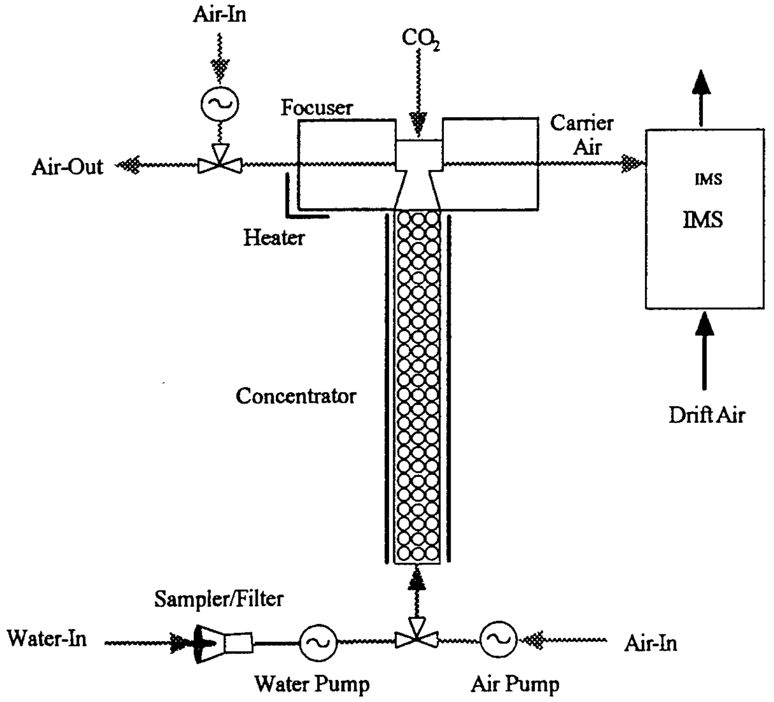


Figure 1. Water Sampling System Schematic

In this configuration, the sampling tube, which contains an inlet hose and particulate filter, utilizes a pump to collect a sample of water. The water sample is passed through the concentrator which is filled with glass beads coated with a thin polymeric film to enhance adsorption of the explosive analyte. After the sample has passed through the concentrator, the concentrator is drained, and air is pumped through the column to remove excess water. The concentrator column is then heated to desorb the analyte which is transported via carrier air to the focusing stage of the concentrator. The focuser utilizes a cold surface to condense and “trap” the analyte. The surface of the cold trap is subsequently heated to desorb the analyte into the carrier air flow for detection by the IMS. To improve cycle time, the system is designed to operate in an overlapped batch mode, with more than one concentrator column. This allows sample collection and separation to occur at the same time as the previous sample analyte is being passed to the IMS. Overall cycle time is a function of the concentrator adsorption and desorption efficiencies which in turn are functions of the polymeric coating chemistry as well as the operational flowrates and temperatures.

Figure 2 is a picture of one of our experimental laboratory systems. A 1/2 inch diameter Tygon tube attached to a peristaltic pump is used for the sampler section. A typical pump rate is 200-500 ml/min of water. The concentrator is a 3/8 inch diameter (I.D.), 6 inch long stainless steel tube filled with 3 mm diameter glass beads. The beads are coated with a 0.1% wt. coating of gas chromatography stationary phase (OV-225, Alltech Associates, Inc.). The temperature of the concentrator is controlled independently of the focusing block and cold trap. Heat is applied to the external surface of the concentrator tube with a heat strip while two cartridge heaters are used to heat the stainless steel focusing block. Temperature range for desorption is 175 to 200 °C. Temperatures are monitored with thermocouples attached to the individual components. The cold trap consists of a coil of 1/16" nickel tubing inserted into the focusing block. The trap was cooled by flowing dry nitrogen through a liquid N_2 bath and then through the tubing. (It is intended that CO_2 cartridges or thermoelectric devices be used to cool the trap in the field version). Carrier air flow rate into the IMS is 100 ml/min. The IMS used in these experiments is a PCP Model 111 Ion Mobility Spectrometer (PCP Inc., West Palm Beach, Fl.).

