

AN EXPLOSIVE VAPOR GENERATOR BASED ON
CAPILLARY GAS CHROMATOGRAPHY

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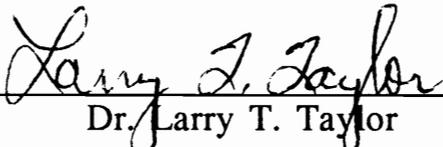
George Allen Reiner

Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

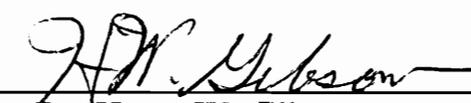
DOCTOR OF PHILOSOPHY
in
Chemistry

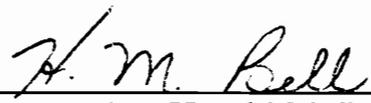
APPROVED:


Dr. Harold M. McNair, Chairman


Dr. Larry T. Taylor


Dr. John G. Mason


Dr. Harry W. Gibson


Dr. Harold M. Bell

November, 1990
Blacksburg, Virginia

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George Allen Reiner

Committee Chairman: Dr. Harold M. McNair
Chemistry

(ABSTRACT)

An explosive vapor generator which produces transient "clouds" of explosive vapors for use in the evaluation of commercial explosive vapor detection systems has been developed based on a capillary gas chromatograph. The design of the vapor generator replaces a flame ionization detector on the gas chromatograph with an effluent heater system to provide a cloud of explosive vapor while preventing condensation onto the walls of the capillary column.

This vapor source has been successfully used to produce vapors of dinitrotoluene (DNT), trinitrotoluene (TNT), and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX). The chemical composition of the output was confirmed by both ion mobility spectrometry, and quadrupole mass spectrometry. Adsorptive effects of TNT and RDX were studied in order to optimize the injection parameters, achieving detection limits three orders of magnitude lower than previously reported. The quantitative output of the system was verified using thermal tube desorption gas chromatography.

Acknowledgements

In a work such as this, there are obviously many people who have assisted in various forms, and I hope than I can adequately acknowledge their contributions. First, I would like to thank Dr. Harold M. McNair, my major professor, for his guidance and for the opportunity to perform research under him. Second, I would like to thank several of my chemistry graduate student colleagues for their support through friendship and technical conversations. These graduate students include Dr. Lee Polite, Dr. James Frazier, Dr. Bill Wilson, Dr. Henry Rasmussen and Nick Snow from Dr. McNair's research group, and Joe Hedrick and Leah Mulcahey from Dr. Taylor's research group. Of special note are Greg Slack and Cheryl Heisey, graduate students who assisted in testing various modifications of the vapor generator, as well as Nick Snow and Leah Mulcahey, who assisted in proof-reading this dissertation.

Third, I would like to thank the monetary support of Mr. Louis Wasserzug of the Naval EOD technology center in Indian Head, MD., Ms. jennelle Derrickson and Mr. Carmen Munafo of the FAA technical center in Atlantic City, NJ, and Mr. Henry Odom of the Naval Surface Warfare Center in Dahlgren, VA. It was the support of these people through NSWC contract #N60921-83-G-A165 B042 that enabled this research.

Fourth, I would like to thank the technical advice and support of Mr. Frank Conrad and the explosive vapor detection group at Sandia National Laboratories in Albuquerque, NM. Mr. Conrad and his group were

instrumental in getting this project started on the right track. Throughout this project, Mr. Conrad's straight-forward advice was greatly appreciated.

Fifth, I want to acknowledge the assistance of Dr. Robert V. Foutz from the Virginia Tech Statistical Consulting Center. Dr. Foutz developed the statistical testing procedure used in chapter 4 of this dissertation.

Sixth, I wish to acknowledge the many teachers whose efforts have touched my life and work including: Dr. Neidig, Dr. Cornelius, Dr. Dahlberg, Dr. Moe and John Uhl of Lebanon Valley College; as well as Mr. Stuckey, Mrs. Jones and Mr. Yenser of Lebanon High School. I only wish that space permitted me to detail the many contributions each of the above teachers has made to my education.

Seventh, I want to thank Emma B. Reiner, my mother, Emma A. Reiner, my sister, Robert D. Reiner, my brother, and Kristen G. Reiner, my wife for their support and sacrifices while I pursued higher education. Kristen has also helped as a proof-reader of this dissertation.

Finally, I wish to dedicate this dissertation to the memory and in honor of the two John Reiners in my life. Dedicated to the memory of John H. Reiner, my father, who despite having only made it through the eighth grade, had the foresight to make the necessary sacrifices to enable me to complete my education. Dedicated to the honor of John A. Reiner, my son, whose arrival this past year has not only added an entire new dimension of happiness to my life, but also was the major motivating factor in my completion of this work.

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Chapter 1. Introduction

1.1 Bomb Detection

The advent of easily concealed plastic explosives as well as the escalation of terrorist sponsored bombings during the 1970s and 1980s has focused attention on various ways of preventing terrorist bombings (1). As part of an effective anti-terrorist program, the problem of explosives detection presents interesting opportunities to the analytical chemist. Different analytical methods of explosives detection can be divided into four primary groups, including tagged identification, untagged identification, bulk detection and vapor detection (2).

Tagged identification of explosives primarily involves incorporating chemical additives into explosives during manufacture. These additives, which are easily detected, can be chosen to assist either with detection or with identification of the explosive to which it is added. Normally, electric blasting caps, commonly used for detonators, are tagged for detection, and packaged explosives are tagged for identification (3). Although it is important for packaged explosives to be detectable, detonators are tagged for detection because they are essential parts of bombs which, due to high design tolerances, are much more difficult for terrorists to manufacture (4). Many techniques can be used in the tagging of packaged explosives for identification of source (5-9).

Untagged identification of explosives involves the use of common analytical techniques to determine the source of an explosive material. This type of explosives detection is primarily used for post blast analysis of residues (10). Techniques included in this form of analysis include liquid chromatography/ion mobility spectrometry (11), electron paramagnetic resonance spectroscopy (12) and inductively coupled plasma atomic emission spectroscopy (13). Chromatographic techniques, including gas chromatography (14-21), liquid chromatography (20, 22), supercritical fluid chromatography (23, 24) and thin layer chromatography (25) are often used for untagged analysis of these compounds. Very recently, tandem mass spectrometry (26) and ion trap mass spectrometry have been used for untagged explosive analysis (27).

The next two modes of explosive detection, bulk detection and vapor detection, are used primarily for search applications; that is, looking for an undetonated explosive device. The bulk detection mode is used mostly for detection of explosives in articles such as packages, baggage and the like. In this type of search situation, analytical techniques which would normally be unusable on a personal search are permitted. Most of the techniques employed for bulk detection involve x-ray techniques (28-30), nuclear magnetic resonance (31, 32) and thermal neutron activation analysis (33, 34). Thermal neutron activation analysis (TNA) has been quite successful in bulk detection and is now the method used to scan airline baggage at several major United States airports.

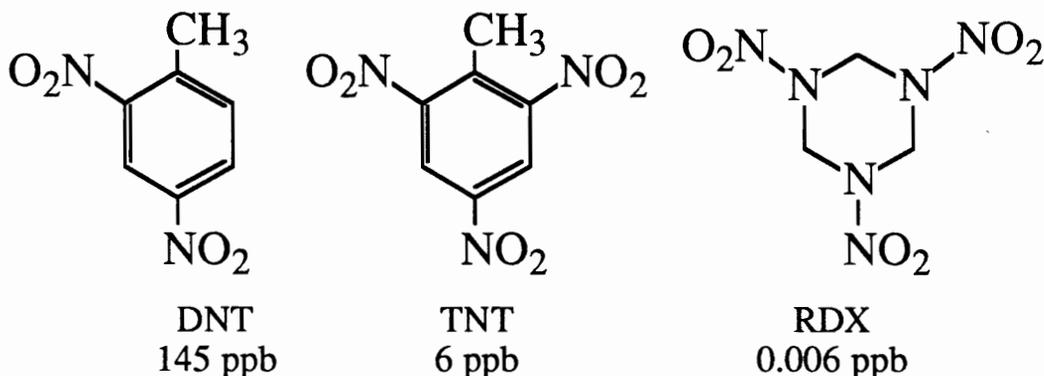
Despite the success of TNA analysis in the area of bulk detection, few people would willingly submit for body scanning by thermal neutrons. For this reason, the last mode of explosive detection, vapor detection, is needed to permit searches for bombs carried by people. Currently techniques for vapor detection include mass spectrometry (35-40), ion mobility spectrometry (41, 42), animal olfaction (43-46), spectroscopic techniques (47-49) and gas chromatography/electron capture detection (50-52). Portable explosive vapor detectors are usually based on ion mobility spectrometry (IMS) or gas chromatography/electron capture detection (GC/ECD) systems.

1.2 Naval EOD Technology Center Study

During the spring of 1988 we were approached by a representative of the Naval Explosive Ordnance Disposal Technology Center (NAVEODTECHCEN) at Indian Head, MD, who was interested in having us study the sensitivities of portable explosive vapor detection systems. This project had two major goals: to compare the sensitivities of several commercially available portable explosive vapor detection system relative to each other, and as a benchmark, to relate the sensitivity of the best explosive vapor detection system to the sensitivity of a commercial GC/ECD system .

Although there are a wide range of explosives available (53), this study involved only three characteristic compounds. The compounds, which are representative of the majority of explosive classes, are 2,4-

dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX). The structures and relative vapor pressures at room temperature in parts-per-billion for these three compounds are given below.



These explosives were chosen to span the representative range of vapor pressures. DNT, a component of some dynamites, represents some of the more volatile explosives without encountering handling problems common to nitroglycerine and ethylene glychol dinitrate. TNT was chosen to represent explosives having low vapor pressures. RDX is a compound commonly used in the plastic explosives which have very low vapor pressures. Due to the very low vapor pressure of this class of explosives, RDX was expected to be the most difficult compound to detect using vapor techniques.

In order to perform the testing requested by NAVEODTECHCEN, a source of explosive vapors was needed. This vapor generator needed to be able to produce quantities of explosives which were reproducible, pure and chemically unadulterated. Additionally, the ability to easily calibrate the

output of the vapor generator would be useful. The development and characterization of a vapor generation system suitable for this study is one objective of this dissertation

1.3 Historical

In 1976, Peter Pella of the National Bureau of Standards reported an explosive vapor generator based on a glass column which was packed with explosive coated solid support material (54). This column was placed in a constant temperature bath, and fed with dry nitrogen. As the nitrogen passed over the solid support, the vapor pressure of the explosive coating caused the effluent nitrogen to contain the equilibrium vapor pressure of the explosive. Explosive vapor detection systems could then be placed at the outlet of this column to test the ability of the detection systems to respond to the explosive. This vapor generator, as well as all of the vapor sources described below, employed various temperature and flow control devices to provide stable, accurate and reproducible temperatures and flow rates.

In 1978, at the New Concepts Symposium and Workshop on Detection and Identification of Explosives, a session on vapor characterization, calibration, and standards had three presentations which involved methods of generating explosive vapors. The first of these, by Martin Cohen and others, used a dilution tunnel to achieve low parts per billion vapor concentrations (55). This dilution tunnel is constructed of corrugated aluminum pipe having dimensions of 2 ft ID by 26 ft in length. An 18 inch fan propels air through this tunnel from the outlet end.

A sample generator is placed at the inlet end of the tunnel. This sample generator works by pumping a known concentration of explosive in solution through a needle which ends in a heated aluminum block. An evaporation channel which was bored into the block provides a long evaporation path over which a gas stream is introduced. The gas stream moves the evaporated explosive vapor out of the aluminum block and into the turbulent flow of the tunnel. Monitoring of the vapor concentration by the vapor detector in question takes place inside the tunnel, at a distance of 10 to 15 tunnel diameters (20 to 30 feet) from the sample generator (55).

Another vapor generation method presented by Frank H. Jarke and others employed explosive vapor containers constructed from 600 mm ID by 1000 mm long glass pipe cylinders (56). These containers were fitted with steel plates on each end. Inside surfaces of the explosive vapor containers were silanized to minimize adsorption of the explosives onto the walls of the container. Explosive samples were placed in a receptacle inside the container. Helium was purged through the container while barrel heaters were employed to control the temperature of the system. The explosive laden vapor stream could then be monitored by vapor detection systems (56).

A third vapor generator presented at the new concepts symposium was presented by Cecelia Carter of Sandia National Laboratories (57). A beryllium-copper block heated by a cartridge heater was used for temperature control. A tapered aluminum insert, which contained the explosive material, was inserted into the heated block. The explosive

material, coated on an inert solid support, was packed into a 32 mm ID channel in the center of the aluminum insert. Zero air passed through the channel, picked up explosive vapors and transported the vapors to a mixing chamber for dilution. In the mixing chamber a 0.18 mm ID jet injects the explosive laden air coaxially into a tube of 0.5 μ m porous sintered nickel tubing. Air enters the chamber through the porous nickel tubing and dilutes the concentration of the explosive laden air (57).

In 1986, B. C. Dionne and others published a paper on the vapor pressures of explosives in which they describe another vapor generator apparatus (58). This design placed a military explosive sample into an explosives canister which was then set in a thermostated sand bath and insulated. A regulated flow of dry nitrogen was passed across the face of the explosive and through the explosives canister. With time, equilibrium was obtained between the explosive vapors and the carrier gas which then exited the explosives canister through a heated transfer line (58). This vapor generator is diagramed in figure 1. At the beginning of the NAVEODTEHCEN study, this vapor generator was commercially available from Thermedics, Inc., and was one of two systems considered for use in the study.

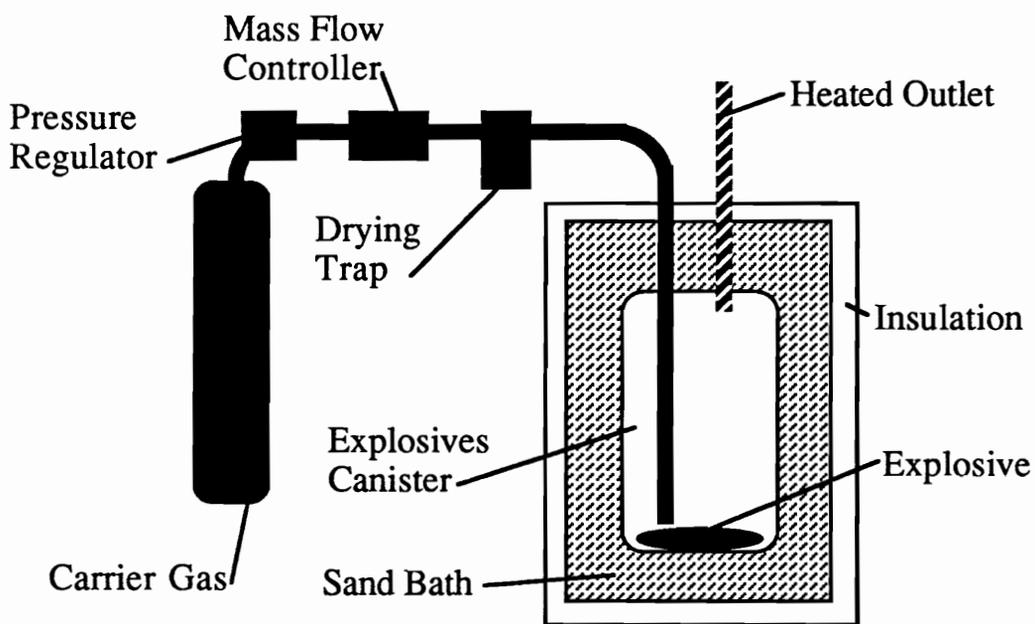


Figure 1. Schematic Diagram of the Thermedics Vapor Generator (58).

