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# Unexploded Ordnance Classification Sensor for Underwater Applications

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# Unexploded Ordnance Classification Sensor for Underwater Applications

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## Abstract

This report describes Sandia's continuing development of a small, portable, ion mobility spectrometer and associated automated sampling system that is intended for UXO detection in a shallow marine environment by trace chemical signature detection. The sensor development activities under this project were divided into three main subtasks. First, a thorough performance comparison was made between the (prototype) Electronic Research Group (ERG) IMS and the proven PCP 111 instrument for detection of explosives desorbed from SPME fibers. Since the majority of the relevant ordnance items contain 2,4,6-trinitrotoluene (TNT) as the main charge, TNT was selected as the analyte for this performance comparison. Second, a prototype automated actuator for the SPME preconcentrator was designed and constructed. Third, the automated preconcentration apparatus was combined with a small IMS detector and operated in the laboratory to demonstrate the overall sensor concept. The performance of the ERG and PCP as instruments for detection of TNT is discussed first. The automation of the SPME preconcentration apparatus is then described, followed by a description of the operation of the combined system in laboratory tests.

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# Unexploded Ordnance Classification Sensor for Underwater Applications

## Introduction

The U.S. Navy's current capabilities for detection and localization of underwater targets such as ordnance items, includes sonar and visible light imaging systems, trained marine mammals, and human divers. The imaging systems are subject to significant clutter: many "suspicious objects" are detected as well as actual ordnance items. The use of marine mammals and humans to detect and classify potential underwater targets carries severe risks. This report summarizes efforts conducted by Sandia National Laboratories personnel to refine the use of Ion Mobility Spectrometry (IMS) for classification of underwater targets by detection of trace amounts of explosives emanating from such targets.

Prior to the start of the efforts reported here, Sandia researchers had demonstrated that ion mobility spectrometry can be used in conjunction with solid phase microextraction (SPME) sampling to detect certain unexploded ordnance (UXO) items in a shallow ocean environment [1]. This demonstration was accomplished using Sandia-modified, commercial, benchtop laboratory instrumentation. Under the Lockheed Martin (LM)/Sandia Shared Vision Program, a multi-phase project has been identified to develop a small, rugged sensor, based on the SPME/IMS technology, that can potentially be used for maritime explosives detection. The potential terrestrial applications of such a sensor package are discussed in a companion report [2]. This report describes Sandia's continuing development of a small, portable, ion mobility spectrometer and associated automated sampling system that is adaptable for use in an unmanned undersea vehicle (UUV). This system is intended for UXO detection in a shallow marine environment by trace chemical signature detection.

The previous demonstrations of detection of explosives from UXO items in marine environments were made using a Sandia-designed adsorption / desorption system that was interfaced to a PCP Model 111 ion mobility spectrometer. The adsorption / desorption system used commercially available, manually actuated SPME samplers. The PCP instrument is a mature design that has been used for several years for analysis of explosives [3]. However, the volume, mass, power requirements, and vibration susceptibility of the PCP 111 preclude its use in portable applications. In order to pursue a mechanical design compatible with future IMS packaging concepts, including UUV applications, work on this project has concentrated on the characterization and development of a commercial prototype IMS instrument obtained from Electronics

Research Group (ERG), Las Cruces, NM. This instrument was acquired by Sandia National Laboratories prior to the Lockheed Martin (LM)/Sandia Shared Vision Program, but had not been thoroughly characterized as an explosives sensor.

The PCP instrument has been demonstrated to successfully detect UXO items when used with SPME preconcentration. Our ultimate goal of a remotely operable sensor system for maritime UXO applications will require automation of the preconcentration cycle. In addition, sufficient detection sensitivity of the IMS spectrometer must be maintained, while increasing the mechanical robustness and reducing the size and power requirements of the instrument. Accordingly, the sensor development activities under this project were divided into three main subtasks. First, a thorough performance comparison was made between the (prototype) ERG IMS and the proven PCP 111 instrument for detection of explosives desorbed from SPME fibers. Since the majority of the relevant ordnance items contain 2,4,6-trinitrotoluene (TNT) as the main charge, TNT was selected as the analyte for this performance comparison. Second, a prototype automated actuator for the SPME preconcentrator was designed and constructed. Third, the automated preconcentration apparatus was combined with a small IMS detector and operated in the laboratory to demonstrate the overall sensor concept. This report is organized in accordance with these subtasks. The performance of the ERG and PCP as instruments for detection of TNT is discussed first. The automation of the SPME preconcentration apparatus is then described, followed by a description of the operation of the combined system in laboratory tests.

# IMS Instrument Performance Comparison

## IMS Principle

The principle of operation of IMS has been discussed elsewhere [4]. Briefly, a conventional IMS operates at atmospheric pressure and consists of a method for ionization of molecules and a method of injecting the resulting ions 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 $\mu$ 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 magnitude of this current pulse is proportional to the number of ions striking the collection electrode. Ultimately, this current is ideally proportional to the mass of analyte injected into the inlet of the instrument. The conditions required in order

$$R = \frac{\mu}{\Delta\mu} = \frac{\Delta t}{t} \qquad \text{(eq. 1)}$$

to obtain this ideal proportionality are discussed further below. The resolution of the IMS or the ability to distinguish ions of different mobilities is given by:
where $\Delta t$ 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 of resolution. Increasing the field gradient can restore the resolution. For the experiments reported here, pure vapors of TNT were introduced to the ionization region of the various instruments. Thus, resolution is a secondary issue for the data discussed herein. However, it is important to note that for eventual field use of the instrument, the ability to resolve TNT from other possible analytes is vital.

## Ionization of the Analyte

The method used to ionize the analyte molecules is important to the discussion of the data presented below. Radioactive $^{63}Ni$ (a beta emitter) is used as the ionization source. The gas flow in the inlet of the IMS was doped with dichloromethane, $CH_2Cl_2$, by inserting a permeation tube into the gas carrier line. This dopant, which was present at a concentration of approximately 5 parts-per-billion in the carrier gas, is ionized by the electrons emitted from the $^{63}Ni$ source, and provides a reservoir of $Cl^-$ 'reactant ions' in the IMS ionization region. Reaction of the $Cl^-$ ions with neutral TNT molecules provides an effective means of producing negatively charged TNT molecular ions [5,6]. The depletion of the reactant ions when high concentrations of analyte are injected is a significant factor contributing to the limited effective dynamic range of IMS instruments.

This effect can be qualitatively observed in the data shown in Figure 1, where a representative response of the PCP IMS instrument to explosives is displayed.