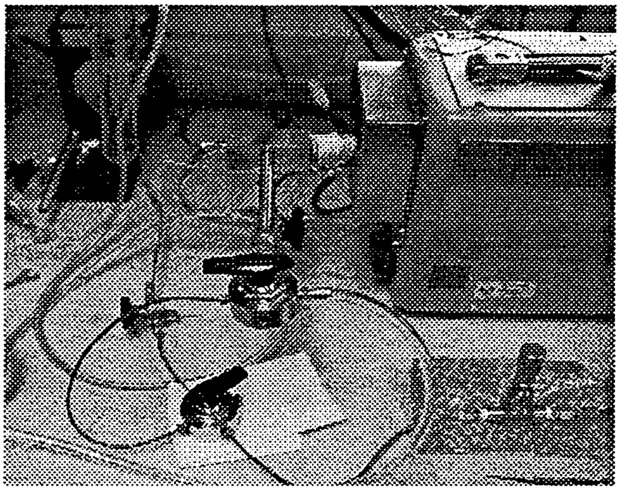


Figure 2. Experimental Laboratory System

Initial experiments to evaluate the system's functional performance have been conducted with 2,4,6-trinitrotoluene (TNT), a common explosive found in mines and UXO. TNT was dissolved in demineralized water and diluted to target concentrations. (Previous work has shown that the adsorption characteristics of TNT on polymeric solid phase materials are not substantially different for de-mineralized water and seawater[3]). The concentrator was loaded "off-line" for these experiments as follows:

1. 500 mL of TNT solution was pumped through the bead column at a rate of 200 mL/min;
2. 500 mL of de-ionized water was then pumped through the concentrator as a rinse solution to flush any non-adsorbed TNT from the system;
3. room temperature air was blown through the bead column at 25 PSI for 90 seconds to remove excess water.

After loading, the concentrator tube was screwed into the focusing block. Tests were conducted with and without the cold trap. Initial tests with the cold trap gave poor results with considerable tailing in the IMS signal. Work on optimizing gas flow and temperature ramp rates is in progress. The best results have been obtained without the cold trap simply by operating the carrier gas in a stop-flow mode through the concentrator. A typical stop-flow test sequence was as follows:

1. focusing block at temperature (175 to 200 °C);
2. install loaded concentrator tube into focusing block, wrap with heater strip;
3. bring bead bed up to desorption temperature, no carrier gas flow through bed;
4. purge concentrator tube with carrier gas at 100 mL/min directly into the IMS.

Figure 3 shows a typical IMS spectrum obtained using the above conditions to concentrate, desorb, and detect the TNT signal from a 90 ppb solution in water.

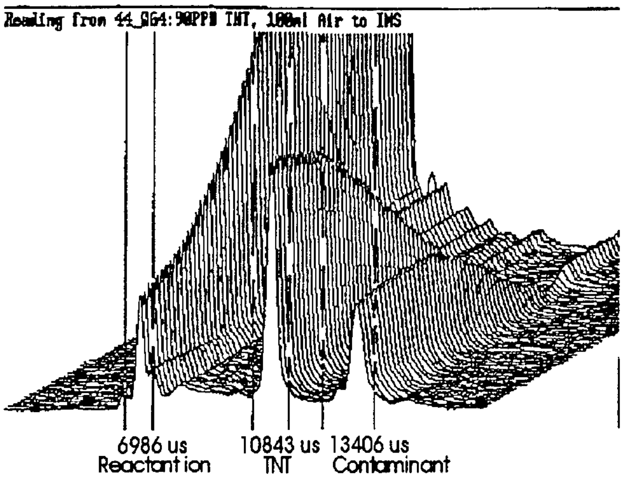


Figure 3. **IMS Spectrum from 90 ppb TNT in water**

The IMS spectrum is plotted in 3 dimensions with signal intensity vs. drift time (microseconds) shown on the *y-x* axes. The third component, plotted on the *z*-axis (from back to front) gives signal duration, corresponding to desorption time. Three ion peaks are shown in this spectrum: a reactant ion due to ionization of gaseous air molecules (e.g. O_2^-); the desorbed TNT signal, and an unidentified contaminant. (For a full discussion of reactant ion chemistry, see Klassen, et.al.[4]).

3. SOIL SAMPLING SYSTEM

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 purpose. 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. Table 1 shows some of the features associated with these mines. Table 2 gives the results of surface swipe analyses.

Table 1. Characteristics of the TM62-P Anti-Tank Mine

Origin	Dimensions	Case Material	Explosive Charge	Fuzing
Former Soviet Union	125 mm height x 320 mm diameter	Various plastics	TNT (5.7 Kg)	magnetic or pressure (200 Kg)

Table 2. Surface Swipe Analysis of TM62-P Anti-Tank Mines

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

It is assumed that the explosive signature flux from buried mines will be derived from two sources: 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 which were then analyzed by high performance liquid chromatography (HPLC). The results of these analyses are presented in Table 2 as nanograms (ng or 10^{-9} g) per square centimeter surface area. These data are in agreement with the range of values previously reported for mine surface contamination[5]. Following completion of the swipe tests, the unfuzed mines were buried at the test site as shown in Figure 4.