The second vapor generator considered for use in the NAVEODTEHCEN study was a modification of Pella's original design which was being used at Sandia National Laboratories in the fall of 1988 (59). The Sandia modification added a small amount of crystalline explosive as a regenerant to the bed of packed explosive coated solid support. This regenerant served to prevent loss of vapors once the explosive on the surface of the support was exhausted. This modification of Pella's design also replaced the constant temperature bath with a heated beryllium-copper block as described earlier by Sandia (57). Finally, the modification increased the length of the column from 190 cm (74.8 inches) to 118 inches, decreased the outer diameter from 0.64 cm (0.252 inches) to 0.125 inches and changed the column material from glass to stainless steel tubing (60).

The common feature of all the available vapor generation methods was that a continuous stream of explosive vapors was available at the outlet of each system. This continuous stream of vapors has certain advantages and disadvantages which will be discussed in the following section.

1.4 Characteristics of Continuous Stream Vapor Generators

The outlet of a continuous stream explosive vapor generator produces a constant concentration of explosive, which does not vary with time once the unit has reached equilibrium. This is shown graphically in figure 2. This continuous output has three important consequences in terms of the sampling of the outlet stream by an explosive vapor detection system. These consequences must be taken into account in order to avoid having the results of a comparative test of vapor detectors skewed in favor of one of the detectors over the others.

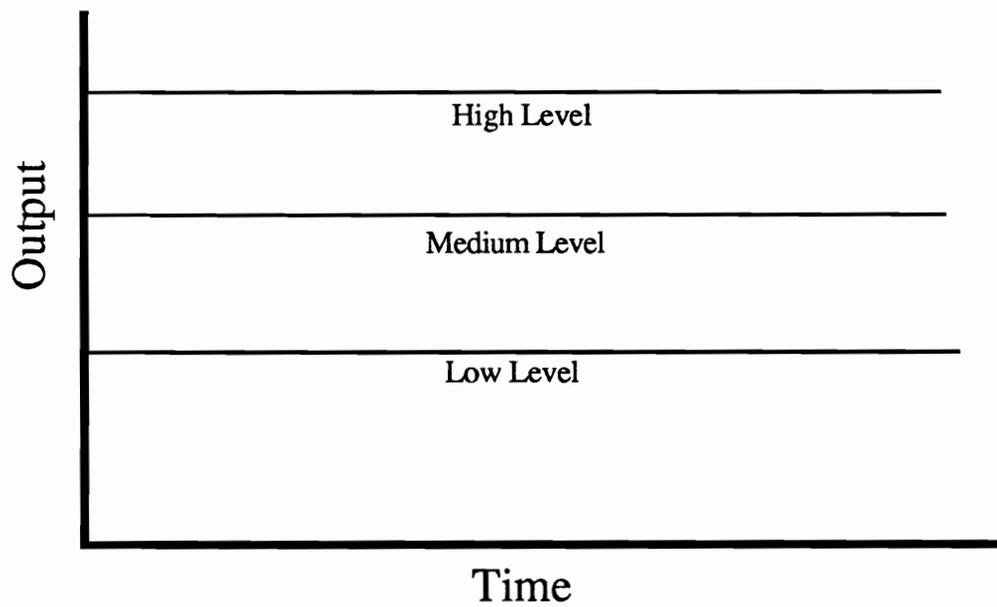


Figure 2. Output vs. Time for Typical Continuous Stream Vapor Generator.

The first consequence is that since the equilibrium vapor pressure of an explosive is exponentially related to temperature, control of temperature is vitally important to the stability of the output. In several of the vapor generation methods described above, temperature control was too poor to consider using the system. For example, the two foot by twenty six foot aluminum pipe by Cohen had no temperature control to prevent adsorption onto the walls of the pipe. The large 600 mm by 1000 mm explosives container by Jarke which employed two barrel heaters for temperature control gave no indication of insulation despite having to heat a 300 liter volume. The Thermedics unit using an explosives canister immersed in a sand bath also had a relatively large volume to thermostat. All three of these designs used time to assist in temperature control. Before these systems were used for testing vapor detectors, they equilibrated for time periods ranging from several hours to several days. Since the NAVEODTEHCEN study needed a variety of levels evaluated within a relatively short period of time, these vapor generators were not considered for this study.

The second consequence of continuous stream vapor generators is that they permit an unlimited sampling time. This gives an unfair advantage to detection systems which sample for long periods of time since they see a greater mass of explosive. Additionally, many of the explosive vapor detectors available use preconcentrator devices (60,61). When preconcentrators are used, the output of a vapor generator system could be trapped onto the surface of the preconcentrator, and later desorbed

resulting in an effectively higher signal than would occur if the preconcentrator were not used (61).

The last consequence of using continuous stream vapor generation methods is that by permitting long sampling times, coating the interior surfaces of the explosive vapor detector with explosive is possible. This coating of the interior surfaces is known as "priming," which results in a detector responding to a much lower level of explosive than if priming were not taking place. This effect is demonstrated in Pella's original paper (54), and is illustrated in figure 3.

Figure 3 shows the response of one of Pella's vapor detectors increasing with time for several levels of explosive vapor. This graph shows that although none of the levels of explosive could initially trigger an alarm, after fifteen seconds, three out of the four levels could trigger an alarm. Although this shows the detector system in the best light, fifteen seconds are not always available for detection of an explosive. For example, the Federal Aviation Administration has required that any explosive vapor detector being considered for airport deployment must be able to scan 10 people and their luggage per minute. This allows six seconds per person or three seconds per piece of carry-on luggage (62).

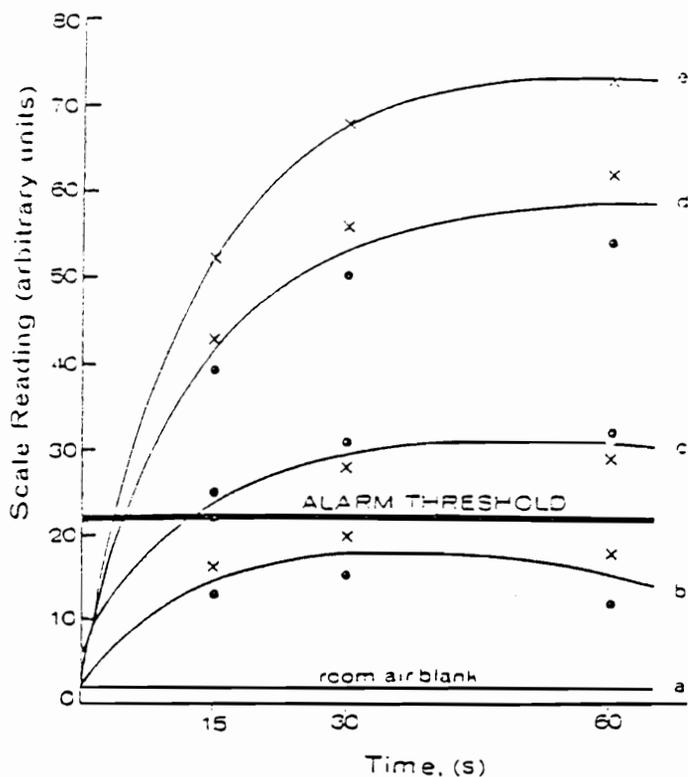


Figure 4. Response of instrument A to various concentrations of TNT

(a) blank; (b) 0.21 ppb; (c) 0.40 ppb; (d) 1.0 ppb; (e) 1.3 ppb. Symbols (●) and (x) represent replicate measurements

Figure 3. Graph of Instrument Response vs. Sampling Time from Pella's Paper (54).

There is another side to the priming issue. If the internal plumbing of a vapor detector is very active, explosive vapor might be lost to the walls of the internal walls of a system and result in a decrease in sensitivity. Many of the explosive vapor detection systems tested for the NAVEODTEHCEN study use Teflon tubing for internal plumbing in an effort to minimize adsorption. However, Peterson and Conrad have shown that explosive molecules can adsorb to Teflon (63).

The final concern about continuous vapor generators was the issue of purity. Most of these methods use military grade explosive as the vapor source. Military grade explosives also contain other volatile compounds such as plasticizers, binders and the like to aid in packaging the explosive. If the output of the Thermedics vapor generation system were used, alarms might be caused not only by the explosive chemical, but also by other volatile compounds capable of generating a signal in the detector.

1.5 Transient Output Vapor Generators

The sampling problems as well as the purity problems with continuous stream vapor generation can be solved by switching to a transient vapor generation system. A transient vapor generation system would have an output versus time plot similar to that of figure 4. Here different levels of explosives would be represented by different curve heights and different areas under the curve. Instead of explosive vapors exiting the vapor generation system as a stream, the vapors would be produced as a cloud of explosive.

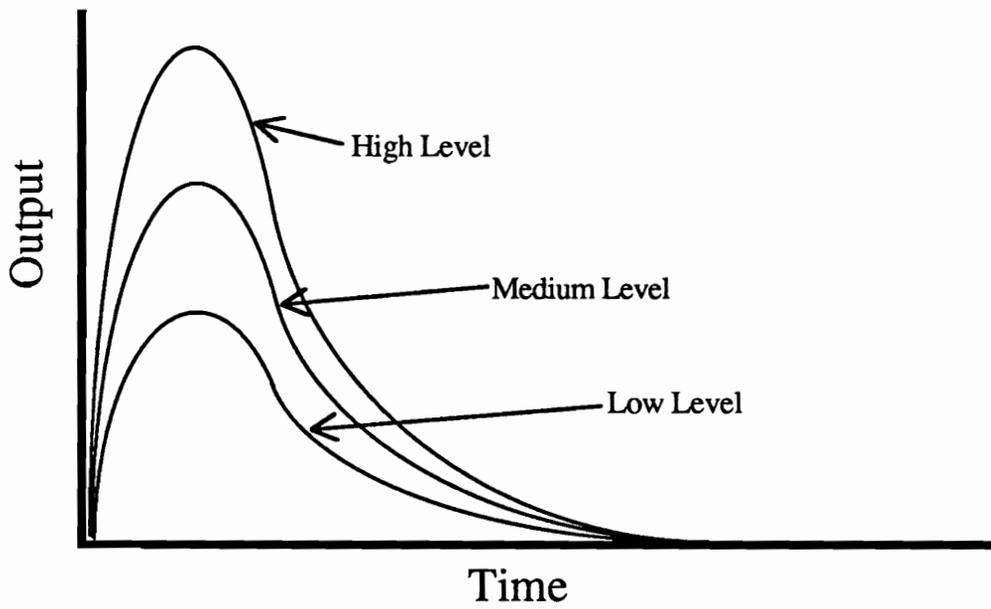


Figure 4. Graph of Output vs. Time for Typical Transient Vapor Generator.

A transient vapor generator could solve the sampling problem by decreasing the duration of the cloud of explosive to a time which is less than the sampling time of any of the vapor detectors. The decreased duration of the cloud would ensure that each of the vapor detectors was exposed to the same mass of explosive vapor. Since the explosive vapor cloud is transient, increased sampling time beyond that of the vapor cloud duration would not result in priming.

By preceding the vapor generator with a suitable purification technique such as gas chromatography, the purity problem could be solved. In this case, even if military grade explosive were used in the vapor generator, the explosive chemical would have a characteristic retention time which could be sampled by any explosive vapor detector. Sampling only during the elution of the explosive chemical would ensure that only these chemicals (DNT, TNT & RDX) would cause alarms.

1.6 Research Objective

In order to perform the testing requested by NAVEODTECHCEN, a source of explosive vapors was needed. The objective of this research is to develop a vapor generation system suitable for this study. The resulting vapor generation system should be capable of producing explosive vapors which are reproducible to enable comparative testing. The vapor composition should be only the pure explosive chemical without interferences from additives of packaged explosives.

By employing capillary gas chromatography as the basis for a vapor generation system, these needs have been met. A GC based vapor generator was assembled and tested. The chemical output of the system was verified, and a procedure for calibration of the system was demonstrated. Finally, instrumental conditions were optimized by analyzing the GC/ECD system to identify and minimize adsorptive sites in order to ensure maximum efficiency of the system, and to push the detection limits for TNT and RDX below those obtainable in an un-optimized system.

Chapter 2: Experimental

2.1 Gas Chromatograph

The Gas Chromatograph (GC) used in this research was a Hewlett Packard (Avondale, PA) model 5890. This instrument was equipped with an electron capture detector (ECD), a flame ionization detector (FID), and a split/splitless capillary injector. The electron capture detector was a constant current type which employed a radioactive source containing 15 mCi of ^{63}Ni . This detector could be operated with either Nitrogen or Argon/Methane as a make-up gas. The flame ionization detector had three interchangeable flame jets to accommodate different column diameters and flow rates. The split/splitless capillary injector was a backpressure-regulated flow system using a time-programmed splitless valve for purging the injector chamber.

Auxiliary equipment installed on this gas chromatograph included a Hewlett Packard (HP) Series 300 GC Chemistry Station, and a Hewlett Packard model 7673A automatic injector. The chemistry station was based on a HP model 9000 desk top computer system using HP's Pascal based operating system. This system both controlled the GC and performed data acquisition and manipulation. The HP chemistry station had macro programming capability permitting the user to submit files of commands to be executed as a batch process. This system coordinated all the automation

of the GC system, serving as the control device for not only the GC, but also for the automatic injector.

The HP 7673A automatic injection module was a mechanical syringe mounted on top of the injection port. The unit had a turret with space for five vials of liquid. Two of these were used for solvent and waste reservoirs. The other three vial positions were available for samples. The mechanical design of this unit permitted a very fast injection time in which the needle dwell time in the hot injection port was 100 msec. This system permitted increased reproducibility for injection into the GC. The basic GC conditions are given in table 1. A chromatogram obtained, using these conditions, from a mixture of 200 pg each of DNT, TNT and RDX in 2-propanol is given in figure 5.

2.2 Gas Chromatograph/Mass Spectrometer

The coupled gas chromatograph/mass spectrometer (GC/MS) system used in this research was a HP 5890 GC similar to the unit described above coupled to a HP 5970 Mass Selective Detector. This unit was also equipped with a Series 300 MS Chemistry Station. Additionally, this unit used a HP 59822A ion gauge controller to measure the vacuum inside the mass spectrometer (MS) manifold. The HP 5890 GC portion of this unit was equipped with a FID and a split/splitless capillary injector. The chemistry station installed on this unit was identical to the one described above for the GC except that it was loaded with mass spectrometry software. This chemistry station was therefore capable of both controlling the GC, the MS and also data acquisition and manipulation.

Table 1. Basic GC Conditions.