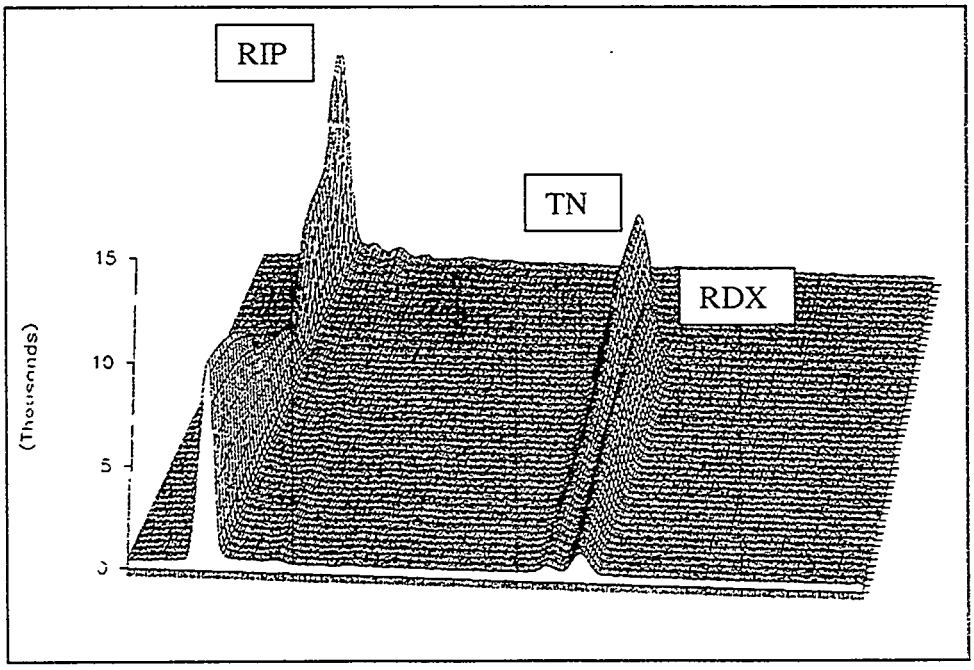


**Figure 1: PCP IMS Response to TNT and RDX**

The vertical axis in the figure is proportional to the ion current, while the horizontal axis for each trace in the figure is proportional to the time required for ions to traverse the drift tube. The multiple traces in the figure represent multiple ion mobility spectra, acquired as a function of elapsed time. The earliest spectra are displayed in the 'rear' of the perspective rendering, and more recent spectra in the 'front'. This method of displaying the IMS response plainly shows the depletion of the reactant ion peak (RIP) due to reaction of $Cl^-$ ions with TNT and RDX vapors in the ionization region. This figure was produced using the commercial data acquisition software provided by PCP. Integration of the TNT or RDX peaks at a given elapsed time following injection would ideally provide a value proportional to the concentration of explosive vapor in the ionization region at that time. However, the measured IMS signal is affected not only by the concentration of the analyte, but by the depletion of the reactant ions. We will return to a more quantitative consideration of this effect during the discussion of the IMS response data for the various instruments.

Since the PCP 111 had been previously demonstrated to have sufficient sensitivity for the detection of explosive devices in marine environments, the goal in comparing the sensitivity of the ERG IMS to the PCP instrument was to verify that the smaller device has sensitivity comparable to the PCP,. In order to enable a useful comparison of instrument sensitivities, it was required that the instrument operating parameters for each device be appropriate for maximizing the measured response to the test compound, TNT. In addition, it was required that a consistent method of data reduction be used for all instruments under evaluation. Finally, handling of extremely small quantities of analyte (picograms) in a reproducible fashion is nontrivial. Thus, Sandia developed and verified a method for reproducibly dosing SPME fibers with controlled picogram-nanogram masses of TNT. Each of these requirements will be discussed. Because reproducible delivery of measured masses of TNT is a *sine qua non* for the other tasks, the SPME delivery of TNT will be addressed first.

## SPME Delivery of TNT

The responses of the IMS instruments were calibrated by a 'round-robin' format using multiple Solid-phase microextraction fibers (SPME's) exposed to static samples of aqueous 2,4,6-trinitrotoluene. This method was chosen because the preconcentrator stage to be used in the prototype fieldable detector system relies on SPME fiber extraction of explosives from seawater. The mass loading of TNT on the SPME fibers used for detector characterization was calibrated by comparison to solution-phase TNT injections in a Hewlett Packard Model 6890 Gas Chromatograph (GC), equipped with a micro-Electron Capture Detector. The procedure used and results for reproducible dosing of the SPME fibers are summarized here. GC analysis methods for nitroaromatic explosives have been discussed in detail by other authors [7].

SPME fibers coated with 65µm polydimethylsiloxane-divinylbenzene were used in these experiments (Supelco, Cat # 57310-U). These are the manually actuated style with 24 gauge needles. The SPME fibers were mounted in the manual holder supplied by Supelco (Cat # 57330-U). To hold the SPME fibers mounted in the manual holder, an aluminum fixture was made such that five fibers could be dosed at once. A layout template for the fixture is shown in Figure 2. The aqueous solutions used to dose the fibers were contained in I-Chem 8oz. wide mouth amber jars (2-7/8" dia. X 3-3/8" height). For each concentration of dosing solution, 100 ml was placed into the jars. A standard laboratory ring stand was used to support the fixture fitted with fibers throughout the dosing sequence. A stopwatch was used to monitor dosing time.

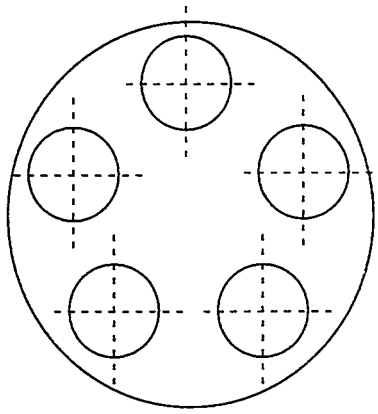

**Figure 2: Schematic of SPME Holder**

In order to insure that the SPME fibers are free of analyte subsequent to analysis, they are "conditioned" according to the manufacturer's recommendation by extended bakeout in flowing carrier gas. The fibers were placed in a heated manifold (220°C) through which dry nitrogen is passed at a flow rate of 5 to 10 ml/min. Construction of this conditioning manifold will not be discussed here, but a picture of a finished unit is included in Figure 3. Conditioned fibers were periodically verified to be "clean", that is, to contain no TNT or interferant compounds, by desorption into the HP6890 gas chromatograph inlet.

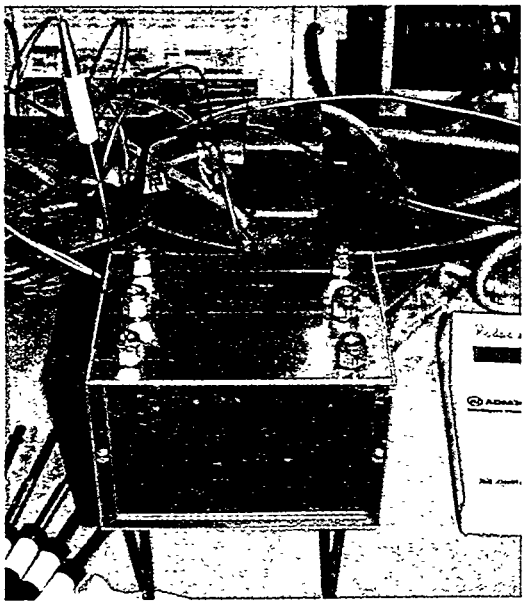

**Figure 3: SPME Conditioning Oven**

The aqueous solutions used to dose the SPME fibers are prepared by means of serial dilution of a TNT stock solution. The stock solution was prepared gravimetrically by dissolving 3X recrystallized TNT in de-ionized water. The concentration of this stock solution is typically 80-90 µg/ml. The stock solution is assayed prior to preparation of the dosing solutions using high-pressure liquid chromatography (HPLC) using EPA Method 8330. As a specific example, for the experiments performed to obtain the results shown below, an intermediate stock solution of 11.5 µg/ml TNT was prepared. Serial dilutions (using HPLC grade water) by factors of 10 yielded solutions with concentrations spanning the range 1.15 µg/ml to 1.15 ng/ml TNT.

An illustration of the experimental set-up prior to actual dosing is shown in Figure 4. The lid is removed from the jar containing the dosing solution, the SPME fibers are extended from their sheaths,

and the five-place holding fixture is carefully lowered such that the fibers are submerged in the solution. At the instant the fibers come in contact with the solution, the stopwatch is started. The fixture is clamped into position, and the solution is allowed to stand undisturbed for the dosing period. Although stirring or other agitation will increase TNT uptake, agitation is not used in this method. Presumably, agitation increases TNT uptake in the fibers by disruption of the depleted boundary layer of solution surrounding the SPME devices. However, in this simple apparatus, agitation was difficult to control in a reproducible manner, and lead to increased variance in repeated dosing of SPME fibers. Dosing is conducted at room temperature (approx. 23°C). Immersion times between 90 seconds and 10 minutes were used to obtain the data plotted in Figures 5 and 6.