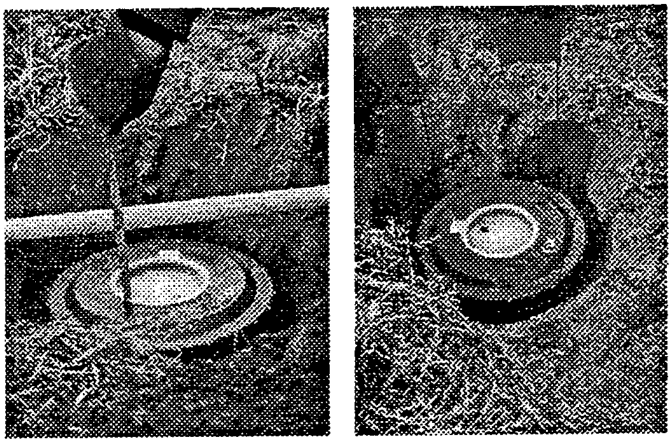


Figure 4. Mine Emplacement at the Sandia Test Site

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 surface[6]. 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 5 shows the results of soil analyses taken from the vicinity of a buried landmine.

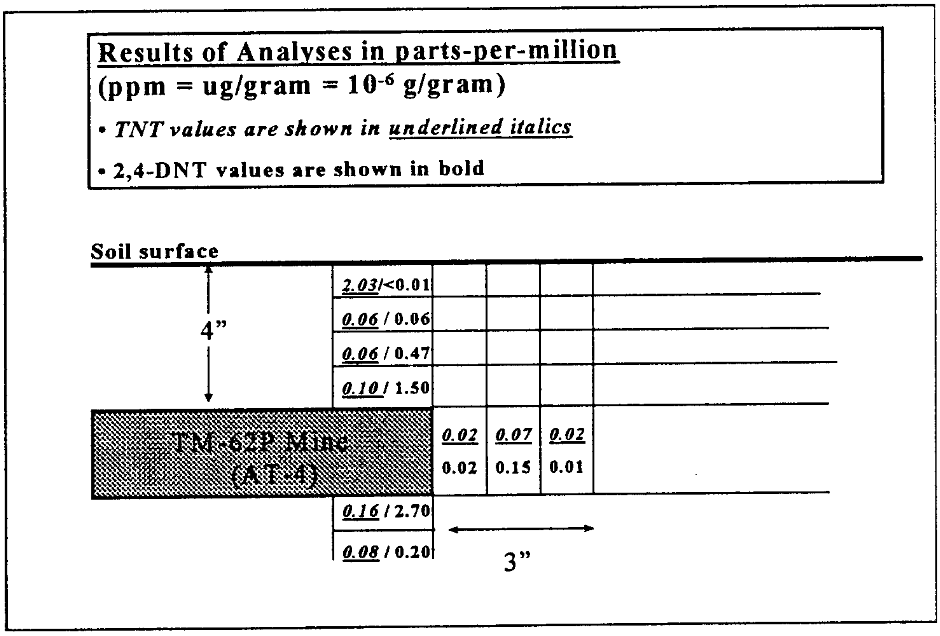


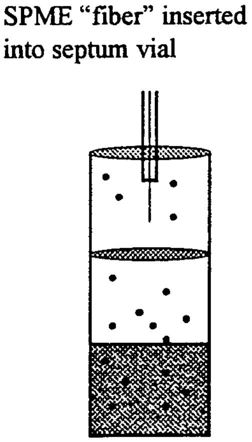
Figure 5. Results of Soil Analysis from Vicinity of Buried Landmine

To obtain the soil samples, a sampling profile was established by digging down to the edge of the mine with a trowel, exposing the edge of the mine, then digging a trench away from the mine. The exposed soil "wall" was sampled at incremental depths with the tip of a clean trowel. The mine was then completely uncovered and removed from the hole in order to sample underneath. 20-50 grams of soil were taken at each sampling point and transferred to amber glass bottles. Individual soil samples were mixed and sieved (<2mm) in the laboratory and stored in a freezer at -15 °C. Representative samples for analysis were extracted with acetonitrile then analyzed by gas chromatography with electron capture detector (GC/ECD). The GC results were confirmed by ion mobility spectrometry (IMS).