Injector	200°C Splitless for 30 sec. 5 psi head pressure (1.3 ml/min.) 100 ml/min. purge vent flow 3 ml/min. septum purge flow
Auto Injector	10 solvent washes 2 sample washes 2 sec. viscosity delay 10 sample pumps 1 µl injection volume
Column Oven	75°C for 2 min.; 20°C/min. to 200°C; hold for 2 min.
Column 1	HP Ultra 1 (polymethylsilicone) 5 m x 0.2 mm x 0.33 µm df
Column 2	HP Ultra 2 (95% methyl, 5% phenyl, polysiloxane) 5 m x 0.2 mm x 0.33 µm df
Detector	250°C (ECD) 195°C (FID/Vap. Gen.) 60 ml/min. make-up flow

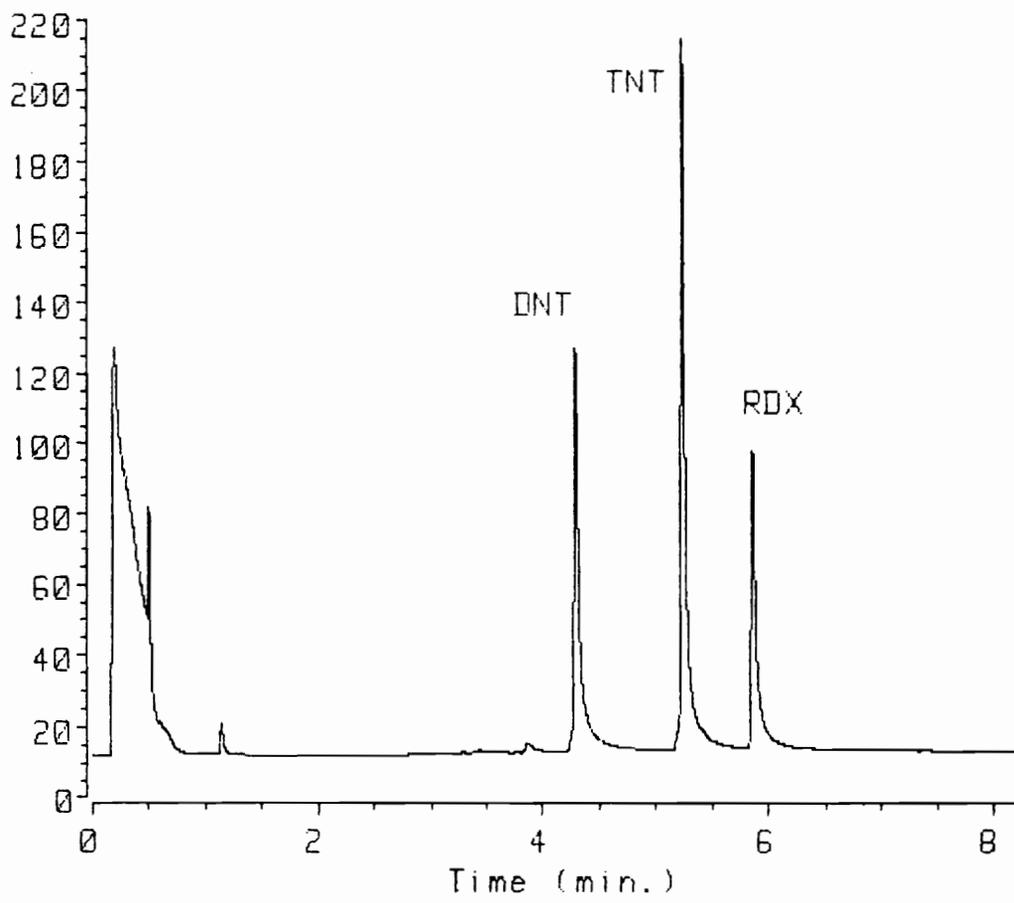


Figure 5. Chromatogram of 200 pg mixture of DNT, TNT and RDX using basic GC conditions.

The HP 5970 Mass Selective Detector (MSD) was a bench top mass spectrometer which had an electron impact (EI) source, a quadrupole mass analyzer, and a continuous dynode electron multiplier (EM). The unit had the capability of monitoring or scanning mass to charge ratios ranging from 10 to 800 amu with a resolution of 1 amu. The electron impact source was operated with an electron energy of 70 eV. This source had two filaments which were selectable to permit continuous use in the event of the failure of one filament. The quadrupole mass analyzer used molybdenum rods which were hyperbolic in cross section and had a length of 203 mm. The electron multiplier voltage could range from 0 to 3000 V; a preamplifier on the EM provided a dynamic range of five decades.

The MSD used a vacuum pumping system which consists of an air-cooled turbomolecular pump which was backed by a two stage mechanical pump. The ion gauge controller monitored the vacuum up to 1×10^{-3} Torr.

The interface connecting the GC to the MSD was a capillary direct interface. This type of interface permitted the fused silica capillary column to be inserted through the wall of the GC and directly into the EI source of the MSD. This interface controlled the temperature of the transfer portion of the capillary column. The temperature is set and controlled by the GC or by the chemistry station through the GC.

The mass selective detector required periodic tuning. This operation calibrated the mass axis, adjusted the ion source voltages, and optimized the

electron multiplier voltage. For all mass spectrometry work in this research, perfluorotributylamine was used as a calibration compound for all tuning operations. The GC/MS Conditions are given in table 2.

2.3 Ion Mobility Spectrometer

The ion mobility spectrometer (IMS) ionizes compounds entering the inlet and measures the drift times for the ions which have been accelerated against a flowing gas. The IMS unit used was the model "Phemto Chem-110" from PCP Inc. (West Palm Beach, Florida). This unit was equipped with the model RGS-4 Recirculating Gas Supply, and the model SF-12 Air Sampler. The temperature of the IMS was held at 190°C. Both the carrier and the drift gases were compressed air which had been dried using molecular sieve. The carrier flow was 200 ml/min, and the drift flow was 500 ml/min. These flows were set using the recirculating gas supply.

Table 2. GC/MS Conditions.

GC Conditions	Same as for Table 2-1
Transfer Line	195°C
Ion Source Pressure	8.0×10^{-5} Torr
Electron Energy	70 eV
EM Voltage	2600 Volts

2.4 Thermal Tube Desorber

A Thermal Desorption Unit (TDU) Model 890 from Dynatherm Analytical Instruments Inc. (Kelton, PA) was used to calibrate the capillary GC based vapor generator. This unit was purchased through Supelco, Inc., and was used with both the GC and the GC/MS units described above. This unit used a fused silica transfer line having an inner diameter of 0.2 mm, and a length of 1 m. The transfer line was connected to an HP Ultra 1 column described above using a Supelco GlasSeal connector which was sealed using Polyimide sealing resin from Restek (Bellefonte, PA). The TDU operated in three modes: a sample preparation mode, a direct injection mode and a desorption mode. The carrier flow for this system was 15 ml/min, and the auxiliary flow was 50 ml/min; both flows were helium which was treated as described below.

The TDU transfer line and the valve were held at 180°C for TNT; the desorption temperature was 190°C for 4 min. For work with RDX, the transfer line and valve were held at 160°C and the desorption temperature was 160°C for 4 min.

The desorption tube used was a 4 mm ID Supelco thermal desorption tube having a length of 11.5 cm. This tube was packed with quartz wool beginning at a distance of 1.5 cm from the inlet end and ending a distance of 5.5 cm from the inlet end. When placed in the TDU, the inlet end was placed into the unit first. All sampling with the thermal desorption tubes

was performed with a Supelco model SP-13P personal sampling unit set to have an inlet flow of 100 ml/min.

2.5 Analytical Balances

Two analytical balances were used during this work. Initial work was performed on a Mettler (Highstown, NJ) model H33AR analytical balance. This mechanical balance had a range from 0 to 160 g with a readability of 0.1 mg. This balance was later replaced by a Mettler model AE100 analytical balance. This electronic balance had a range from 0 to 109 g with a readability of 0.1 mg. The second unit was also equipped with a built-in 100 g calibration weight and had user selectable integration time and stability detection. All weighings used weighing paper or weighing dishes supplied by Fisher Scientific (Pittsburgh, PA). Weighings performed on the AE100 used an integration time value of 3 (6 sec.) and used the most sensitive stability detection setting.

2.6 Solutions and Chemicals

All solutions used for this work were prepared using standard analytical techniques. All stock solutions were prepared in Pyrex[®] brand volumetric flasks ranging in size from 10 to 250 ml. All stock solutions of 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) were prepared in Pyrex[®] brand volumetric flasks for light sensitive materials ranging in size from 50 to 250 ml. Dilute solutions were made in either volumetric flasks or directly into HP amber autosampler vials. These autosampler vials were sealed with Kimble brand

aluminum crimp top seals fitted with PTFE silicone septa purchased through Fisher Scientific.

The measurement and transfer of small liquid samples was performed using an Eppendorf Digital PipetteTM model 4710 made by Brinkmann Instruments, Inc. (Westbury, NY) and purchased through Fisher Scientific. Three different sizes of pipettes were used, having ranges of 0.5 to 10 μ l, 10 to 100 μ l, and 100 to 1000 μ l. These units were fitted with Eppendorf or FisherBrand disposable tips purchased through Fisher Scientific.

The solvents used in this work were Fisher Optima Grade Methanol and 2-propanol. Samples of the explosives 2,4-dinitrotoluene (DNT), TNT and RDX were supplied (pre-purified by recrystallization) by the Naval EOD Technology Center (NAVEODTECHCEN) located in Indian Head, MD. The purity of the explosive samples was confirmed using GC/MS and GC/ECD.

2.7 Consumables

The carrier gas used with both the GC and the GC/MS systems was Airco (Murray Hill, NJ) grade 5.0 (99.999%) helium. The make-up gas used for the ECD in the GC system was Airco grade 5.0 nitrogen. Both of these gasses for the GC/ECD were purified using a Supelco (Bellefonte, PA) heated gas purifier prior to entering the GC system. The carrier gas to the GC/MS was used without purification. The consumables used in both the GC and the GC/MS included LB-2 thermogreen septa and M-2A

graphite/vespel (40%/60%) ferrules, both purchased from Supelco. Hamilton (Reno, NV) model #701 10 μ l syringes purchased from Supelco were used for manual injection into the GC/MS. Hamilton model #80377 10 μ l syringes purchased from HP were used for automatic injection into the GC.

2.8 Capillary GC Based Vapor Generator

The transient explosive vapor generator, which was based on a capillary GC system was built by modifying the HP 5890 GC in the following manner. First, the tower assembly of the FID was removed, and the capillary flame tip was replaced with a larger diameter flame tip designed for packed column use. This larger aperture permitted the capillary column to be inserted through the flame jet and extended outside of the GC 9.5 cm. To prevent condensation of the explosives vapors on the walls of the exposed capillary column, a heater was designed for the exposed portion of the capillary column. This heater is shown in figure 6.

The heater consisted of the following parts: the inner portion was a piece of 2 mm ID soft glass tubing, 9.5 cm in length. This tube was wrapped in 30 gauge chromel wire, spaced 3 mm between windings. This wire-wrapped tube was placed inside a 4.0 mm ID glass tube, 9.2 cm in length. The ends of the inner tube were flared to hold the heater in place. The wire heater was then connected to the 25.2 volt leads of a 25.2/117 volt step down transformer, fed by a 120 V Variac. The Variac was adjusted to obtain a temperature of 195°C inside the tube when measured by an Omega model HH-81 digital thermometer.

The probes of the detection system were placed within 2 mm of the end of the capillary column which was set flush to the end of the inner glass portion of the heater. To prevent air currents from interfering with detection of the explosive vapors, a piece of glass tubing, 3 cm in diameter was placed around the heater about 3 to 4 cm above the FID base.

A diagram of the entire system, including GC, TDU and effluent heater assembly, is given in figure 7. For simplicity, computer cables are omitted from this figure. Figure 7 indicates how the detector systems under study were clamped into place above the effluent heater assembly.

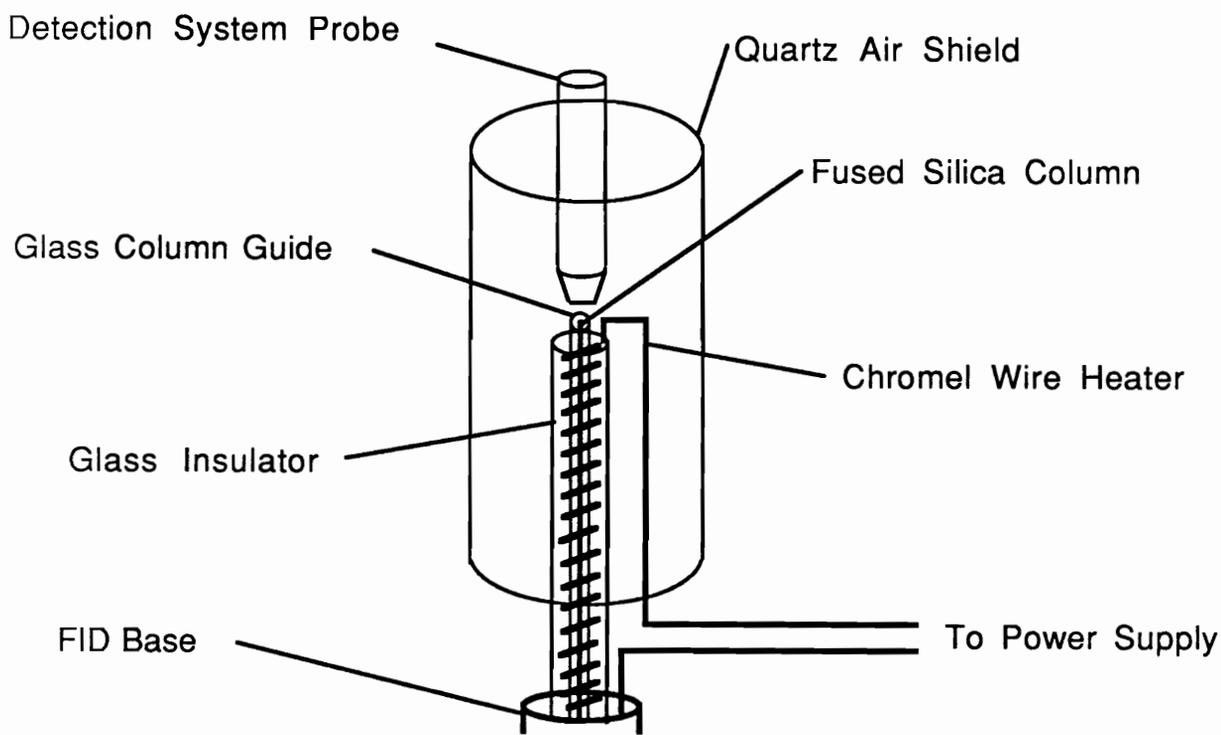


Figure 6. Fused Silica Column Heater.

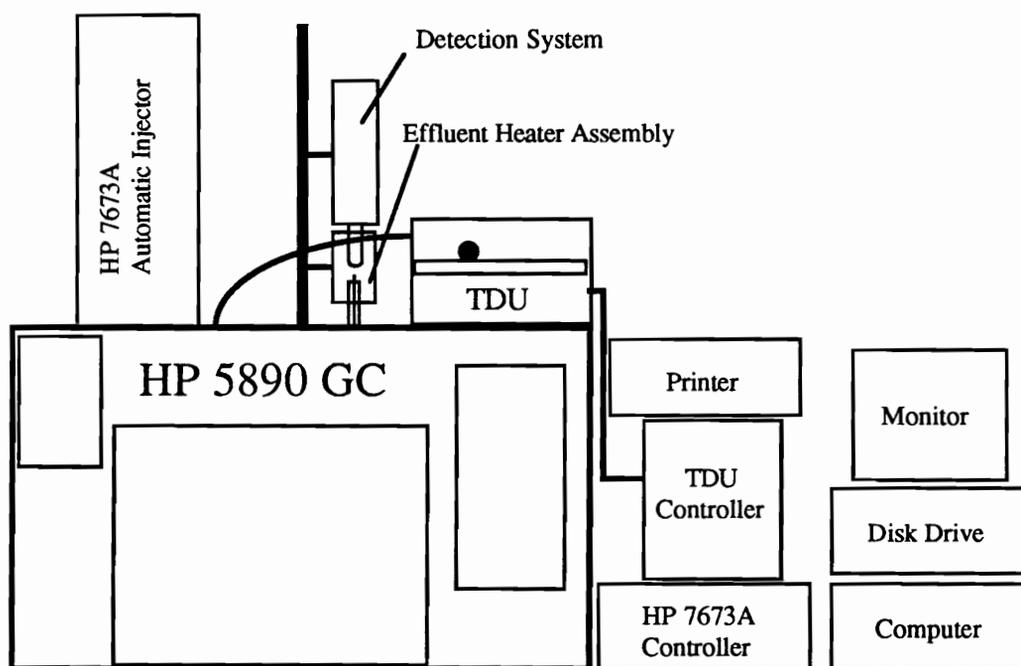


Figure 7. Diagram of Capillary GC Based Explosive Vapor Generator.