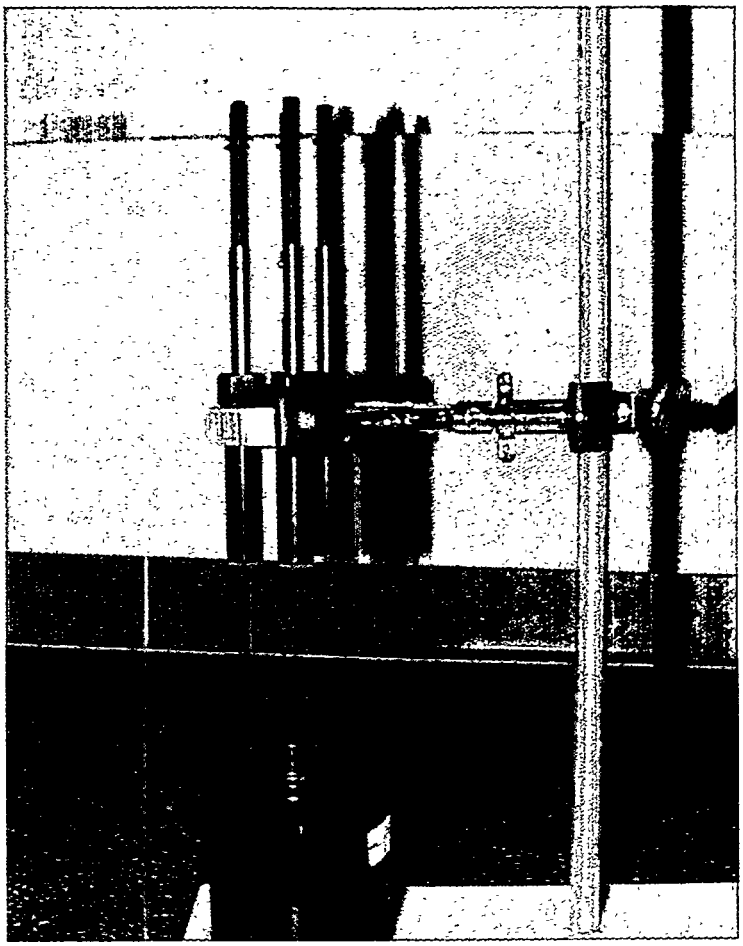

**Figure 4: SPME Dosing Arrangement**

To determine the actual TNT uptake by the SPME fibers during a dosing run, analysis of the fibers by gas chromatography with electron capture detection was used. A Hewlett-Packard model 6890 GC fitted with a 7 meter Restek RTX225 column (0.530 mm ID, 0.10 μ film thickness) was used in these analyses. The inlet was operated in splitless mode at a temperature of 220°C. Carrier gas flow was set to 7.4 ml/min of helium. The temperature program was: 100°C for 2 min., ramp up at 10°C/min to 200°C and hold for 7 min. The ECD was operated at 225°C. A makeup gas flow of 60 ml/min of nitrogen was used.

Plots of TNT mass on individual SPME fibers, as measured by GC-ECD, vs. the product of (aqueous solution concentration) x (dosing time) yield a linear relationship over a wide range of dosing conditions. The representative data shown in Figure 5 were obtained over a period of three weeks. The plot shown in Figure 6 is an enlargement of the low-level dosing region. Figure 6 shows typical variations in TNT uptake over several experiments widely spaced in time.

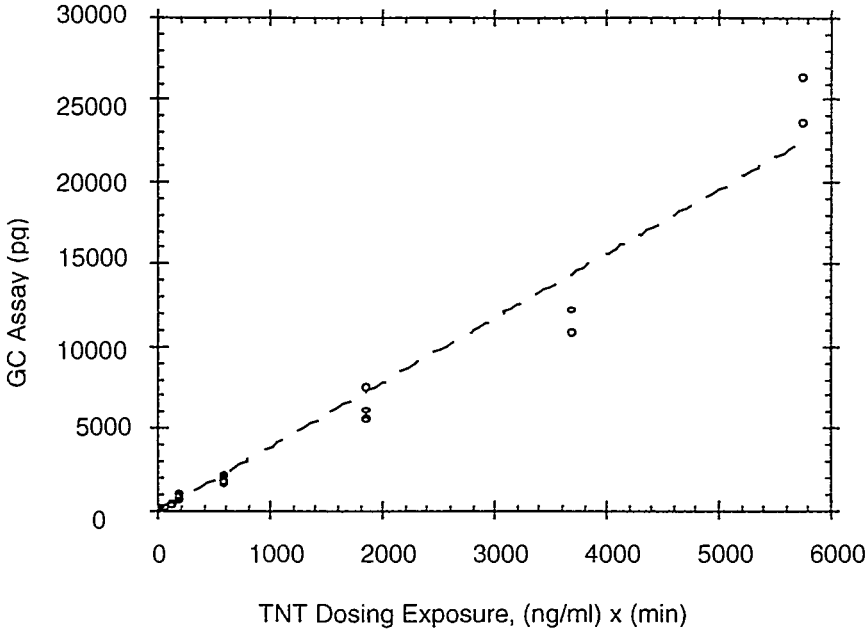


**Figure 5: SPME TNT Mass Dosing Results**

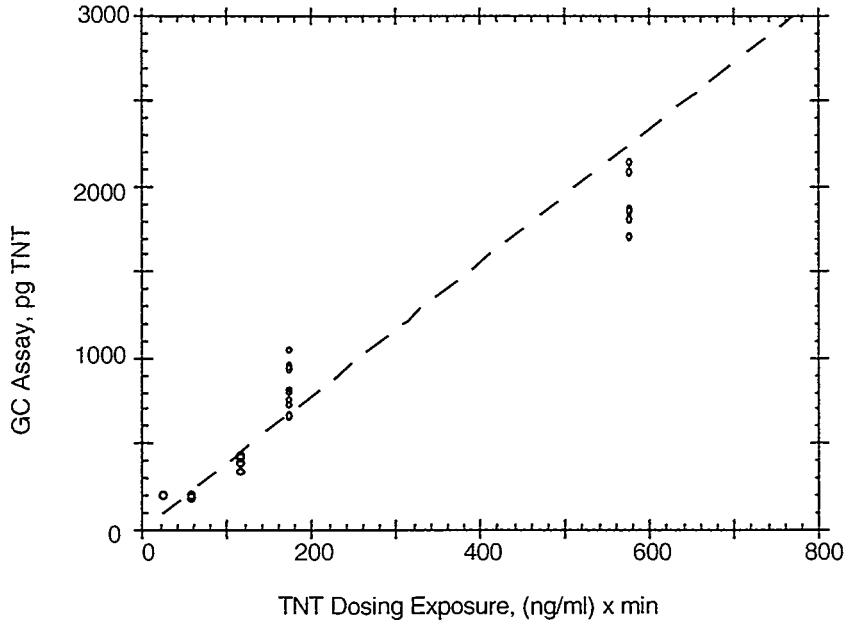


**Figure 6: SPME TNT Mass Dosing Results (Low Total Mass)**

When these dosing experiments were initiated, the set of five SPME fibers in use were evaluated for fiber to fiber uptake variation by identically dosing them, and then assaying them via GC. The initial results showed fiber to fiber variation to be approximately 7%

(std deviation/ mean). As the fibers aged through repeated dosing cycles, this variation tended to grow. After repeated dosing, desorption, and reconditioning cycles, duplicate identically dosed fibers have shown fiber to fiber variation of up to 15%. Based on these data, the SPME fibers are estimated to have a useful life of approximately 50 cycles. However, the extended high-temperature conditioning used in these experiments to guarantee avoidance of cross contamination between measurements is believed to contribute significantly to the "aging" of the fibers. Optimization of the high-temperature conditioning cycle could significantly improve fiber life.