2,4,6-trinitrotoluene (TNT) and/or 2,4-dinitrotoluene (DNT) were detected in all of the samples, as shown in Figure 2. Cyclotrimethylenetrinitramine (RDX) was not detected in any of the soil samples, however, the sensitivity of GC/ECD is lower for RDX than for the nitrotoluenes. In general, concentrations decreased with increasing distance from the mine with the exception of the one sample taken at the ground surface which had the highest concentration of TNT. Spencer, et.al.[7], have shown that increased concentration of buried chemicals at the ground surface can result from natural precipitation/evaporation cycles. It is not immediately evident why this should occur for TNT and not DNT in this case.

The results of these analyses show that chemical signatures are detectable in the vicinity of buried landmines. These encouraging results prompted us to conduct a series of experiments to determine the feasibility of extracting and detecting these signatures in the field. Recent developments in chemical separation science have provided analytical chemists with a useful device to extract and concentrate trace quantities of organic chemical compounds from air and water matrices[8]. This solid phase microextraction (SPME) device consists of a syringe type plunger with a fused silica fiber tip. The fused silica fiber is coated with a chemical specific polymeric adsorbent. The adsorbent fiber is placed in an aqueous sample, or in the vapor space above an aqueous sample to collect the organic compounds. The fiber tip is then extended into the inlet of a gas chromatograph (GC) and the compounds are thermally desorbed onto the GC column for analysis.

We have developed a SPME analysis method to extract explosive compounds from soil samples using hot water as a solvent. In this method, as illustrated in Figure 6, water is added to the soil sample in a sealed septum vial and heated to 60 °C to increase the solubility and vapor pressure of the analytes. In this illustration the fiber tip is extended into the vapor "headspace" to acquire the analytes but the tip can also be extended into the aqueous phase .



- TNT is extracted from soil samples with hot water, 60 °C, in a sealed, septum vial.
- SPME fiber is inserted through septum.
- Headspace vapor or aqueous phase analyte is collected on solid phase coating on fiber.
- SPME fiber is removed from vial and thermally desorbed in heated inlet of GC or IMS.

Figure 6. SPME Method for Determination of Explosives in Soils

A series of soil standards were made by mixing uncontaminated soil from the test site with aqueous solutions of TNT and 2,4-DNT. The mixtures were allowed to equilibrate for 24 hours with continuous mixing to ensure complete adsorption to the soil binding sites[9]. The mixtures were centrifuged and filtered, then dried in a light shielded dessicator at room temperature. These contaminated soils were then serially diluted with uncontaminated dirt using a roller mill, to yield contaminated soils with part-per-billion (ppb) concentrations of TNT and DNT (10^{-9} gram/gram soil). These concentrations were representative of those determined in the soil samples from the Sandia minefield, as shown previously in Figure 5.

Figure 7 illustrates the results of SPME/GC analysis of a soil contaminated with 40 ppb of TNT and 4 ppb of 2,4-DNT. The first bar (dry vapor), shows the analyte concentration collected for 30 minutes in the vapor headspace above a *dry* soil sample, heated to 60 °C. The second bar (wet vapor) shows the results of vapor analysis above a *water saturated* soil, heated to 60 °C, after 30 minutes collection time. The third bar shows the results of analysis of the aqueous extraction solution after 30 minutes collection time. These results are consistent with the modeling work by Phelan and Webb[6] which indicate that the vapor phase concentration in soils increases with increasing moisture content.

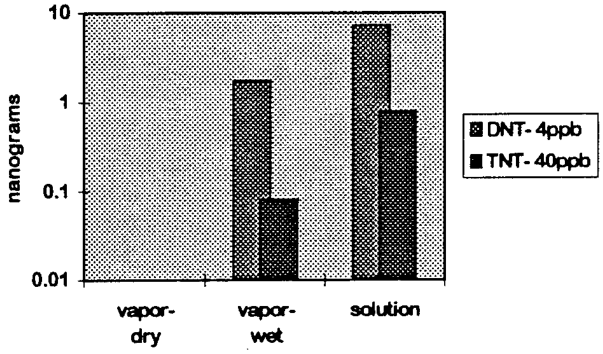


Figure 7. SPME/GC Analysis of Contaminated Soils: Vapor and Aqueous Solution Extracts

The results of these experiments demonstrate that it is possible to extract, collect and detect explosive signatures in soils using a solid phase "probe". We are designing a field-deployable soil/sediment probe that can be coupled with a miniaturized IMS for detection of landmines and unexploded ordnance as illustrated in Figure 8.