2.9 Testing Procedure

Setting up the capillary vapor generator involved removing the GC column from the ECD and installing it into the FID port. This operation exposed the ECD to room air, an operation which tended to de-stabilize the ECD. In order to ensure that the ECD was stabilized prior to testing, the night before performing a test the the column was connected to the ECD; all of the temperature zones activated, and the column oven temperature set at 200°C.

On the morning of a test, the instrument was returned to initial conditions. Before any GC runs were performed, the operating background of the ECD was required to be under 25.0 (arbitrary units), as read from the front panel of the GC. After this condition was met, a manual injection (2 μ l) of the stock solution containing the explosive under investigation was injected and analyzed. This step served two purposes; one was to prime the interior surfaces of the GC with the explosive, and the other was to prove the GC was functioning properly. After injecting the stock solution, the autosampler was used to inject a known mass of explosive as a solution in 1 μ l of 2-propanol. Before a test proceeded, ECD chromatograms were required to show no extra peaks for 1 min on either side of the peak of interest, and the peak areas as quantitated by the series 300 Chem Station for three injections were required to give a percent relative standard deviation of 15% or less.

To carry out a run, the fused silica capillary was removed from the ECD and placed in the FID exit of the oven. The capillary was adjusted with its exit end flush with the end of the fused silica heater, which was clamped above the FID. When the vapor detection system was moved near the GC and stabilized, a known mass of explosive was injected into the GC as a solution in 1 μ l of 2-propanol. The GC run was then started and the vapor detection system was clamped into place 30 sec. prior to the elution time of the explosive. The vapor detection system was then monitored for a response at the elution time of the explosive. Only alarm and clear responses were noted since the signal strengths given by the detection systems were arbitrary and were not comparable from detection system to detection system. One minute after the explosive eluted from the GC, the detection system was removed from the heated outlet.

2.10 Statistical Analysis

Generic statistical analysis were performed using StatView and StatView SE + Graphics from Abacus Concepts (Berkeley, CA) on an Apple (Cupertino, CA) Macintosh Plus and Macintosh IICx computer systems. A specific statistical analysis program which will be described later was written by the author using MicroSoft (Redmond, WA) QuickBASIC and run on an Apple Macintosh Plus computer system.

Chapter 3. Results and Discussion

Section A: Design and Calibration of Capillary Vapor Generator

3A.1 Overview

The evaluation of explosive vapor detection systems required a controlled source of explosive vapors. The first priority was to determine whether a calibration method could be devised to correct some of the deficiencies of the two available vapor generators. Although both the Sandia and the Thermedics vapor generator designs had potential purity problems, the Thermedics design also had problems with temperature control. In light of this, while neither unit appeared ready for off-the-shelf use, the Sandia design seemed the most workable. A gas chromatograph was retrofitted as to perform like the Sandia vapor generator.

When initial experiments with the re-configured GC employing Sandia's design did not work, a move was made from a continuous stream vapor generator to one which gave a transient output. The first version of this vapor generator was a coiled-wire heater surrounding a glass tube containing adsorbent. A small amount of explosive was placed on the adsorbent which was then heated and back-flushed with gas.

Although this unit did not work properly, a modification of this approach was finally used. By using a capillary gas chromatograph and

producing vapors at the column outlet, the vapors could be pre-purified prior to generation. This unit, when built as described in chapter 2 worked well. The output of this unit was verified by both GC/MS and by IMS. This capillary GC based explosive vapor generator was then used in the evaluation of the explosive detectors for NAVEODTECHCEN.

Calibration of the capillary vapor generator was important to verify the efficiency of the vapor generator. Although the capillary vapor generator was initially designed to permit comparative testing of the explosive detectors for NAVEODTECHCEN, the unit would be more useful if calibration would enable the vapor generator to do single unit testing.

3A.2 Verification of Capillary Vapor Generator Output

The problems with the previous vapor generator designs could be divided into two groups: problems in producing vapor of the desired purity, and problems with decomposition or adsorption of explosives due to thermal problems. Both problems were solved by employing gas chromatography as the basis for the next vapor generator.

The gas chromatograph is used to both purify and produce the explosive vapors. This is accomplished by introducing the explosive into the GC as a dilute solution in a suitable solvent, 2-propanol. The capillary column in the GC separates the explosive from the solvent and any impurities. When the column outlet is connected to the effluent heater,

transient clouds of explosive vapor are produced as each compound elutes from the column.

Initial tests with this vapor generator proved the idea was feasible. Positive identification of the output was required to insure that the explosives did not thermally decompose in the system. The identity of the output was verified by using both GC/MS and IMS. Mass spectra of the three explosives used with this vapor generator are presented, as obtained from the GC/MS, in figures 8, 9, and 10 below. Library mass spectra of the explosives are given in figure 11. The IMS results are presented in table 3.

In figure 8, the mass spectrum of DNT shows the molecular ion at m/z 182. The fragment ions shown have been found to match well with library spectra. In figures 9 and 10, the mass spectra of TNT and RDX are shown. Although neither mass spectrum has a molecular ion, this is not a problem considering the high ionization energy. Since both spectra match library spectra very well, decomposition is not likely.

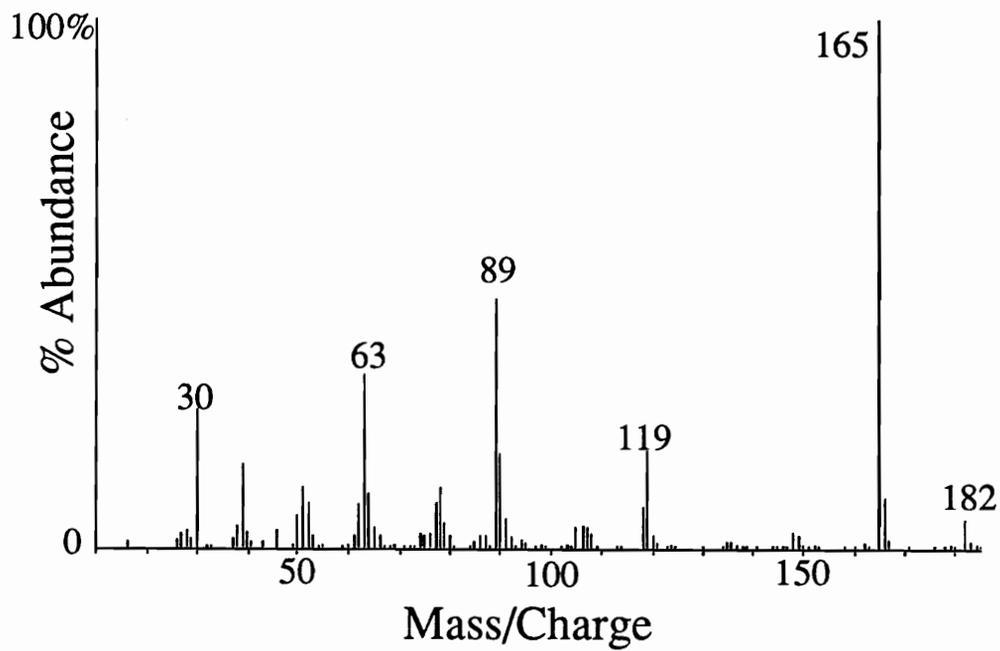


Figure 8. Mass Spectrum of DNT Vapor Generator Output.

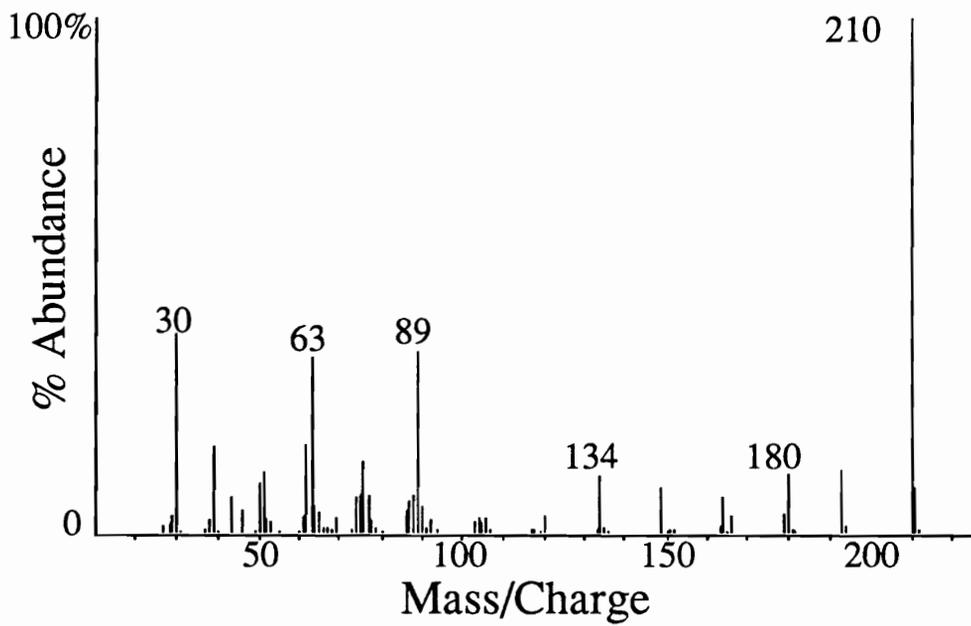


Figure 9. Mass Spectrum of TNT Vapor Generator Output.

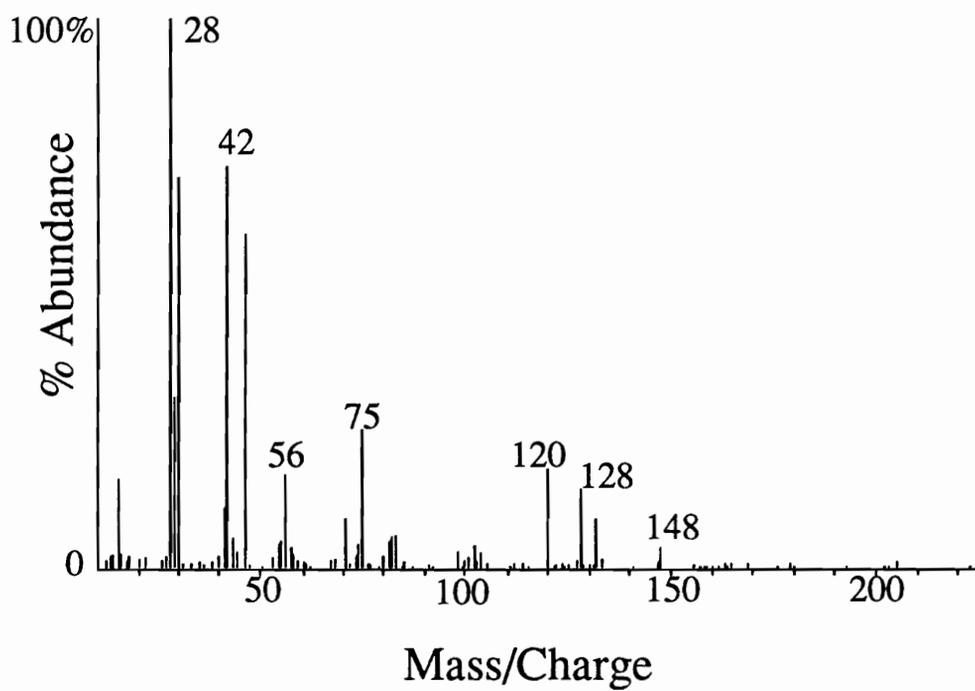


Figure 10. Mass Spectrum of RDX Vapor Generator Output.

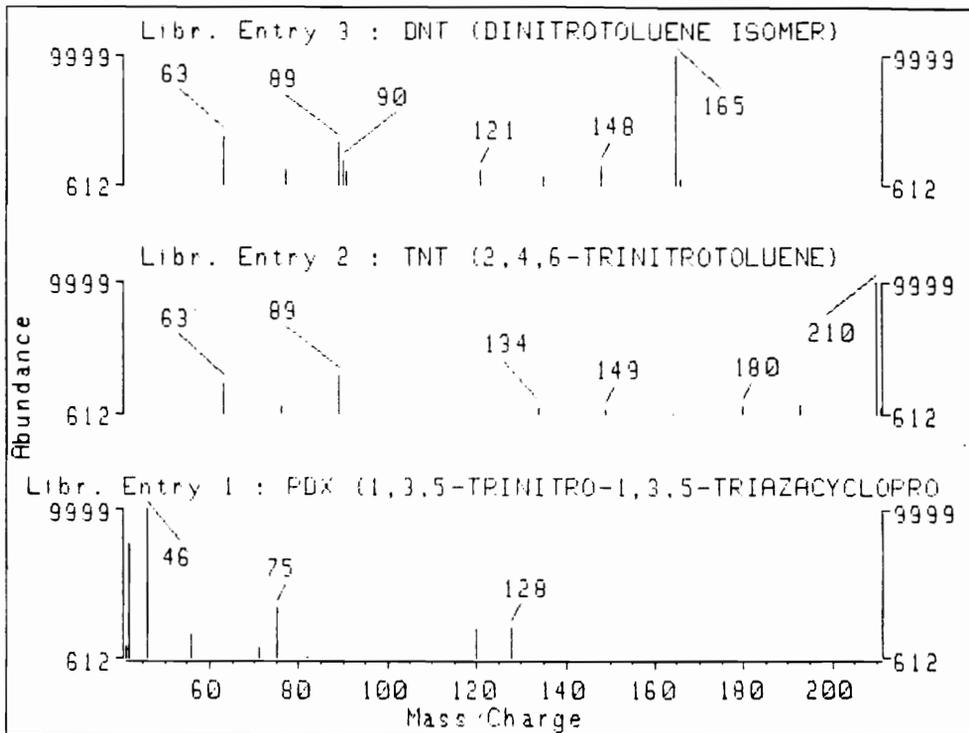


Figure 11. HP MS Chem Station Library Mass Spectra of the Explosives DNT, TNT & RDX.

Table 3. IMS Results for Verification of Vapor Generator Output

Explosive	Vapor Generator Output Drift Time	Headspace Drift Time
DNT	13.89	13.89
TNT	15.07	15.04
RDX	15.94, 16.56	15.92, 16.58

Since RDX has a molecular weight of 222, the lack of ions at m/z values above 130 was a cause of concern. When the injector temperature of the GC/MS was raised to 400°C to deliberately cause the decomposition of RDX, the RDX peak completely disappeared, causing an increase in size of the air peak in the chromatogram. This indicated that RDX probably decomposed to light gases and the lack of higher m/z ions was probably due to the high ionization energy of the GC/MS. However, since this evidence was not conclusive, the output of the vapor generator was also tested by IMS.

For the IMS data in table 3, the output of the vapor generator was collected for all three explosives and submitted to the IMS. Headspace vapor of the three explosives was also collected and analyzed in the same way. As can be seen in the data, the IMS spectra of the headspace vapor matched that of the vapor generator output. If decomposition was occurring, a shift to lower IMS drift times would have been observed in the vapor generator output IMS spectra.

This data taken in consideration with the GC/MS data showed that no thermal decomposition was occurring and that the chemical identity of the vapor produced was that of the explosives which were injected. These results allowed the comparative study to proceed.

3A.3 Calibration of Capillary Vapor Generator

The thermal desorption unit (TDU) described in chapter 2 was used to calibrate the vapor generator. The GC/ECD was first calibrated by

injection of a series of solutions of the explosives in 2-propanol. The direct injection mode of the TDU was then calibrated by injection of the same solutions onto the quartz wool of the desorption tubes, followed by desorption from the quartz wool into the GC. Once the response of the TDU was known, the capillary vapor generator was then calibrated by collecting the output of the vapor generator with the quartz wool desorption tube and subsequently desorbing from the tube into the GC for analysis.