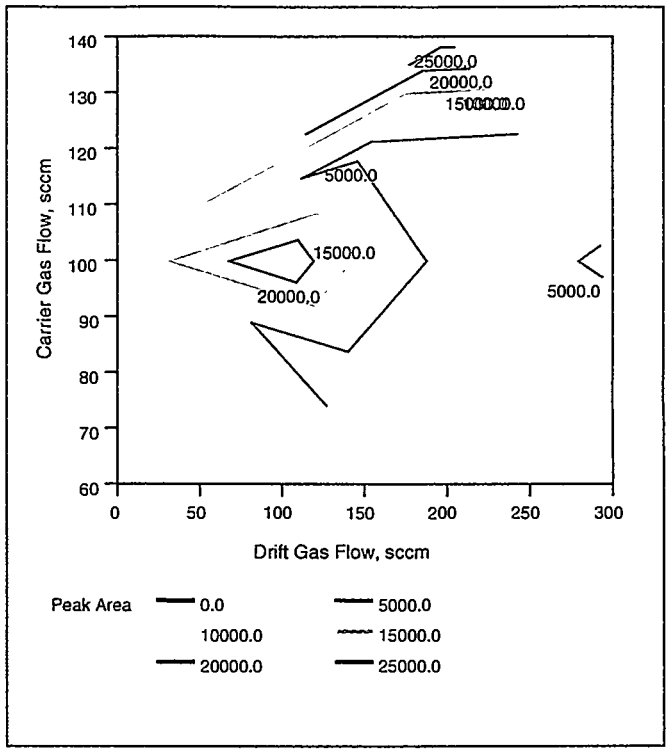


**Figure 7: Contour Plot of IMS TNT Response vs. Gas Flows**

## IMS Response vs. Instrument Operating Parameters

Using the SPME dosing method outlined above, a series of measurements were run on the PCP111 and ERG IMS instruments, using a constant mass of TNT (approximately 400 pg) to test the dependence of the instrumental response on four operating parameters: The inlet temperature (°C), the drift tube temperatures (°C), the carrier gas flow rate (standard cc/min), and drift gas flow rate (standard cc/min). Commercially available statistical experimental design software was used to choose a series of parameter settings for optimization of the IMS instrument response to TNT presented on a SPME fiber. Results of these tests for the PCP111 IMS are summarized in Figures 7 and 8, which display contour plots showing the response of the instrument vs. the operating parameters. Gas flow settings were assumed to be independent of temperature settings. Examination of the instrumental response data supports this assumption.

Based on the response surface in Figure 7, the PCP 111 operating conditions used during the underwater UXO detection field trials (200°C drift tube, 175°C inlet temps; 200 ml/min. drift gas, 100 ml/min carrier gas flows) were not the absolute optimal conditions for TNT detection in this instrument. However, although the gas flows used in those field trials were not optimal for maximum signal, they are what the instrument manufacturer recommends. More importantly, use of those recommended flow settings

allows for a more rapid purging of the instrument, thus preventing lingering background TNT signals. Such signals were observed when the drift and carrier flows were closely matched.

Several attempts were made to measure a sufficient number of instrumental response points in order to construct similar optimization contour plots for the ERG IMS instrument. However, the instrument was found to be susceptible to internal high voltage breakdown, particularly when the drift cell and inlet temperatures were increased. Accordingly, the ERG instrument was disassembled and reassembled several times, with electrical insulators between high-voltage elements of the drift cell replaced each time. The assembly of the ERG cell currently requires the use of sheet mica electrical insulation with thickness on the order of 0.004 inch. After repeated attempts, it was determined that stress cracking in the mica was a contributing factor in the deterioration of the electrical insulation at higher operating temperatures. A complete data set for full response surfaces, analogous to those displayed in Figures 7 and 8, was not obtained for the ERG instrument. Operating parameters used in the determination of the ERG instrumental sensitivity to TNT were based on the available response surface data and on observations of clearing times for TNT following injections at higher masses. The observation of high-voltage breakdown in the ERG cell led us to pursue two additional tasks. The first is characterization of a third cell design, obtained from Professor Gary Eiceman's laboratory at New Mexico State University, Las Cruces. This IMS design will be hereinafter referred to as the NMSU instrument. The second is a series of modifications of the ERG design, in order to avoid electrical breakdown. These modifications will be discussed later in this report.

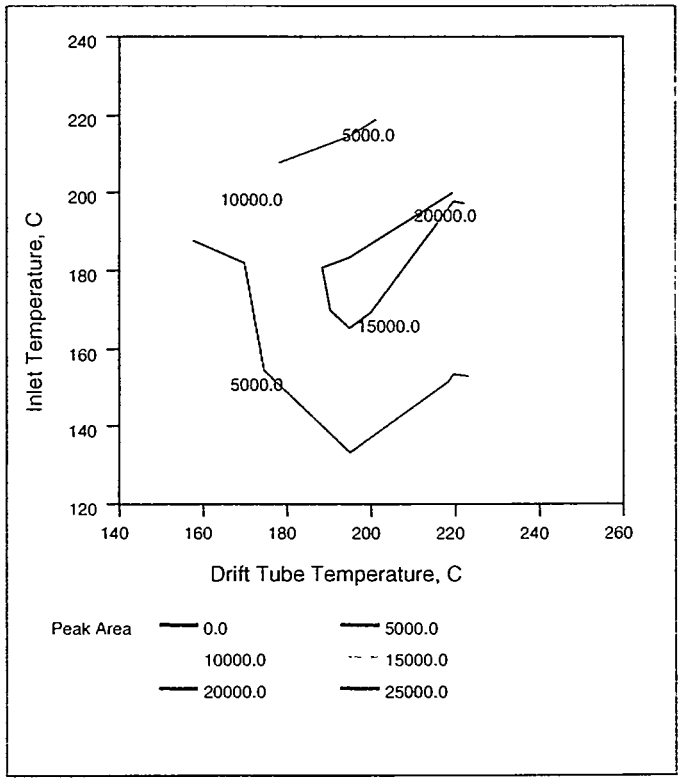


**Figure 8: Contour Plot of IMS TNT Response vs. Temperatures**

## IMS Data Reduction Method

The PCP111 IMS is used as the benchmark for TNT detection, since this instrument has been used to successfully identify underwater UXO items in field tests [8]. A laboratory comparison of the responses of the PCP, ERG, and NMSU instruments for TNT was obtained. The performance data was obtained by repeated injections of TNT into the three instruments, using the SPME fiber doping procedure described in detail above. This provides confidence in consistent analyte mass delivery. In practice, the data for each TNT injection were logged in a manner analogous to the IMS data displayed in Figure 1. Data files contained a series of fifty ion mobility spectra for each TNT injection. In order to compare results between the different instruments, a consistent means of data reduction must be applied. The amplitude of the signal from an IMS instrument is proportional to the ion current flowing through the drift tube at a given elapsed time. Since each instrument used in this study has somewhat different gain in the multiple amplification stages of the electrometer and the A/D converter used to log the data, the vertical axes for signal plots from the instruments are not directly comparable. In order to quantitatively compare the responses of the different instruments, a consistent procedure was used to determine the peak amplitude of the response of a given instrument to a given mass of TNT injected. A drift time interval where no peak appeared was selected, and the mean of the amplitude in this interval was calculated. This mean baseline amplitude was subtracted from the measured amplitude of each point within a fixed drift time interval for the TNT peak, for the highest-amplitude trace captured during data acquisition for each injection. These values were squared, summed, and the square root of the resulting sum was reported as the amplitude of the TNT peak. An example is illustrated in Figure 9, which displays a single IMS spectrum trace from an injection of TNT into the PCP instrument. The large peak at data channel 100 (on the

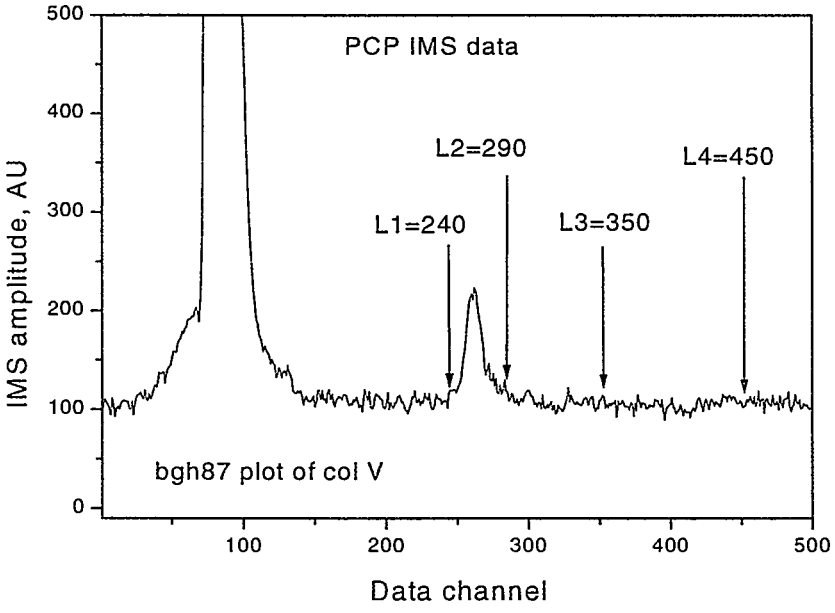


**Figure 9: Data Channels Used for Reduction of PCP IMS Spectra**

horizontal axis) is due to the Cl- reactive ion peak. The TNT peak appears in channels 240-290. The average background levels for PCP IMS spectra were calculated using the data values in channels 350-450. A similar procedure was followed for reduction of data from the ERG and NMSU instruments.