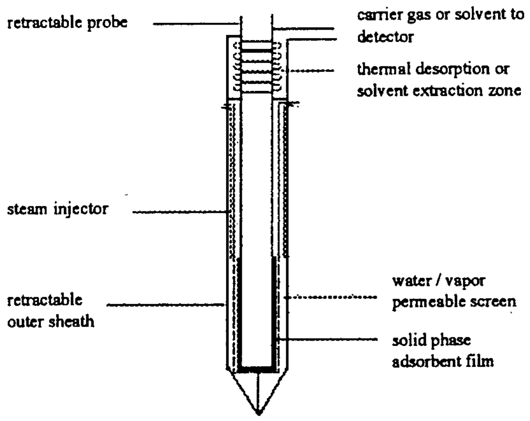


Figure 8. Field Probe Soil Sampler

In this design, hot water or steam is injected into the soil or sediment to create a heated, aqueous, "microenvironment" in which the explosive molecules are extracted from the soil particles and preferentially re-adsorbed to the chemically selective, solid phase coating on the un-sheathed probe. The probe is then retracted and the solid phase is thermally desorbed into the IMS. Alternatively, the solid phase can be solvent "stripped" and the analyte transferred to a liquid phase detector.

In practice, the probe would work in concert with other portable or robotic detectors including magnetometers and ground penetrating radars (GPR). The probe would be used to *classify* buried, mine-like objects as having explosive signatures. This "fusion" of data would greatly reduce the false alarm rate associated with non-explosive, buried clutter.

4. SUMMARY

In principle, we have demonstrated the ability to collect, concentrate, and detect explosive molecules in water and soil at concentrations representative of buried or submerged explosive ordnance. 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. This requirement creates a large energy demand. We are investigating the use of disposable, chemical heat sources for this application. Another technical challenge is the optimization of analyte collection efficiencies. We have had some success with the use of conventional, solid phase adsorbents, however the adsorption kinetics are not optimum for rapid signal acquisition. Also, these materials have been designed for controlled laboratory use and are not robust enough for continued field operation. We are investigating the development of rugged, thin film, solid phase adsorbents for application in our chemical sensor system.

Miniaturization of the various components is a necessity for reducing power consumption and weight. Commercial ion mobility spectrometers that are designed for field use can weigh up to several hundred pounds. We are currently working with Electronic Research Group (ERG, Las Cruces, NM) to adapt an ERG miniature IMS to this application. The working components of the ERG IMS are shown in Figure 9.

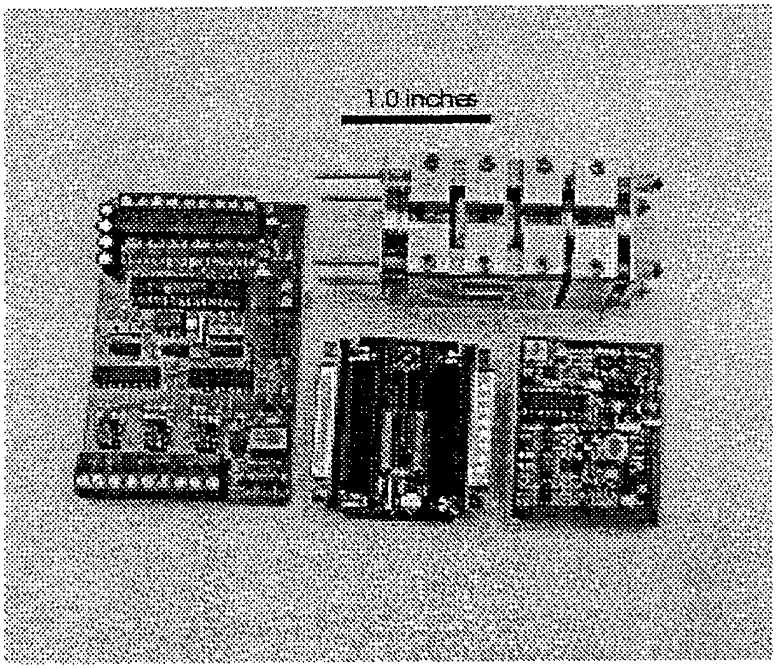


Figure 9. ERG Miniature Ion Mobility Spectrometer

The ERG miniature IMS weighs less than 5 pounds and operates at significantly reduced gas flows relative to other commercially available instruments (milliliters/minute vs. 100's milliliters/minute). The inlet system is adapted from a GC capillary tube (0.5mm diameter). The entire system can be operated from a 12V DC power supply and the current operating software is installed on a laptop computer. We have purchased two of these units for test and evaluation. Preliminary assessments are that the ERG IMS is considerably less sensitive to vibration than our laboratory IMS instruments and should be suitable for field use. We are in the process of miniaturizing our sample collection and concentration components to meet the input requirements of this device. Our goal is to develop a single, IMS based detector system with interchangeable sample introduction modules for use on land or in water.

5. ACKNOWLEDGEMENTS

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