Three solutions of TNT in 2-propanol were made at concentrations of 964 pg/ μ l, 370 pg/ μ l and 94 pg/ μ l. Each of these solutions was first injected into the GC/ECD using the HP 7673A automatic injector and analyzed using the standard GC conditions. The solutions were then injected onto the quartz wool of the thermal desorption tube, desorbed into the GC and analyzed using the basic GC conditions given in chapter 2 but employing a 5 minute initial hold time to permit cold trapping of the TDU output. Finally the solutions were injected into the GC configured as a vapor generator, collected using the Supelco sampling pump, desorbed into the GC using the TDU, and analyzed using the same conditions as for the TDU in the direct injection mode. The data from this experiment is given in table 4, and is graphed in figure 12.

Table 4. Comparison of Peak Areas for TNT Calibration.

Concentration	Area Counts		
	HP Injection	TDU Injection	Vap. Gen.
964 pg	70649	66489	55212
370 pg	31715	27219	23259
94 pg	10524	8133	6886

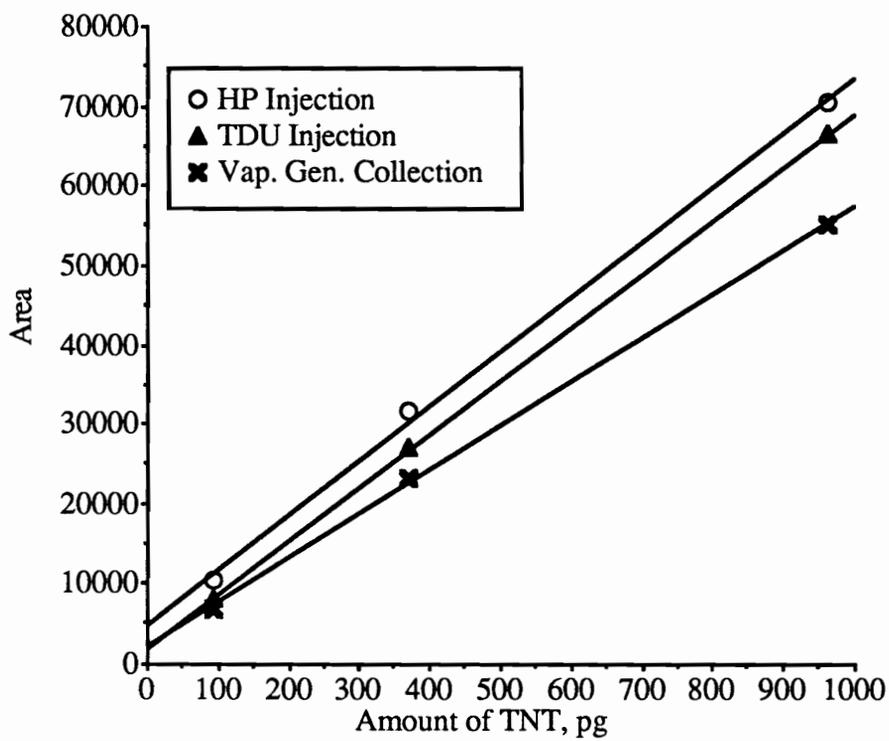


Figure 12. Graph of TNT Calibration Data.

In figure 12, the difference between the line representing direct auto-injection into the HP GC (HP Injection) and the line representing direct manual injection into the TDU (TDU injection) is indicative of the efficiency of desorption from the quartz wool surface and transfer into the GC system. The efficiency of desorption and transfer is 93% for the 964 pg level, 88% for the 370 pg level and 49% for the 94 pg level. Relative standard deviations of 5% for the HP injection, 7% for the TDU injection and 3% for the collection from the vapor generator were determined previously by replicate analysis.

The center line in figure 12 is also the calibration line for the TDU unit. If the area counts from the vapor generator collection are plotted on this line to calculate the amount of TNT collected, then the efficiency of the vapor generator can be calculated, and in turn, calibration of the vapor generator output for TNT is achieved. These results are summarized in table 5. An important assumption is made in this step. The difference between the TDU injection line (figure 12) and the vapor generator collection line represents the sum of the efficiency of the vapor generator and the efficiency of trapping the TNT on the quartz wool surface. In light of Hannum's work (60), assuming an efficiency of 100% for trapping onto quartz wool is reasonable. Table 5 shows that the capillary vapor generator has an average efficiency of 81% for TNT throughout the range of calibration.

Table 5. Efficiency of Capillary Vapor Generator for TNT

Amount Injected	Amount Collected	Efficiency
964 pg	794 pg	82%
370 pg	316 pg	86%
94 pg	72 pg	76%

For the RDX calibration, three solutions were made at concentrations of 9.95 ng/ μ l, 4.00 ng/ μ l and 0.96 ng/ μ l. The same steps described above for TNT solutions were used for the RDX solutions, however, the TDU temperatures were lowered to 160°C as stated in chapter two. Data from the analyses of the RDX solutions are presented in table 6, and graphed in figure 13.

As in the TNT data set, error bars given in figure 13 were obtained by replicate analysis of samples which were not part of the calibration data. For the RDX data set the relative standard deviations were $\pm 7\%$ for the HP injection, $\pm 10\%$ for the injection into the TDU and $\pm 5\%$ for the vapor generator collection.

When comparing the data from the TDU injection to that of the HP injections, the efficiencies of desorption of RDX from quartz wool are 71% for the 9.95 ng level, 63% for the 4.00 ng level and 52% for the 0.96 ng level. When comparing the vapor generator data to the TDU injection data, the efficiency of the vapor generator for RDX can be determined. These efficiencies, which are presented in table 7, give an average vapor generator efficiency of 65% for RDX.

Table 6. Comparison of Peak Areas from RDX Calibration

Concentration	Area Counts		
	HP Injection	TDU Injection	Vap. Gen.
9.95 ng	880155	628953	345842
4.00 ng	358386	216355	95693
0.96 ng	73618	37236	20008

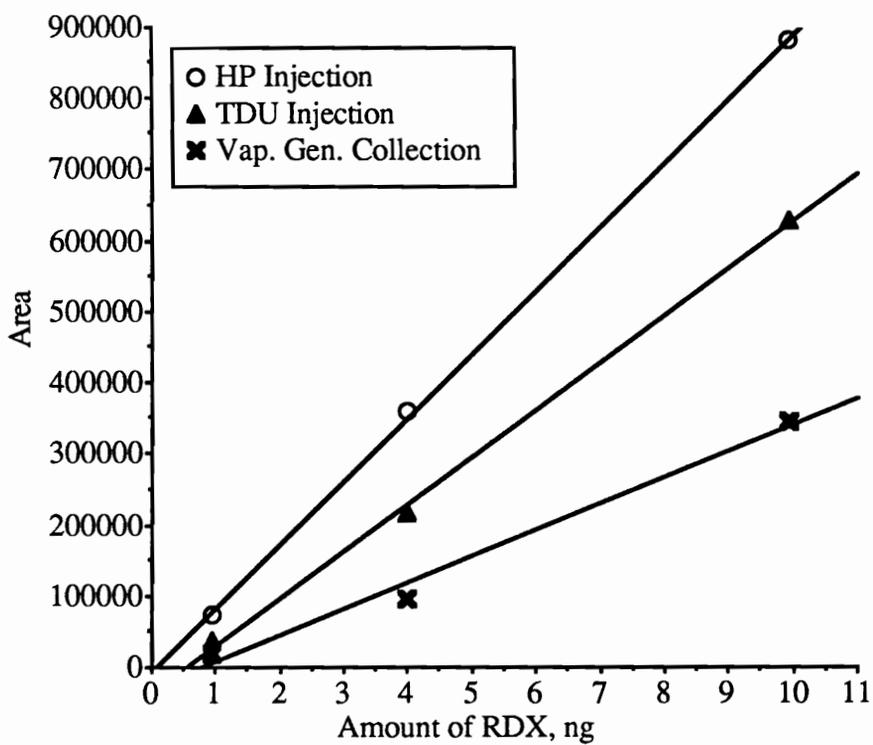
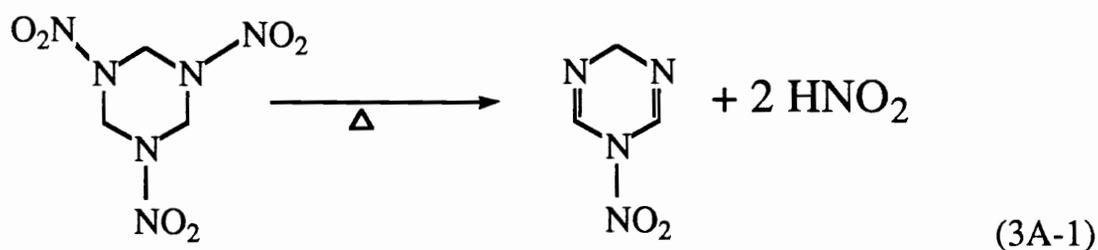


Figure 13. Graph of RDX Calibration Data.

Table 7. Efficiency of Capillary Vapor Generator for RDX.

Amount Injected	Amount Collected	Efficiency
9.95 ng	5.75 ng	58%
4.00 ng	1.98 ng	49%
0.96 ng	0.84 ng	87%

For some reason, although RDX did not decompose in the GC, it did decompose in the TDU producing two peaks as shown in figure 14. The decrease of TDU temperatures to 160°C was done to maximize the second peak which was the retention time for RDX. Testing throughout the range of temperatures from 140°C to 200°C did not eliminate the decomposition. As a result of this decomposition, the areas in table 6 are the sum of both peaks. A possible decomposition reaction given in equation 3A-1. (64)



The GC/MS was used to obtain a mass spectrum of the unknown peak in figure 14. This mass spectrum, which supports reaction 3A-1 is given in figure 15. In this case, a molecular ion is present at a mass to charge ratio of 128. The mass spectra peak at a mass to charge ratio of 83 would represent loss of the final NO₂, and the peak at a mass to charge ratio of 46 is NO₂.

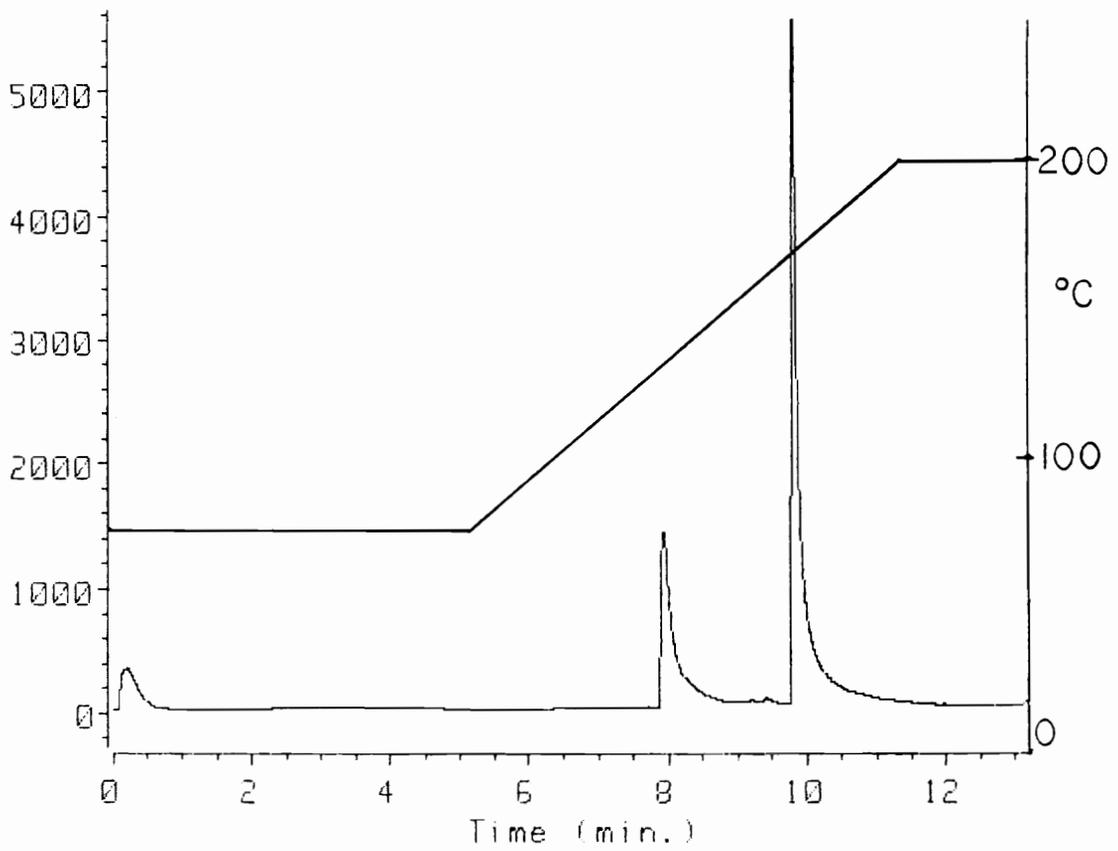


Figure 14. RDX Thermal Desorption Chromatogram.

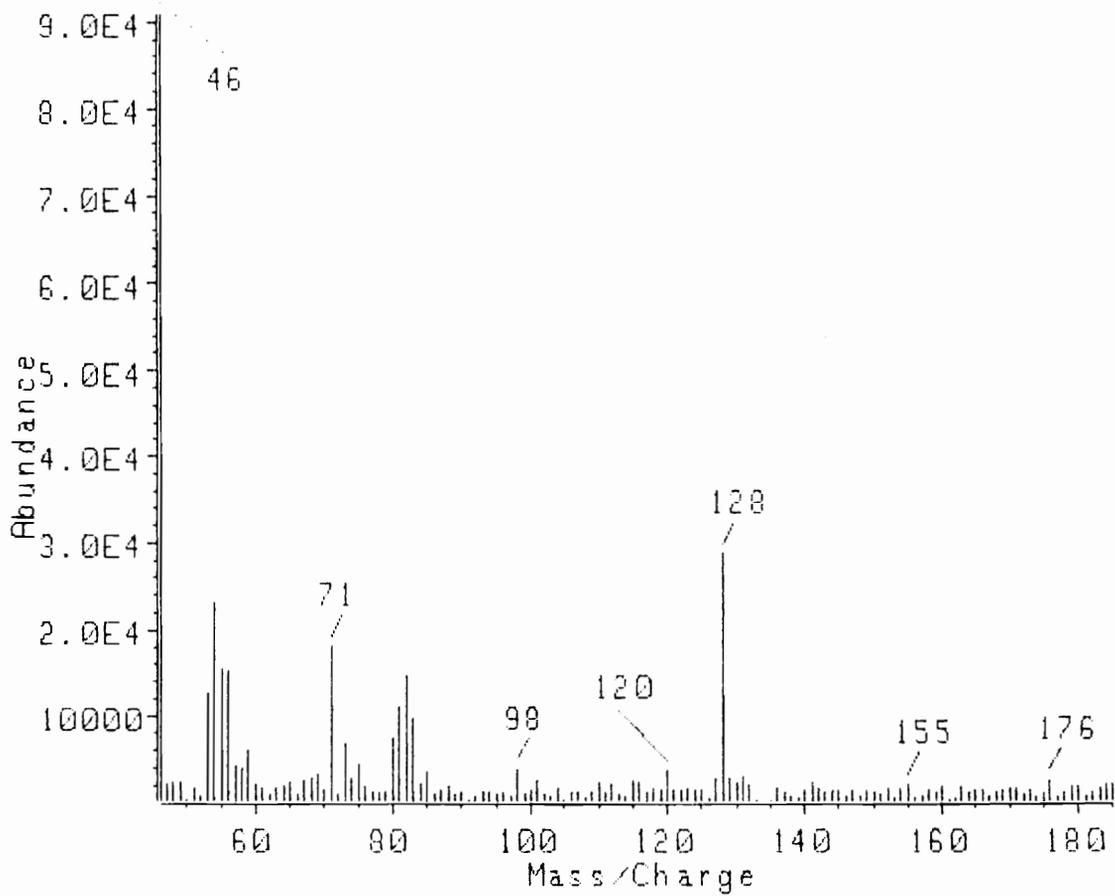


Figure 15. Mass Spectra of Unknown Peak in Figure 12.