Repeated measurements of TNT peak amplitude and of blank injections were recorded. The variance of these repeated measurements was assumed to be normally distributed. Subject to this assumption, the standard deviation of repeated measurements is representative of the noise associated with the measurements. The "noise-limited detection level" for each instrument was estimated from the available data by calculating the upper limit of the standard deviation interval for repeated measurements of blanks, where no TNT was injected.

Comparison of the instruments has been conducted based on a simple IMS response model [4]. This model assumes that the characteristic nonlinear response of an IMS to increasing analyte mass can be attributed to the depletion of dopant ions in the chemical ionization of the analyte. For the negative-ion detection of TNT discussed here, the relevant dopant ion is $Cl^-$, formed by the $^{63}Ni$ beta ionization of $CH_2Cl_2$ dopant gas. Writing the reactant ion, $Cl^-$, as $R^-$ and the product TNT ion as $P^-$:

$$R^- + P \rightarrow R + P^- \qquad \text{(eq. 2)}$$

Assuming that this bimolecular reaction obeys first-order kinetics, then

$$dn_p/dt = -(dn_R/dt) = KNn_R \qquad \text{(eq. 3)}$$

where $n_R$ = reactant ion density, $n_p$ = product ion density, N = neutral analyte vapor density, and K = the first order rate constant for the reaction. Separating the variables and integrating the rate equation yields

$$\int dn_R/n_R = -\int KNdt \qquad \text{(eq. 4)}$$

$$n_R = n_R^0(e^{-KNt}) \qquad \text{(eq. 5)}$$

Assuming conservation of charge in the bimolecular reaction:

$$n_R + n_P = n_R^0 \qquad \text{(eq. 6)}$$

Substituting this relation in the integrated rate equation yields

$$n_P = n_R^0 - n_R = n_R^0(1 - e^{-KNt}) \qquad \text{(eq. 7)}$$

Thus, if the IMS signal is limited by depletion of the reactant ions, then the measured plot of IMS signal vs. TNT injected can be fit to an equation of the form

$$y = a(1-e^{-bx}) \qquad \text{(eq. 8)}$$

with a ~ [Cl-] and b ~ Kt, the chemical ionization probability.

Use of the above fitting equation allows for comparisons to be made in the response of the instruments vs. injected mass, as will be seen below.

The results to date for the characterization data acquired using the three IMS instruments are summarized in Figures 10-13.

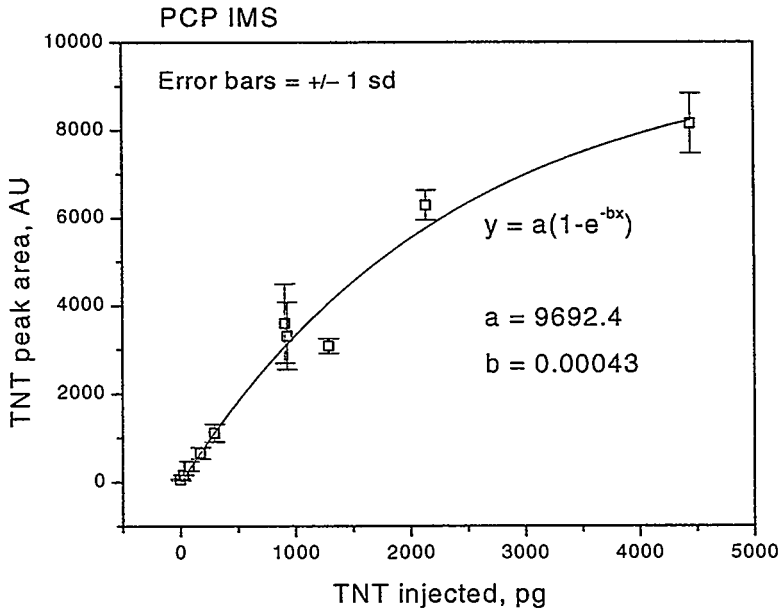


**Figure 10: PCP 111 Response to TNT Injected on SPME Fibers**

In each figure, the available data have been fit to the form of Equation 7, as indicated above. Further, the noise limit of detection based on the available data is presented. Thus it can be seen from a comparison of the figures that the noise limit of detection for the NMSU instrument, as currently configured, is significantly higher than for the other instruments. This analysis does nothing to define the source of the noise. Since each instrument uses different electronic circuitry, the performance difference cannot be directly attributed to the characteristics of the individual IMS cells. Only the overall performance as currently configured can be compared here.

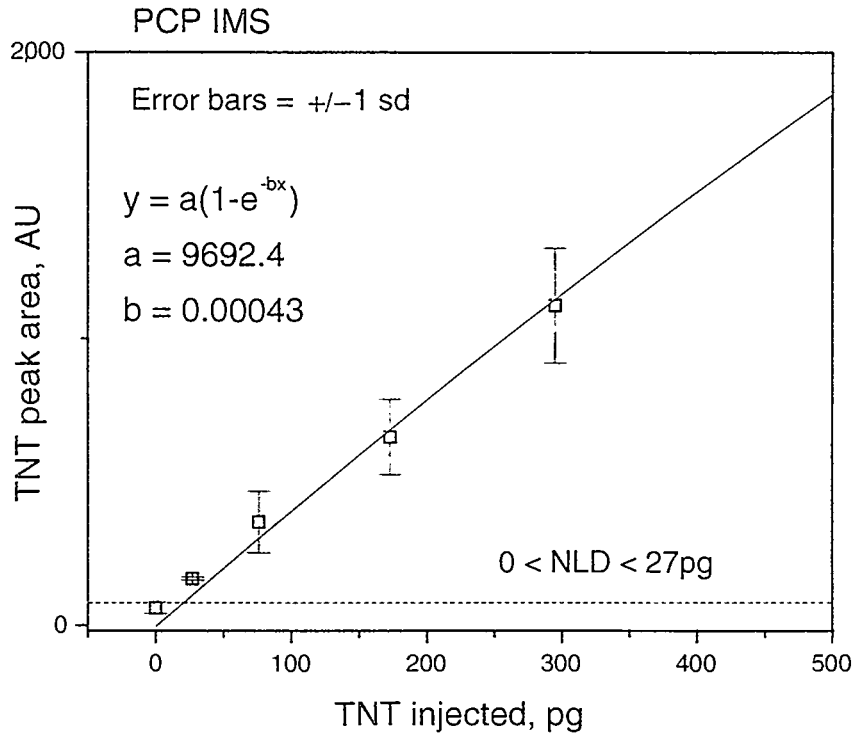


**Figure 11: PCP 111 Response to TNT Injected on SPME Fibers, Detail**

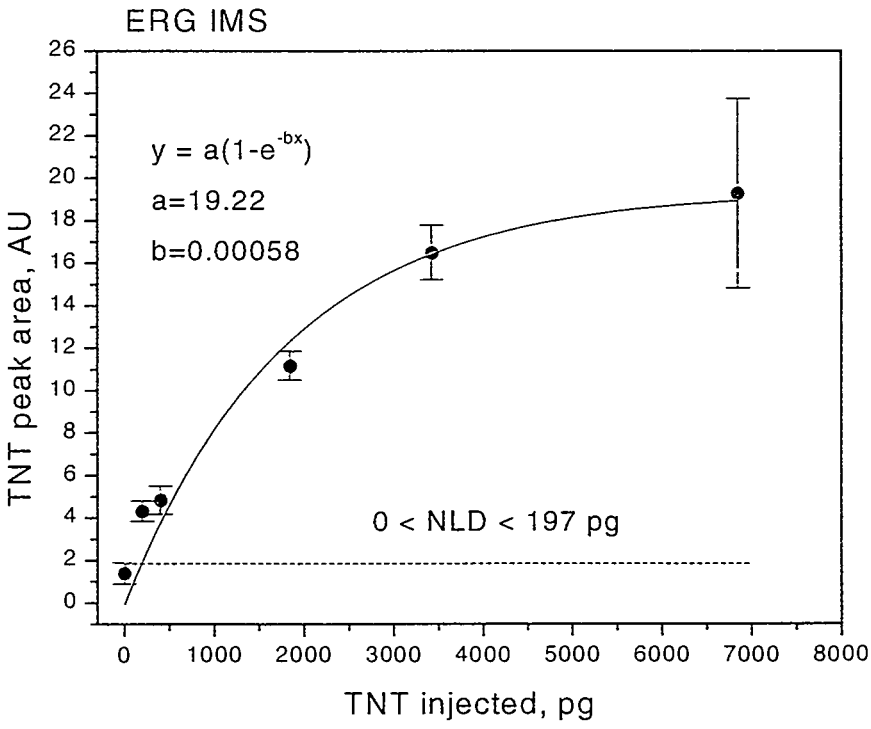


**Figure 12: ERG Response to TNT Injected on SPME Fibers**

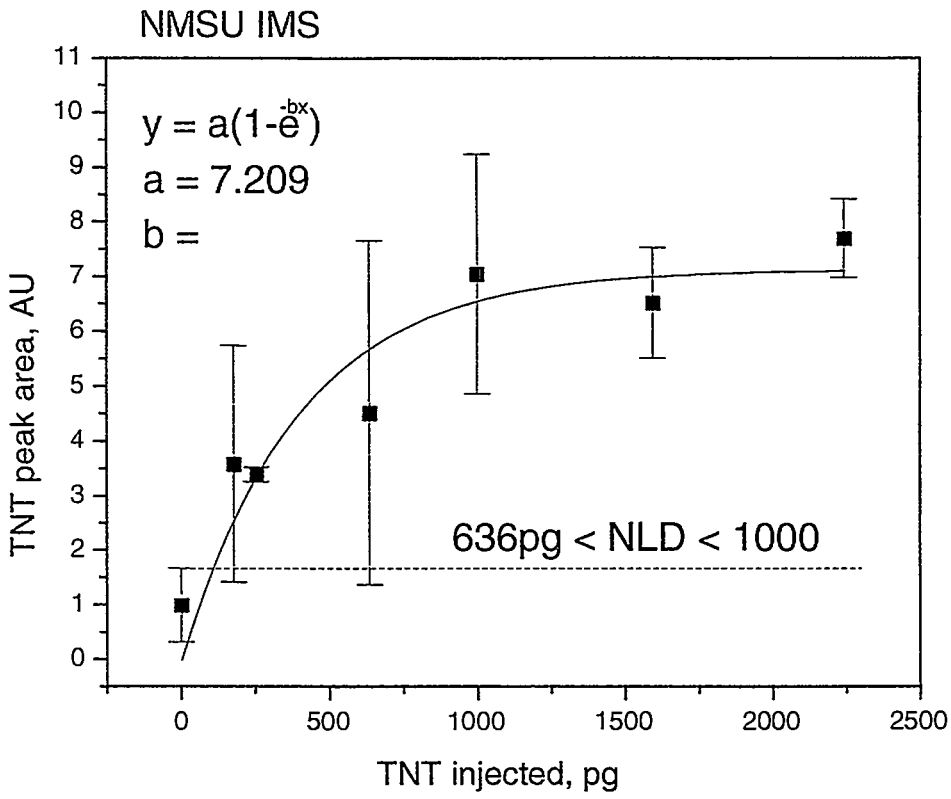


**Figure 13: NMSU Response to TNT Injected on SPME Fibers**

The scale parameter, *a*, of the fits shown in Figures 10-13 has, of necessity, the same arbitrary units as the reported peak amplitude for each instrument. Thus, scaling the response data by the respective values of the *a* parameter results in a dimensionless y-axis plot with maximum amplitude asymptotic to the value 1, as shown in Figure 14. This plot is included in order to compare the dynamic range and slope of response vs. TNT injected for the three instruments tested. There is significant variance in the data, particularly for the NMSU instrument, and therefore the values of the fitting parameters can vary within a rather wide range. Thus the absolute magnitude of the fitting parameter b should not be taken as a quantitative measure of instrumental sensitivity. Given that disclaimer, the plots shown in Figure 5 can be *qualitatively* interpreted to indicate that the PCP111 and ERG instruments are comparable in secondary ionization efficiency, and the NMSU instrument has an ionization efficiency which may in fact be greater than that of the other two instruments. This interpretation cannot separate possible effects contributing to the efficiency of the overall cell design. It is confined by the parameterization assumptions of the model to a description of secondary ionization efficiency in the ionization region of the IMS cells.

In summary, on the basis of the available data it can be stated that the PCP111 has the lowest measured NLD value. The ERG instrument, has comparable performance to the PCP, and has a value for the NLD of 0 < NLD < 197 pg. Based on Sandia National Laboratories' experience with field demonstrations of the IMS technology, this sensitivity should be adequate for detection of some forms of UXO in the marine environment. The performance of the NMSU instrument, based on the data available to date, is poor compared to the PCP111 benchmark and to the ERG instrument, but the poor performance is likely to be attributable to electronic noise sources in the overall system. The secondary ionization efficiency of the NMSU instrument is good, again

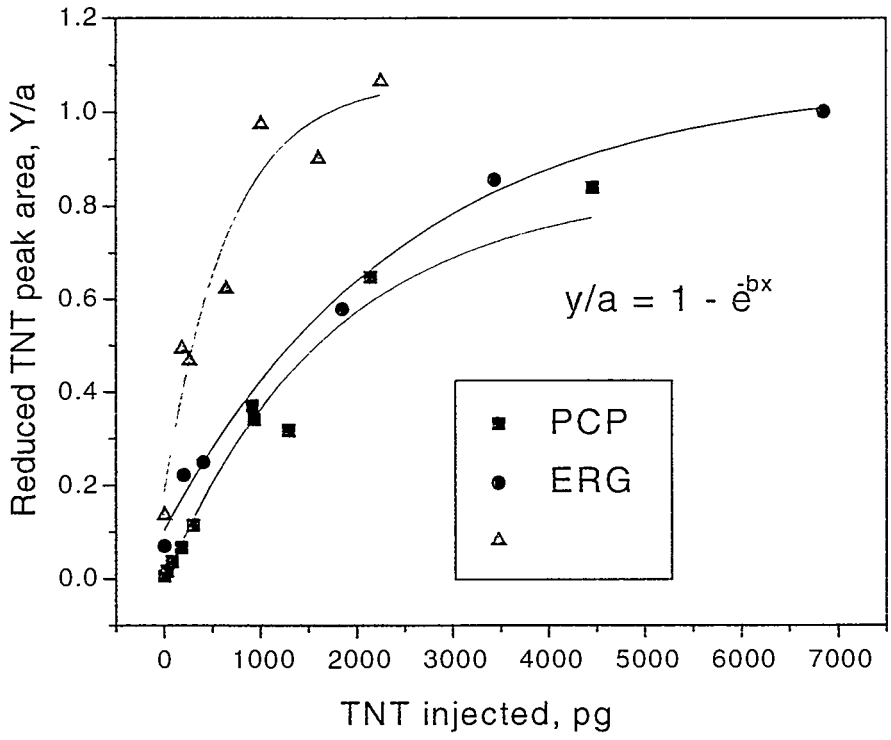


**Figure 14: Scaled Response of the Three IMS Instruments vs. TNT Injected**

based on the limited data available. The reduced response plots of Figure 14 indicate that the NMSU instrument may potentially have the "best sensitivity" of the three instruments, as measured by the steepest slope of response at low analyte mass. The noise limitations, however, dominate this signal response and limit the usefulness of the instrument in the present configuration. The dynamic range of the instruments decreases as the slope of response increases. The IMS response model applied here is based on consideration of the secondary ionization reaction efficiency. However, the overall

performance of the various instruments is due to the ionization efficiency plus contributions from other possible effects (e.g., drift tube and ion collection performance). These various factors in the performance of the three cells are not individually quantified when using this model to interpret the data.