Chapter 3. Results and Discussion

Section B: Initial Testing of Explosive Vapor Detectors

3B.1 Overview

The previous section discussed the successful development of the vapor generator system. It also demonstrated that the system produced vapors of the correct chemical composition. With the development of this system, work could then proceed on testing of the initial four vapor detection systems. The initial testing, as stated in the introduction, was to be of a comparative nature. The information which was important was the relative performance of the vapor detection systems, and relating them to the performance of a commercial GC/ECD system.

In order to achieve these comparisons, a carefully planned statistical design was used. This design involved specifying the order of testing as well as the procedure and protocol for the tests. The statistical design described below uses a randomized, blocked ANOVA to permit valid comparisons on the abilities of the detection systems to detect a given level of explosive.

This section will describe the initial testing which was performed with the vapor generator. Detailed descriptions of the statistics employed will be given. Unfortunately the actual data collected in this section is not

able to be released at the request of the Naval EOD Technology Center in Indian Head, MD. Instead, a sample data table will be presented to illustrate the results obtainable from the vapor generator.

3B.2 Statistics

In order to meet the objective of NAVEODTECHCEN's study, it must be possible to discern a difference between the various explosive detection system's abilities to respond to the explosive vapor being produced by the vapor generator. A statistical test was developed to ensure that any differences found were statistically valid.

Atmospheric conditions such as temperature, pressure and humidity can have a profound effect on the sensitivity of electron capture based detection systems. In order to remove the effect of these variables, the statistical design employs randomized blocking of the data.

The following definitions will be used in the discussion of the statistical design:

Test: One exposure of the vapor generator output to one detection system

Run: A series of tests with each detection system being tested against the same amount of explosive vapor in random order of detection system.

Level: A series of runs performed at the same level of explosive.

Each of the detection systems being tested had its own scale to indicate the relative strength of any alarm. However, since these scales were arbitrary, they were not comparable. As a result of this, only "Alarm" and "Clear" conditions were recorded. Any detection systems which gave caution signals were recorded as alarms.

Because only Alarm and Clear signals were recorded, the data is Boolean (consisting of only 1 & 0) in nature and normal statistical tables do not apply to data sets generated by this experiment. In order to permit statistical comparison, a randomization analysis was employed.

The layout for a typical data table of a given level is given in table 8. In this table, four detection systems are compared. The data for each detector system is contained in the column below the label. A total of twelve tests were performed as a series of three runs. In the case of table 8, detector system C was tested first for run 1, followed by detector systems A, B and D in that order. For run 2, the order of detection systems was A, D, B and C, and for run 3, the order was D, B, C and A. These sequences were determined using random numbers.

Table 8 Typical Data Table Layout

Level X

	System A	System B	System C	System D
Run 1	Test 2	Test 3	Test 1	Test 4
Run 2	Test 1	Test 2	Test 4	Test 3
Run 3	Test 4	Test 2	Test 3	Test 1

The major assumption in the statistical analysis is that the atmospheric variables which might affect the ECD's would change slowly over time. Therefore, within a given run, they would be essentially constant. With this being the case, any positive or negative effects due to humidity, pressure, etc., would affect all detection equally within the run. The statistical analysis then corrects for changes between runs by averaging the data for several runs. For this part of the analysis a standard ANOVA calculation is performed. A brief discussion of this technique follows.

If the columns of data under each detector system were taken as individual data treatments and the runs labeled as different blocks, the data table in table 8 can then be re-written as in table 9 (transposing the axis) which is taken from Wapole & Meyers (66).

In this data table, a total of b runs with k detection systems are tested. Each "y" term is the result of a test. Results of each test were recorded as either a "1" for an Alarm response or a "0" for a Clear response. Each "i" term is a different detector system, and each "j" term is a different run. The results for each detector system (treatment) are totaled and averaged. The same applies for the results for each run (block). A grand total, $T_{..}$, and grand average, $\bar{y}_{..}$, are then calculated.

Table 9. Array for a Randomized Complete Block Design.

Treatment	Block						Total	Mean
	1	2	...	j	...	b		
1	y ₁₁	y ₁₂	...	y _{1j}	...	y _{1b}	T _{1.}	$\bar{y}_{1.}$
2	y ₂₁	y ₂₂	...	y _{2j}	...	y _{2b}	T _{2.}	$\bar{y}_{2.}$
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
i	y _{i1}	y _{i2}	...	y _{ij}	...	y _{ib}	T _{i.}	$\bar{y}_{i.}$
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
k	y _{k1}	y _{k2}	...	y _{kj}	...	y _{kb}	T _{k.}	$\bar{y}_{k.}$
Total	T _{.1}	T _{.2}	...	T _{.j}	...	T _{.b}	T _{..}	
Mean	$\bar{y}_{.1}$	$\bar{y}_{.2}$...	$\bar{y}_{.j}$...	$\bar{y}_{.b}$		$\bar{y}_{..}$

Taken from Wapole & Meyers (66)

For our analysis, we assume that a difference exists between the runs and we are not interested in that difference. However, any differences between detector systems (treatments) are important. In order to test the validity of this difference, a f-test is used. To compute the f statistic, the following sum-of-squares computing formulas are employed based on table 9.

$$SST = \sum_{i=1}^k \sum_{j=1}^b y_{ij}^2 - \frac{T_{..}^2}{bk} \quad (3B.1)$$

$$SST = \frac{\sum_{i=1}^k T_{i.}^2}{b} - \frac{T_{..}^2}{bk} \quad (3B.2)$$

$$SST = \frac{\sum_{j=1}^b T_{.j}^2}{k} - \frac{T_{..}^2}{bk} \quad (3B.3)$$

$$SSE = SST - SSA - SSB \quad (3B.4)$$

The following mean squares are then calculated.

$$S_1^2 = \frac{SSA}{k-1} \quad (3B.5)$$

$$S^2 = \frac{SSE}{(b-1)(k-1)} \quad (3B.6)$$

The f statistic is finally calculated.

$$f_1 = \frac{S_1^2}{S^2} \quad (3B.7)$$

Up to this point, the statistics are the same as for any randomized, blocked ANOVA in which variation in the treatments are the only concern. In a normal analysis, the f statistic is then compared to f tables to determine if a statistically valid difference exists in the data. However, that is not possible due to the Boolean nature of the data in this experiment. To solve this problem, an experiment specific f-table will be generated.

The f statistic calculated above represents that f value of the actual data set. To generate a data-set-specific f table, a null hypothesis is made as follows.

H_0 : Any difference between the detection systems' response is due to differences in their abilities to capture and respond to the explosive vapor.

H_1 : Differences recorded among the detector systems are due only to random phenomena.

To test the null hypothesis, a randomization analysis is carried out. First, the test results from each run are randomly permuted within that run. Second, after all runs in a given level are permuted, another f statistic is calculated and recorded. Third, many (up to a few hundred) permuted f statistics are calculated and recorded. Fourth, these f statistics are sorted forming the f-table. Fifth, the f value for the actual data set is compared to the generated f-table.

If the f value for the actual data exceeds 90% of the f-values in the generated f-table, then H_0 can be accepted at the 90% confidence level. Likewise, if the f-value of the data exceeds 95% of the values in the generated f-table, then H_0 is accepted at the 95% confidence level, and so forth. If the confidence level associated with the data set is not high enough for the needs of the experiment, then H_0 is rejected and H_1 is accepted.

Obviously, this statistical analysis is very computationally intensive. To facilitate this analysis, a BASIC program was written to carry out these computations. This program is listed in the appendix.

3B.3 Typical Results

With the completion of the statistical design, all was in place to begin comparative testing of the explosive vapor detection systems. Table 10 shows some typical results from this testing with vapors of DNT and TNT. At this point it is a good time note that although this data is typical of what was produced during the initial testing, the actual data is being withheld for later publication by the U. S. Navy, the sponsor of this work.

Table 10 shows four levels of testing. Three different levels of TNT and one level of DNT. For the three levels of TNT testing, table 10 shows that 3 of the four detector systems respond at the higher and middle levels, while none of the detectors respond to the lowest level.

Table 10. Typical Data from Comparative Testing.

Level I, High level of TNT

	System A	System B	System C	System D
Run 1	1	1	1	0
Run 2	1	1	1	0
Run 3	1	1	1	0

Level II, Medium level of TNT

	System A	System B	System C	System D
Run 1	1	0	1	0
Run 2	1	1	1	0
Run 3	1	0	0	0
Run 4	1	1	1	0

Level III, Low level of TNT

	System A	System B	System C	System D
Run 1	0	0	0	0
Run 2	0	0	0	0
Run 3	0	0	0	0

Level IV, Medium level of DNT

	System A	System B	System C	System D
Run 1	1	0	1	0
Run 2	1	1	0	1
Run 3	1	0	1	1
Run 4	1	0	0	0
Run 5	1	1	0	0

In all levels of TNT, detector system D did not respond. Since all other detector systems responded, either of two results can be inferred from his data. First, system D may not be working properly, or second, the design of system D is such that it does not detect TNT. To eliminate the first possibility, all detector systems were given vendor-supplied test samples prior to each level of testing to ensure that they were working properly. As a result of this, based on the data in table 10, an acceptable conclusion is that system D probably can not detect TNT.

So far in the evaluation of the data presented in table 10, there has been no need for the statistical program. This is true whenever a detector system always responds or never responds to a given level of testing. In these cases it is obvious whether or not the system can detect the explosive.

When comparing Systems B and C in level II, two questions arise. First, can systems B and C detect that level of TNT? Second, do they differ in their abilities to detect this level? The answer to the first question is yes. For the purposes of this experiment, any alarm at a level which can be differentiated from the noise of the instrument is an indication that the system can detect that level of explosive. For the answer to the second question, we need to input the data from systems B&C of level II into the program.

The results indicate that the f value of the data ranks 1 out of 16 or at about the 6% confidence level. Since the confidence in the data is so low, this indicates that there is not a statistically significant difference

between the ability of system B and System C to respond to the middle level of TNT.

For level IV of table 10, once again all detector system respond at least once to this level. However, system A responds 100% of the time while systems B, C and D respond 20% of the time. When this data is entered into the statistical program, the result is that the f value of the data ranks 753rd out of 1000 (CL = 75%). Although it appears that system A is better than the others at this level, this conclusion is not statistically valid based on the data collected.

In table 11, three more runs have been performed for level IV in table 10. Once again, system A continues to respond 100% of the time, but the other systems do not.

If this data set is entered into the analysis program, the results are that the f of the data ranks 955th out of 1000 (CL = 95%). In this case a valid conclusion is that there is a difference among the four detectors. Since three of the four alarm 3 out of 8 times and the fourth (System A) alarms 8 out of 8 times, system A is more reliable than systems B, C and D at this level of testing.

If a valid difference were detected among a set of detector systems where the difference was not as obvious as above, pair-wise testing could be employed to discern where the difference existed.

Table 11. Typical Data from Additional Comparative Testing.

Level IV, Medium level of DNT continued

	System A	System B	System C	System D
Run 1	1	0	1	0
Run 2	1	1	0	1
Run 3	1	0	1	1
Run 4	1	0	0	0
Run 5	1	1	0	0
Run 6	1	0	1	0
Run 7	1	1	0	0
Run 8	1	0	0	1

3B.4 Summary of Testing

During this project, comparative testing has been performed on one set of four different commercial detection systems at various levels of three explosives. Following the initial set, three other commercial detection systems (all from the same vendor) have been tested at various levels of two explosives. Finally, three prototype vapor detection systems, two being based on IMS and one being based on MS/MS were tested at various levels of two explosives.

Chapter 3. Results and Discussion

Section C: Optimization of GC Conditions

3C.1 Overview

The successful comparative testing of the explosive vapor detection systems indicated that the capillary vapor generator was a functional unit. Major questions which remained involved characterizing the extent of adsorption in the system and optimizing the system to prevent adsorption as much as possible.

Although the Navy was initially interested only in the comparative testing -- that is, identifying the best of the explosive vapor detection systems -- it soon became apparent that the usefulness of this vapor generator could be expanded by proving the accuracy of the unit in addition to its reproducibility. The study of adsorption in this system helped to ensure accuracy in two ways. First, by collecting linear range data, regions where adsorption was insignificant could be identified. Second, collecting linear range data and minimizing adsorption would be the first step in a calibration of this type of system.

This chapter will compare the amount of adsorption on two different stationary phases as far as adsorption is concerned. After a phase is chosen, initial linear range data will be presented identifying regions where

adsorption is occurring to a significant extent. Following the initial linear range study, an exhaustive analysis of operating parameters is presented. These operating parameters include injection splitless time, injector priming, injector liner configuration, and injector temperature. Finally, the operating parameters test results are used to recommend new parameters for the vapor generator. Once implemented, another linear range data set is taken using the new parameters.

3C.2 Effect of Stationary Phase

In order to study the effects of stationary phase, two sets of linear range data were obtained. One set used the HP Ultra 2 column described earlier, and the other used an equivalent HP Ultra 1 stationary phase in a column having the same dimensions. For each of these data sets, two parameters were calculated and tabulated. The first was the classical limit of detection (LOD), using equation 3C-1. This parameter gives an extrapolated measure of the minimum amount of sample which could be detected with that column and instrument.

$$\text{LOD} = \frac{3S_b}{m} \quad (3C.1)$$

In this equation, S_b represents the standard deviation of 20 or more blank readings and m is the slope of the height vs. amount line in the trace region (less than 50 pg/ μ l). For this experiment, the S_b was calculated by obtaining a 2 second sample of the baseline while the data acquisition rate was 10 Hz, and measuring the peak to peak baseline noise during this time sample. Since a peak to peak measurement spans five standard deviations

(67), one fifth of this peak-to-peak measurement is equal to one standard deviation. The value for m was obtained by plotting the height of the TNT peak vs. the amount of sample injected for the trace region of the data set. By taking the slope of the height vs. amount line as opposed to the area vs. amount line, the values for both S_b and M will each have the same units (frequency) and will thus cancel each other in the LOD equation.

The second parameter used to measure the effect of stationary phase was a value we defined as the Lowest Level Detected (LLD). This is simply defined as the lowest value of a decade series of injections which produced an integratable peak on the chromatogram. The results from these two parameters for each column are tabulated in table 12 below.

In this table, the LOD calculation gave a value of 9 fg for the Ultra 1 phase and a value of 20 fg for the Ultra 2 phase. When evaluating LOD data, a factor of 3 is generally needed for the difference to be considered significant. (67)

A large difference is observed for the LLD results. The Ultra 1 phase gave a detection at 92 fg (figure 16) while the lowest detection given by the Ultra 2 phase was at 500 fg. Although it is not possible to statistically test this difference, the difference is significant because the Ultra 2 phase did not give detections at the 92 fg level. In addition to the large difference shown by the LLD calculations, the raw data shows that there generally was much more tailing of TNT on the Ultra 2 phase than there was on the Ultra 1 phase. Based on these results, all subsequent work was done on the HP Ultra 1 phase.

Table 12. Effect of Stationary Phase.