## Automated Sampling

The characterization of the IMS instruments described above was conducted using manually operated SPME sampling apparatus to inject TNT into the instruments. The field demonstration described in reference 1 utilized a simple sampling scheme, with a water flow channel located near the inlet of the IMS. The sample water flow was separated from both the IMS inlet and from the manually-actuated SPME fiber holder by standard methylsilicone septa. This arrangement is illustrated schematically in Figure 15. Water flow rates on the order of 1 liter/minute were used in the field demonstrations. The protective syringe containing the SPME fiber was first injected through the outer septum, after which the SPME fiber was extended into the water flow. Sampling times on the order of 2-5 minutes were used to detect actual UXO items in St. Andrews Bay, Panama City,Florida [1]. After sampling, the SPME fiber was retracted into the protective syringe, and a further linear translation of the syringe was performed in order to extend the assembly through the second septum, and into the heated inlet of the IMS. At that point, the SPME fiber was again extended from the syringe, and the sample desorbed into the IMS. Therefore, two independent, coaxial linear translations of the SPME apparatus are required for each sampling cycle. One of the tasks conducted under the Lockheed-Martin/Sandia National Laboratories Shared Vision project was automation of these linear translations, with the ultimate goal of placing the sampling cycle under software control in order to allow autonomous operation of the combined sampler/sensor system.

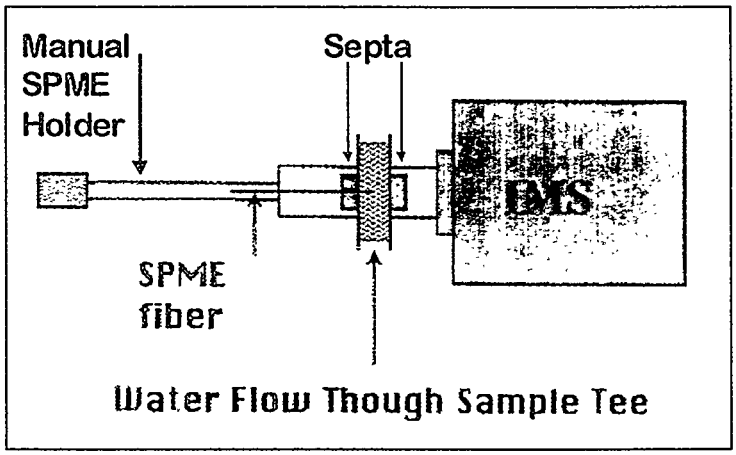


**Figure 15: Schematic Layout of Manual SPME Sampling System**

The prototype automated SPME interface operates essentially identically to the manual device. The operational sequence is relatively simple. First, the SPME fiber, which is encased in a hypodermic needle, is inserted through a septum into the water stream. The

SPME fiber is then extended and allowed to absorb explosive from the water. After a sufficient amount of time, the SPME fiber is withdrawn into the needle, which is then translated into the desorption region of the IMS. The SPME fiber is then exposed to desorb any explosives. At the end of the desorption cycle, the SPME fiber is retracted, the needle moved to the initial location, and the system is ready for additional cycles. These two required linear translations have been automated. The prototype was constructed using commercial off-the-shelf components where possible, and will need to be ruggedized to allow successful installation into a portable field UXO classification sensor. The drive mechanism for the device is based on a cam system for the primary translation (movement of the protective syringe through the septa) and a direct drive for the secondary translation (extension of the SPME active surface into the flowing analyte stream and into the inlet of the detector). We anticipate that in the next-generation device the secondary translation will also be cam-driven. Thus, the control logic for operation of the device will consist of two on/off lines, one for the primary translation and one for the secondary. A design layout for the automated sampling apparatus is shown in Figure 16, which is reproduced as a full-page image for clarity.

## Combined System Demonstration

On December 15, 1999, successful detection of TNT in a flowing analyte stream was demonstrated using the automated sampler in conjunction with the NMSU IMS cell. The NMSU cell was used for this demonstration because the ERG cell had been disassembled for the purpose of making mechanical modifications described below. During the automated sampler demonstration, the SPME fiber was exposed to the analyte stream for 10 seconds prior to injection. Typical exposure times for the field demonstrations previously conducted by Sandia National Laboratories were on the order of 2 to 5 minutes. The analyte matrix used was "Instant Ocean", a commercial product used to produce salinity in saltwater aquariums. This artificial ocean water was spiked with TNT for the demonstration. Aliquots from the original TNT concentration and a second concentration produced by dilution in "real time" were post-analyzed by HPLC. The original concentration was 8.47 micrograms TNT/g $H_2O$, and the second, diluted concentration was 0.18 micrograms TNT/g $H_2O$. TNT signals were observed in "real time" for SPME injections following exposure to both solutions. Digitized instrument response data were captured during the demonstration runs, analogous to the manner described above the instrument characterization data displayed in this report. The combined system (NMSU IMS cell plus prototype automated sampling system) is shown in Figure 17.