	HP Ultra 1 phase (100% Methylsilicone)	HP Ultra 2 phase (5% Phenyl, 95% Methylsilicone)
LOD (K=3)	9 fg	20 fg
LLD	92 fg	500 fg

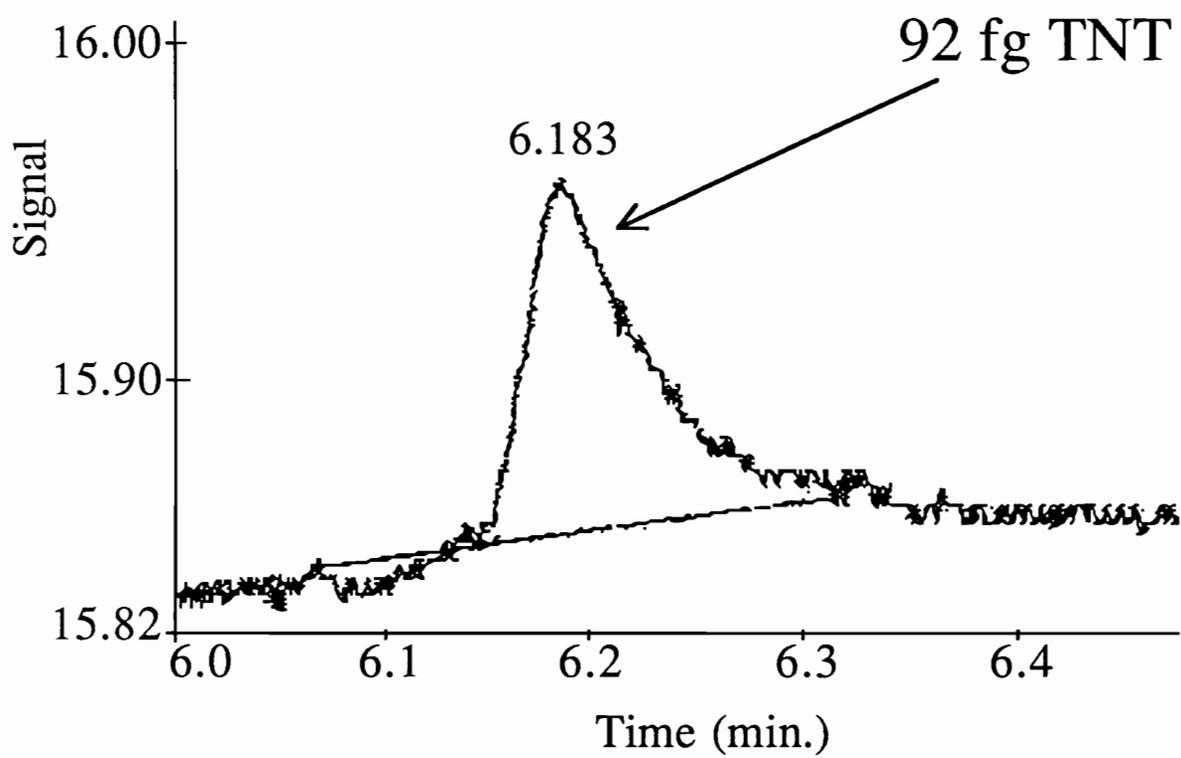


Figure 16. Chromatogram of 92 fg/ μ l TNT in 2-propanol.

3C.3 Combined TNT and RDX Data

The initial combined TNT and RDX data is shown in figure 17. The solutions used to prepare this line ranged in concentration from 39.5 fg/ μ l to 4.00 ng/ μ l. This data shows that both TNT and RDX have the same response in an ECD. The straight line and zero intercept give no indication of adsorption. However, if area/pg is plotted against the log of the amount, as in figure 18, the region where adsorption occurs becomes evident.

Figure 18 shows that the higher concentrations all have a constant area/pg value of about 40 area counts/pg of explosive. When adsorption is significant, this value drops drastically, first to a value less than 40, then to essentially zero as the adsorption processes predominate. For TNT, adsorption begins at 3.95 pg/ μ l and leads to no signal at 365 fg and below. In the case of RDX, adsorption becomes significant at 39.5 pg/ μ l and leads to no signal at 3.95 pg/ μ l and below.

Although both TNT and RDX share the same calibration line, figure 18 shows that the GC can detect a smaller amount of TNT than RDX. In terms of the previous study (table 12), both compounds should have similar LODs but would have different LLDs.

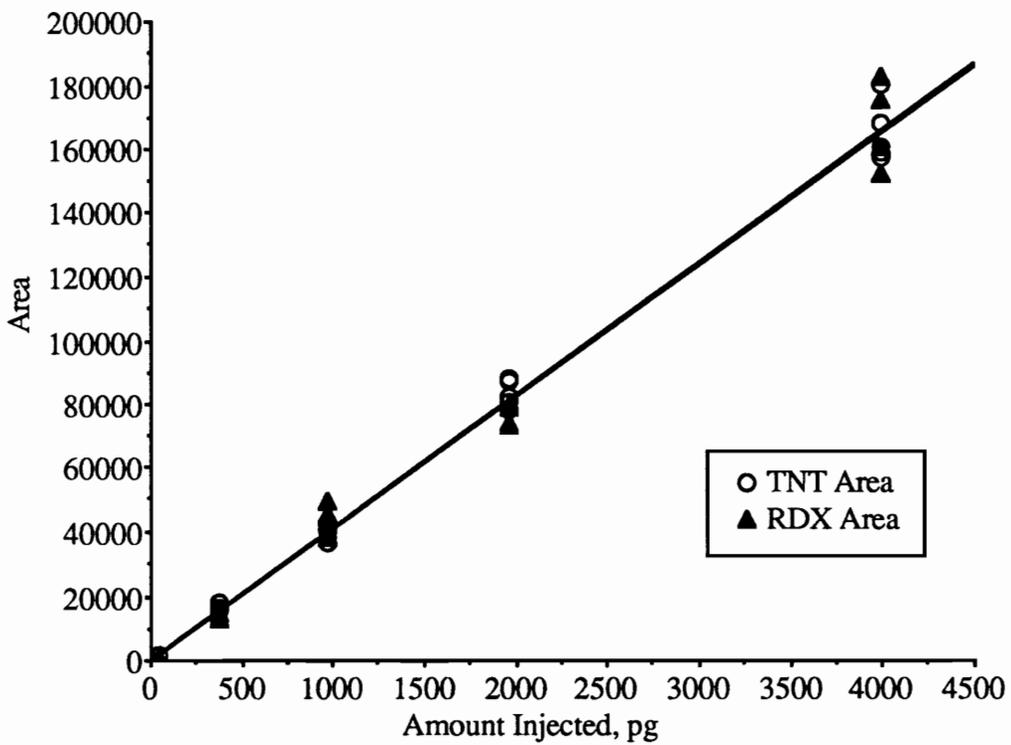


Figure 17 Area vs. Amt. Injected for TNT & RDX, Basic Conditions

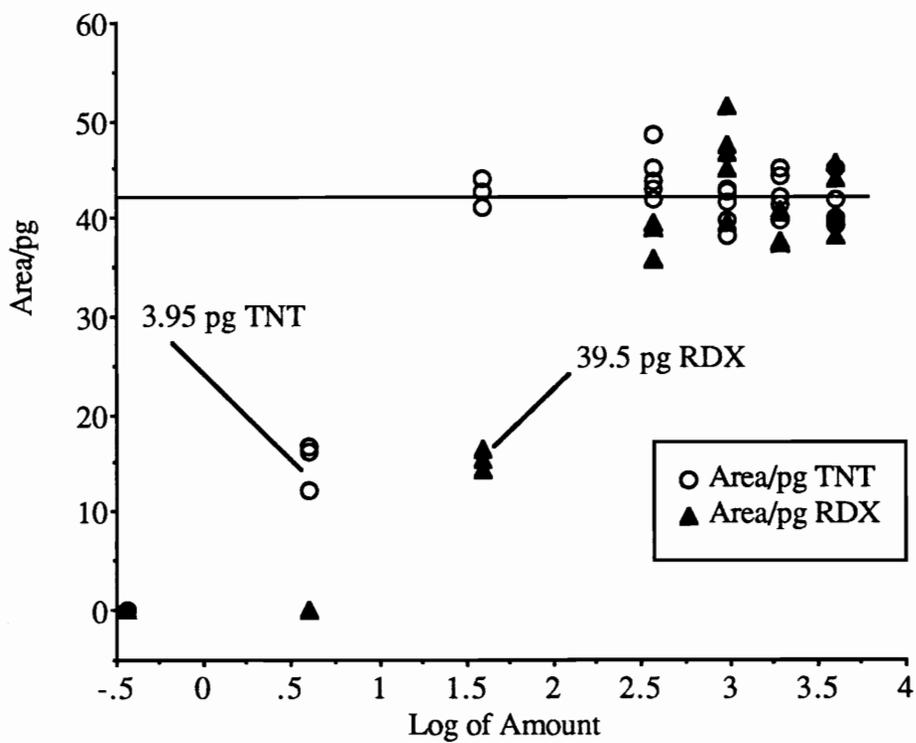


Figure 18 Area/pg vs. Log(Amount) for TNT & RDX, Basic Conditions.

An explanation for the difference between the LLD for TNT in the previous section, which was 92 fg, and the LLD for TNT in this section which is 3.95 pg is needed. These two studies were completed approximately 6 months apart. In the first study, which was performed during the winter, a new column was used for the stationary phase experiment. The data for the initial combined TNT and RDX line (figure 17) was performed on a previously used column of HP Ultra 1 phase during the summer when the humidity was very high. The twenty-fold difference in TNT's LLD for these experiments is likely caused by the increased adsorption due to contamination of the instrument with time. The increase in humidity during the summer might have also quenched the ECD signal (due to back diffusion into the ECD cell), resulting in additional loss of sensitivity.

With this study completed, the information needed to optimize the experimental parameters is in place. The optimization will take place at level of 39.5 pg of RDX, a region where adsorption was found to be significant.

3C.4 Optimization of Injection Parameters

In order to optimize the injection system, the effect of changes in splitless time, liner configuration (including the effect of priming) and injection temperature were studied. Each of these studies involved changing the parameter in question over a range of values. Replicate analysis of the 39.5 pg/ μ l of RDX in 2-propanol solution were performed

at each setting of the parameter in question. The results of these analyses were then treated using Analysis of Variance (ANOVA) as implemented by StatView SE + Graphics on the Apple Macintosh Plus computer system. This ANOVA implementation is the same as described in Miller and Miller. (68)

The first parameter tested was the splitless time for the injection. The values tested were 15, 30 and 45 seconds. At each splitless time a series of three replicate injections were made, and the RDX peak was integrated. The area counts for these peaks are presented in table 13. The results of the ANOVA of these area counts are presented in table 14. The ANOVA generates an f value of 1.396 with 2 and 6 degrees of freedom for the "within sample" and "between sample" mean squares respectively. The critical value of f for these degrees of freedom is 5.143. Since the f value of the data set does not exceed the critical f value, there is no significant difference among the different splitless times at the 95% confidence level. In table 14, the p value of 0.3179 indicates that a significant difference exists only at the 68% confidence level. In other words, the probability of any difference between the data sets being due to random variation is 0.3179, which is a very high probability.

Table 13. Data from Splitless Time Study.

Splitless Time	Area Counts
15 sec	933
15 sec	826
15 sec	906
30 sec	850
30 sec	760
30 sec	813
45 sec	773
45 sec	919
45 sec	789

Table 14. StatView Output for Splitless Time ANOVA.

One Factor ANOVA X₁ : Splitless Time Y₁ : RDX Area

Analysis of Variance Table

Source:	DF:	Sum Squares:	Mean Square:	F-test:
Between groups	2	10732.564	5366.282	1.396
Within groups	6	23066.193	3844.366	p = .3179
Total	8	33798.758		

Model II estimate of between component variance = 507.306

The fact that there is no significant difference between the splitless times is not surprising. Generally in capillary GC, 95% of the sample is transferred to the column during the early stages of a splitless injection. (69) The difference that would be expected would only represent 5% of the sample at most. Since there is not a significant difference, a splitless time of 15 seconds was chosen to minimize the possibility of thermal decomposition in the hot injection port.

The second parameter tested was the effect of priming the injection port. Priming was accomplished by slowly injecting 80 μg of RDX in 2 ml of 2-propanol over a period of 30 sec. This saturated the injection port with RDX vapor which would hopefully temporarily cover any active sites. After the priming injection, a temperature ramp was initiated to clean the RDX from the column. Following the temperature ramp, a blank run was performed to ensure that the GC was clean.

Table 15 shows the data collected from this test. Again, this data was treated using ANOVA, the results of which are presented in table 16. These results show that there is a very significant difference in the area counts due to the priming. The probability that any difference is due to random variation is 0.004, which means that the difference is significant at the 99.6% confidence level.

Table 15. Data from Priming Experiment.

Primed?	Area Counts
Yes	545
Yes	493
No	365
No	354
No	407
No	353

Table 16. StatView Output for Priming ANOVA.

One Factor ANOVA X₁ : Primed Y₁ : Area Counts

Analysis of Variance Table

Source:	DF:	Sum Squares:	Mean Square:	F-test:
Between groups	1	29669.913	29669.913	35.402
Within groups	4	3352.335	838.084	p = .004
Total	5	33022.248		

Model II estimate of between component variance = 10811.936

The fact that priming the injector port produces such a large difference in the area counts is not surprising. The injector liner in use at at this time was the commercial HP splitless liner. This liner is usually shipped with minimal treatment to make the liner inert. Since the glass used is an active surface which is capable of trapping explosives as shown by Hannum (60), there is the potential for the explosives to adsorb to the glass liner surface. The priming temporarily covers these active sites and causes the liner to become more inert.

The results from the priming test indicate that priming greatly reduces adsorption for the HP liner, however, other injection liners are available which are more inert than those commercially available from HP which might have been better than the primed HP liner. These liners were the subject of the next test. A combined experiment was devised to test the effect of priming on each of several injection liner configurations. This combined experiment was accomplished by performing replicate analyses RDX using each of the injection liner configurations in a non-primed and primed state. The results of these analysis were statistically analyzed using a 2 way ANOVA.

The designed test involved seven liner configurations including four treatments of the HP splitless liner and two liners commercially available from Restek (Bellefonte, PA), a company which markets treated injection liners. The liner configuration test was broken down into two groups of liners. One group contained four configurations with non-primed and

primed surfaces for a total of eight sets of data and the other group contained three liner configurations for a total of six sets of data.

For each set of data, area, height and area to height ratio were used in separate ANOVAs. Table 17 presents the data from the first group of liner configuration tests. Table 18 lists the results of the ANOVA of the area data. Table 19 contains the results of the height data ANOVA, and table 20 has the results of the area/height ANOVA.

Table 18 shows that there is a very high probability of a difference due to liner configuration (99.99% confidence level) as far as the area data was concerned. However, there was no significant difference due to the effect of priming for these liner configurations, giving an 83% confidence level for the area data. The bottom portion of table 18 shows the incidence table for the area data set, which gives the number of replicate analyses and the average area counts for each combination of liner type and priming type. Although the top portion of table 18 shows no difference due to priming, the bottom portion of table 18, does show that differences are present. Table 19 shows similar data for the peak heights, however, table 20 shows a significant effect due to priming for the area/height calculations (99.99% confidence level). The incidence table at the bottom of table 20 shows that in all cases, the area/height increased with priming.

Table 17. Liner Configurations Group 1 Data.