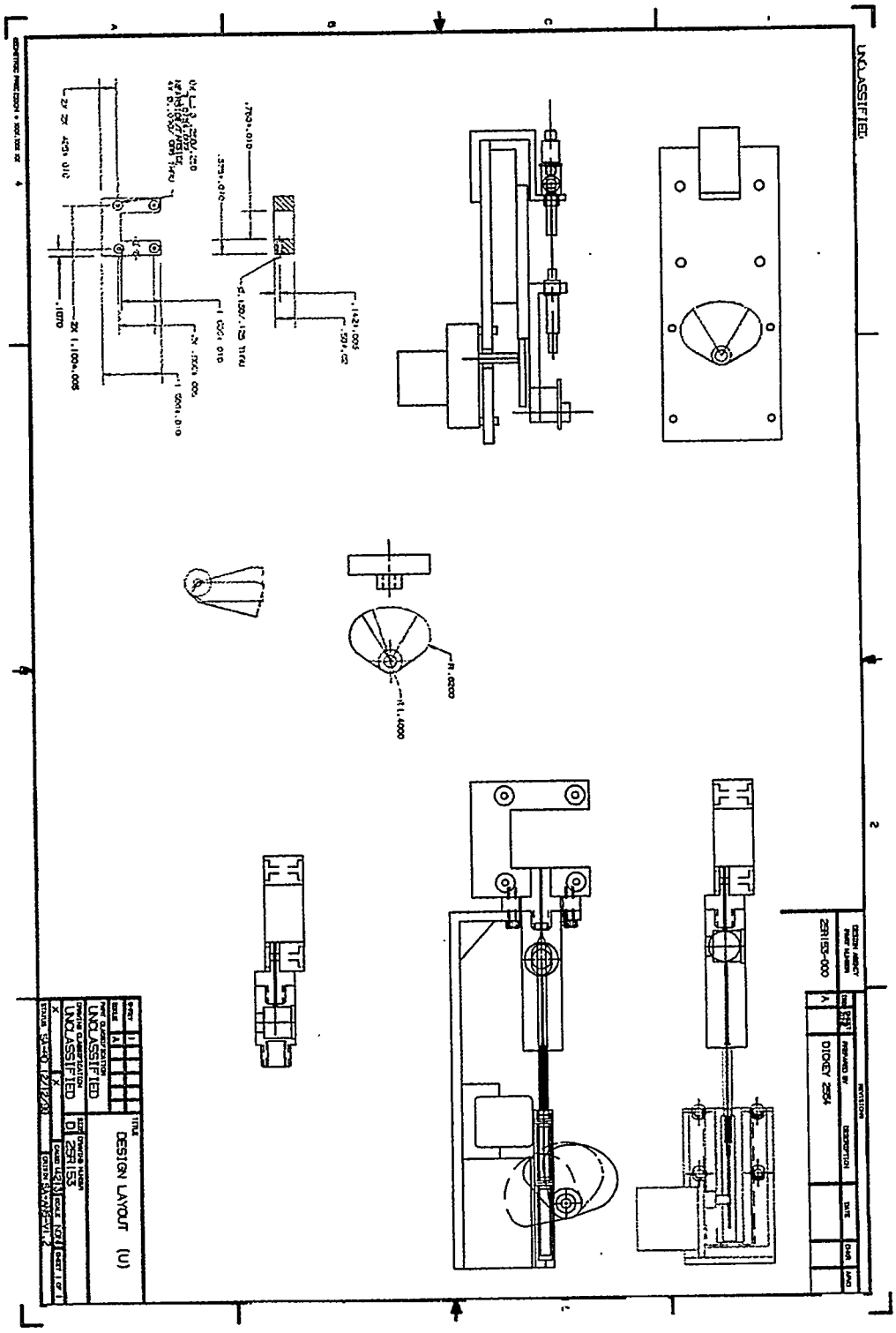


**Figure 16: Automated Sampler**

# Modifications of the ERG Design

The IMS performance characterizations reported herein indicate that the sensitivity of the ERG IMS cell is adequate for the task of classifying undersea UXO items. However, this cell repeatedly exhibited intermittent high-voltage breakdown during the course of these measurements. To address this problem, we have reviewed the design and operation of the ERG cell with high-voltage component designers from Sandia National Laboratories' Firing Set and Optical Engineering Department. This review resulted in four recommendations for improving the breakdown resistance of the ERG cell. These recommendations were intentionally limited to changes that could be incorporated without radical changes in the mechanical design of the instrument. Thus, options which would require re-characterization of the device as an explosives detector were avoided. During January 2000 we implemented three of the four recommendations. The fourth requires a significant redesign of the instrument control electronics, and was therefore judged to be impractical in the limited time remaining under Phase I of this Shared Vision project.

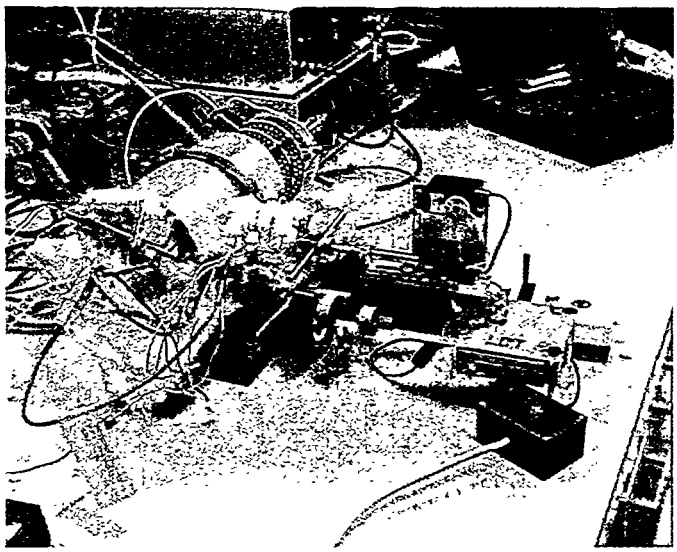

**Figure 17: Automated SPME Sampling System Mounted on NMSU IMS**

The design changes can be briefly described as follows. The ERG cell is a miniaturized version of a standard IMS drift tube design, and thus consists of several electrodes in a "stack", separated by insulators. This stack of mechanical components, with heating elements, insulation, gas handling, and control circuitry removed, is shown in Figure 18.

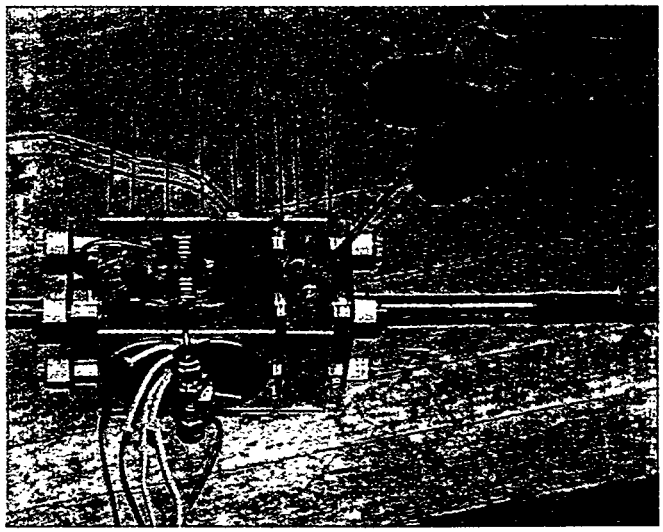

**Figure 18: ERG IMS Drift Cell**

The gradual change in voltage along the drift tube results in moderate voltages between adjacent electrodes. However, at the ends of the stack the voltage gradient is relatively high. The original ERG design used natural mica insulation

of approximately 0.004 inch thickness to support a voltage difference of ~2kV at specific points. The resulting gradient, ~500 volts/mil, is near the dielectric breakdown for almost all materials normally considered "good insulators". Therefore, special attention was paid in the design review to these points in the electrode stack. It was recommended that the metal electrodes at these points, which had been fabricated with minimal dimensional radii at "corners", should be re-machined in order to make the radii larger than the thickness of the insulators. This is a standard means of avoiding breakdown due to high local fields. In addition, a second layer of mica was added at these points to increase the total thickness of the insulation, and to reduce the possibility of localized breakdown due to defects in the natural material. This could be accomplished without extensive dimensional redesign of other mechanical components of the drift tube. Third, the faces of the metal electrodes at these points were polished to remove any machining asperities that might result in high local electric fields.

The fourth recommendation resulting from the design review was a redesign of both the mechanical electrode stack and the high-voltage power supply, so that the drift cell could be operated as a bipolar rather than unipolar device. This would lower the voltage with respect to ground by a factor of two. However, the extensive mechanical redesign required to electrically isolate both ends of the stack, rather than one end as in the current unipolar design, was deemed impractical within the one-month time frame available. In addition, modification of the high voltage supply to a bipolar design would be required. Therefore, work on this modification has been deferred until a later date.

# Summary

The U.S. Navy has an operational need for low-cost sensors capable of classifying targets detected by sonar or other sensors as ordnance, or as non-explosive objects. Prior to the work reported here, Sandia National Laboratories researchers had successfully demonstrated UXO identification in shallow ocean environments using a combination of trace explosives preconcentration and ion mobility spectrometry (IMS) detection. This work has pushed the technology toward the long-term goal of an autonomous, low-cost, field-deployable IMS sensor for maritime UXO classification. Our objectives have been to improve the mechanical and electronic robustness of the sensor, decrease the size, and automate the sampling and preconcentration cycle, while maintaining explosives detection capability adequate for the classification of underwater UXO.

The previous demonstrations of UXO identification were made using a PCP111 ion mobility spectrometer as the explosives sensor. Laboratory characterization of this instrument found that the effective detection limit of this device for TNT desorbed from SPME fibers was <27 pg. By comparison a small IMS sensor, considered as a candidate for incorporation into an autonomous field detection system, displayed a TNT detection limit of <197 pg. The IMS response data were evaluated using a simple model that attributes the characteristic limited dynamic range of these detectors to depletion of reactant ions in the chemical ionization of the TNT analyte.

The sensitivity of the small IMS cell should be sufficient for classification of UXO items in marine environments, given sufficient sampling time. However, the small IMS design suffered operational failures in the laboratory due to intermittent high-voltage breakdown. The device has been modified in an attempt to reduce these failures.

We have demonstrated a laboratory prototype system that incorporates an automated solid-phase microextraction (SPME) sampler and a reduced-size IMS cell design. We have demonstrated that the detection capability of such a system is adequate for UXO identification. The technology is now of sufficient maturity that a packaged, submersible, field-deployable IMS sensor and preconcentration unit can be confidently designed and prototyped. The ultimate goal of deployment on an autonomous underwater platform will require interface design input from the owner(s) of candidate platforms.

In addition to the maritime UXO application, we have prepared a study of other potential commercial and military applications of ruggedized, miniaturized IMS chemical detectors, including CBW defense, counterterrorism, agricultural, environmental, law enforcement, and forensic applications. This study has identified additional high-payoff applications for the IMS technology. The results of that study have been presented in a companion report [9].

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[9] "IMS Applications Analysis", Philip J. Rodacy, Robert J. Simonson, Stephen D. Reber, and Bradley G. Hance, Sandia National Laboratories, in press, 2000.

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