Liner Configuration	Primed?	Area Counts	Height	Area/Height
HP Commercial	No	404	7.83	51.7
HP Commercial	No	519	9.59	54.1
HP Commercial	No	418	7.19	58.1
HP Commercial	No	354	6.28	56.3
HP Commercial	No	443	7.04	62.9
HP Commercial	Yes	481	7.17	67.1
HP Commercial	Yes	421	6.09	69.2
HP Commercial	Yes	350	4.60	76.2
HP Commercial	Yes	329	4.40	74.8
HP Commercial	Yes	321	4.27	75.1
HP Heat Treated	No	535	6.19	86.4
HP Heat Treated	No	548	6.11	89.7
HP Heat Treated	No	642	7.83	82.0
HP Heat Treated	No	529	6.31	83.9
HP Heat Treated	No	636	8.15	78.1
HP Heat Treated	Yes	711	8.73	81.4
HP Heat Treated	Yes	692	8.26	83.8
HP Heat Treated	Yes	639	7.66	83.4
HP Heat Treated	Yes	654	7.67	85.2
HP Heat Treated	Yes	559	6.34	88.1
HP Acid Treated	No	178	2.41	73.9
HP Acid Treated	No	188	2.02	93.0
HP Acid Treated	No	130	1.48	87.5
HP Acid Treated	No	216	2.70	80.1
HP Acid Treated	No	211	2.61	80.9
HP Acid Treated	Yes	585	7.52	77.9
HP Acid Treated	Yes	545	6.78	80.3
HP Acid Treated	Yes	453	5.34	84.8
HP Acid Treated	Yes	526	7.02	74.9
HP Acid Treated	Yes	543	7.15	76.0
Restek 2 mm GN	No	1085	18.75	57.9
Restek 2 mm GN	No	916	16.01	57.2
Restek 2 mm GN	No	776	12.93	60.0
Restek 2 mm GN	No	731	11.87	61.6
Restek 2 mm GN	Yes	672	8.72	77.1
Restek 2 mm GN	Yes	658	9.19	71.6
Restek 2 mm GN	Yes	606	7.78	78.0
Restek 2 mm GN	Yes	678	8.98	75.5
Restek 2 mm GN	Yes	566	7.09	79.8

Table 18. Liner Configurations 1 Area ANOVA StatView Output.

Anova table for a 2-factor Analysis of Variance on Y 1 : RDX Area

Source:	df:	Sum of Squares:	Mean Square:	F-test:	P value:
Liner Type (A)	3	983575.465	327858.488	63.545	.0001
Primmed? (B)	1	10269.624	10269.624	1.99	.1683
AB	3	430723.154	143574.385	27.827	.0001
Error	31	159944.272	5159.493		

There were no missing cells found.

The AB Incidence table on Y 1 : RDX Area

Primmed?:		No	Yes	Totals:
Liner Type	HP Comme...	5 427.534	5 380.546	10 404.04
	HP Heat Tr...	5 578.058	5 650.81	10 614.434
	HP Acid Tr...	5 184.7	5 530.278	10 357.489
	Restek 0.2...	4 877.187	5 636.018	9 743.204
	Totals:	19 497.906	20 549.413	39 524.32

Table 19. Liner Configurations 1 Height ANOVA
StatView Output.

Anova table for a 2-factor Analysis of Variance on Y 2 : RDX Height

Source:	df:	Sum of Squares:	Mean Square:	F-test:	P value:
Liner Type (A)	3	251.23	83.743	46.453	.0001
Primmed? (B)	1	7.367	7.367	4.087	.0519
AB	3	155.792	51.931	28.807	.0001
Error	31	55.885	1.803		

There were no missing cells found.

The AB Incidence table on Y 2 : RDX Height

Primmed?:		No	Yes	Totals:
Liner Type	HP Comme...	5 7.585	5 5.305	10 6.445
	HP Heat Tr...	5 6.916	5 7.734	10 7.325
	HP Acid Tr...	5 2.246	5 6.761	10 4.503
	Restek 0.2...	4 14.889	5 8.349	9 11.256
Totals:		19 7.542	20 7.037	39 7.283

Table 20. Liner Configurations 1 Area/Height ANOVA StatView Output.

Anova table for a 2-factor Analysis of Variance on Y 3 : Area/Height (RDX)

Source:	df:	Sum of Squares:	Mean Square:	F-test:	P value:
Liner Type (A)	3	2741.557	913.852	49.809	.0001
Primmed? (B)	1	513.667	513.667	27.997	.0001
AB	3	859.2	286.4	15.61	.0001
Error	31	568.755	18.347		

There were no missing cells found.

The AB Incidence table on Y 3 : Area/Height (RDX)

Primmed?:		No	Yes	Totals:
Liner Type	HP Comme...	5 56.623	5 72.489	10 64.556
	HP Heat Tr...	5 84.028	5 84.373	10 84.201
	HP Acid Tr...	5 83.076	5 78.763	10 80.919
	Restek 0.2...	4 59.186	5 76.403	9 68.751
Totals:		19 71.336	20 78.007	39 74.757

The effect of priming is not clear based on the ANOVA results alone. To further investigate the effect of priming, individual t-tests were performed on each liner configuration sub-set of group 1. These tests serve the purpose of determining if any significant difference in the sub-sets exist that might not be evident as a result of the 2 way ANOVA. The results of the t-tests are summarized in table 21.

The top portion of this table gives the probabilities that any differences are due only the random variation. In order for a difference to be statistically significant, this probability must be less than 0.05 for the 95% confidence level. The bottom portion of table 21 indicates if the difference was positive, negative or not significant (Not Sig.). This table shows that the effect of priming, if any, is different for each liner configuration. The differences given in table 21 are both positive and negative which is the reason that the ANOVAs were unable to detect these differences.

Table 21. Liner Configurations 1 t-Test Results.

Probabilities of effects due only to random variation

Liner Configuration	Area Counts	Height	Area/Height
HP Commercial	.2843	.0211	.0003
HP Heat Treated	.0804	.2073	.8826
HP Acid Treated	.0001	.0001	.2802
Restek 2mm GN	.0141	.0027	.0001

Positive or Negative Effects

Liner Configuration	Area Counts	Height	Area/Height
HP Commercial	Not Sig.	Negative	Negative
HP Heat Treated	Not Sig.	Not Sig.	Not Sig.
HP Acid Treated	Positive	Positive	Not Sig.
Restek 2mm GN	Negative	Negative	Negative

The results from tables 18 and 19 clearly show that the Restek 2 mm gooseneck liner in an un-primed state was the most inert in terms of peak area and height which are valid measures of irreversible adsorption. However, another measure of adsorption in a GC system is the area to height ratio which gives an indication of the reversible adsorption. A lower area/height ratio indicates less reversible adsorption if all other factors are the same. In terms of area to height ratio, the best performance was the HP commercial liner in an un-primed state (table 20). The HP commercial liner therefore had the least amount of reversible adsorption, while the Restek 2 mm gooseneck liner had the least amount of irreversible adsorption. Since reversible adsorption results primarily in poor chromatographic performance, and highest area and height was needed for this study, the Restek 2 mm gooseneck liner was chosen for additional testing in the second group.

With the above results in mind, the second group of liner configurations included the 2mm Restek liner to permit valid comparison with the other two liners. The second group of liners included a 2 mm Restek gooseneck liner, a 4 mm Restek gooseneck liner and a HP liner which has been silylated. These liners were tested both in un-primed and primed states.

The data from the replicate analyses of the RDX solutions is presented in table 22. The data was statistically analyzed using a 2-way ANOVA, the output of which is given in tables 23, 24 and 25 for area, height and area/height respectively. Tables 23, 24 and 25 all show

significant effects due to the liner configurations. Table 23 does not show an effect on the area due to priming, however, unlike group 1, the height data in table 24 shows a significant effect due to priming. The sub-sets of the liner configurations were also tested using a t-test, which is summarized in table 26.

From the bottom portions of tables 23 and 24, the area and height values show that the Restek 2 mm gooseneck injection liner in an un-primed state was the most inert. This liner also gives the lowest area/height value of the second group (table 25), which also indicates that this liner was the most inert. Since the Restek 2 mm gooseneck liner was also the best of group 1, this liner was chosen for subsequent work with the vapor generator.

Table 22. Liner Configurations Group 2 Data.

Liner Configuration	Primed?	Area Counts	Height	Area/Height
HP Silylated	No	118	1.18	99.9
HP Silylated	No	113	1.27	89.0
HP Silylated	No	92.6	1.00	93.0
HP Silylated	No	166	1.72	96.5
HP Silylated	No	81.3	.93	87.2
HP Silylated	Yes	400	3.73	107
HP Silylated	Yes	338	3.19	106
HP Silylated	Yes	379	3.73	102
HP Silylated	Yes	275	2.83	97.2
Restek 2 mm GN	No	679	12.49	54.4
Restek 2 mm GN	No	584	9.93	58.9
Restek 2 mm GN	No	562	8.28	67.9
Restek 2 mm GN	No	595	8.42	70.7
Restek 2 mm GN	No	522	7.67	68.0
Restek 2 mm GN	Yes	455	5.63	80.8
Restek 2 mm GN	Yes	515	6.42	80.2
Restek 2 mm GN	Yes	463	5.82	79.5
Restek 2 mm GN	Yes	514	6.67	77.0
Restek 2 mm GN	Yes	502	6.14	81.8
Restek 4 mm GN	No	479	6.70	71.6
Restek 4 mm GN	No	412	6.31	65.3
Restek 4 mm GN	No	445	5.89	75.6
Restek 4 mm GN	No	494	6.02	81.9
Restek 4 mm GN	No	459	5.45	84.2
Restek 4 mm GN	Yes	387	3.52	110
Restek 4 mm GN	Yes	422	3.92	108
Restek 4 mm GN	Yes	394	3.76	105
Restek 4 mm GN	Yes	422	4.00	105
Restek 4 mm GN	Yes	428	3.94	109

Table 23. Liner Configurations 2 Area ANOVA StatView Output.

Anova table for a 2-factor Analysis of Variance on Y 1 : Area

Source:	df:	Sum of Squares:	Mean Square:	F-test:	P value:
Liner Type (A)	2	457039.04	228519.52	148.135	.0001
Primmed? (B)	1	6154.722	6154.722	3.99	.0577
AB	2	148389.169	74194.585	48.096	.0001
Error	23	35480.773	1542.642		

There were no missing cells found.

The AB Incidence table on Y 1 : Area

Primmed?:		No	Yes	Totals:
Liner Type	HP Silylated	5 114.143	4 348.125	9 218.135
	Restek 2 m...	5 588.58	5 489.832	10 539.206
	Restek 4 m...	5 457.896	5 410.374	10 434.135
Totals:		15 386.873	14 420.966	29 403.332

Table 24. Liner Configurations 2 Height ANOVA
StatView Output.

Anova table for a 2-factor Analysis of Variance on Y 2 : Height

Source:	df:	Sum of Squares:	Mean Square:	F-test:	P value:
Liner Type (A)	2	140.247	70.124	91.16	.0001
Primmed? (B)	1	8.788	8.788	11.425	.0026
AB	2	37.898	18.949	24.633	.0001
Error	23	17.692	.769		

There were no missing cells found.

The AB Incidence table on Y 2 : Height

Primmed?:		No	Yes	Totals:
Liner Type	HP Silylated	5 1.219	4 3.371	9 2.176
	Restek 2 m...	5 9.358	5 6.137	10 7.748
	Restek 4 m...	5 6.075	5 3.829	10 4.952
Totals:		15 5.551	14 4.523	29 5.054

Table 25. Liner Configurations 2 Area/Height ANOVA
StatView Output.

Anova table for a 2-factor Analysis of Variance on Y 3 : Area/Height

Source:	df:	Sum of Squares:	Mean Square:	F-test:	P value:
Liner Type (A)	2	3560.273	1780.137	64.706	.0001
Primmed? (B)	1	2622.559	2622.559	95.327	.0001
AB	2	597.659	298.83	10.862	.0005
Error	23	632.756	27.511		

There were no missing cells found.

The AB Incidence table on Y 3 : Area/Height

Primmed?:		No	Yes	Totals:
Liner Type	HP Silylated	5 93.132	4 103.002	9 97.518
	Restek 2 m...	5 63.971	5 79.87	10 71.921
	Restek 4 m...	5 75.727	5 107.213	10 91.47
Totals:		15 77.61	14 96.244	29 86.606

Table 26. Liner Configurations 2 t-test Results.

Probabilities of effects due only to random variation

Liner Configuration	Area Counts	Height	Area/Height
HP Silylated	.0001	.0001	.0206
Restek 2 mm GN	.0091	.0066	.0011
Restek 4 mm GN	.02	.0001	.0001

Positive or Negative Effects

Liner Configuration	Area Counts	Height	Area/Height
HP Silylated	Positive	Positive	Positive
Restek 2 mm GN	Negative	Negative	Positive
Restek 4 mm GN	Negative	Negative	Positive

The last parameter to be tested was the injection port temperature. Temperatures ranging from 160°C to 240°C at intervals of 20°C were used to analyze in triplicate a solution of 39.5 pg/μl of RDX in 2-propanol. The data from these analyses are presented in table 27. An ANOVA was used to test for a statistically valid difference among the five injection temperatures. The results of this ANOVA are presented in table 28. This table shows that the highest area resulted from an injection temperature of 220°C with a close second highest resulting from a temperature of 240°C. Testing did not proceed past the leveling off point at 220°C to 240°C because at temperatures above 205°C, the decomposition of RDX becomes a concern (53). In order to minimize the possibility of decomposition, 220°C was chosen as the best injection temperature.

Table 27. Data from Injection Temperature Experiment.

Injection Temperature	Area Counts
240°C	137
240°C	162
240°C	194
220°C	169
220°C	159
220°C	182
200°C	106
200°C	98.0
200°C	115
180°C	51.4
180°C	25.4
180°C	52.8
160°C	45.7
160°C	12.3
160°C	21.9

Table 28. StatView Output for Injection Temperature ANOVA.

One Factor ANOVA X₁ : Inj. Temp. Y₁ : Area

Analysis of Variance Table

Source:	DF:	Sum Squares:	Mean Square:	F-test:
Between groups	4	53046.79	13261.697	42.183
Within groups	10	3143.849	314.385	p = .0001
Total	14	56190.638		

Model II estimate of between component variance = 4315.771

One Factor ANOVA X₁ : Inj. Temp. Y₁ : Area

Group:	Count:	Mean:	Std. Dev.:	Std. Error:
A (240C)	3	164.56	28.78	16.616
B (220C)	3	169.913	11.783	6.803
C (200C)	3	106.266	8.405	4.853
D (180C)	3	43.182	15.434	8.911
E (160C)	3	26.644	17.204	9.933

3C.5 Results of Optimization

The injection temperature experiment completed the optimization of the vapor generator. Table 29 summarizes the changes in GC conditions which were made as a result of the optimization experiments. With the changes made on the instrument, another set of combined TNT and RDX data was obtained. A graph of this data is shown in figure 19. The LOD Values for both data sets from the old and new conditions as well as the LLD values are tabulated in table 30. As can be seen from this set, although the extrapolated LODs did not improve much, the LLDs improved drastically. The LLD for TNT changed from 3.95 pg to 39.5 fg, which is an improvement of two orders of magnitude. For RDX, the LLD changed from 39.5 pg to 0.365 pg which again was an improvement of two orders of magnitude.

The literature was searched for the best detection limits for TNT and RDX in a GC/ECD system. Douse (16,21) reports values for the minimum detectable levels (MDL) of 5 pg for TNT and 10 pg for RDX using GC/ECD. Since Douse does not define the MDL, comparing the MDLs to the LLDs resulting from this work gives a two order of magnitude improvement for TNT and a one-and-one-half order of magnitude improvement for RDX. If Douse's MDLs are compared to the LODs resulting from this work, then a thousand-fold improvement is realized in this work for both TNT and RDX.

Table 29. Changes in Parameters as a Result of Optimization.

Parameter	Old Conditions	New Conditions
Splitless Time	30 sec.	15 sec.
Priming of Injector	none	none
Splitless Liner	HP Commercial	Restek 2 mm GN
Injection Temperature	200°C	220°C

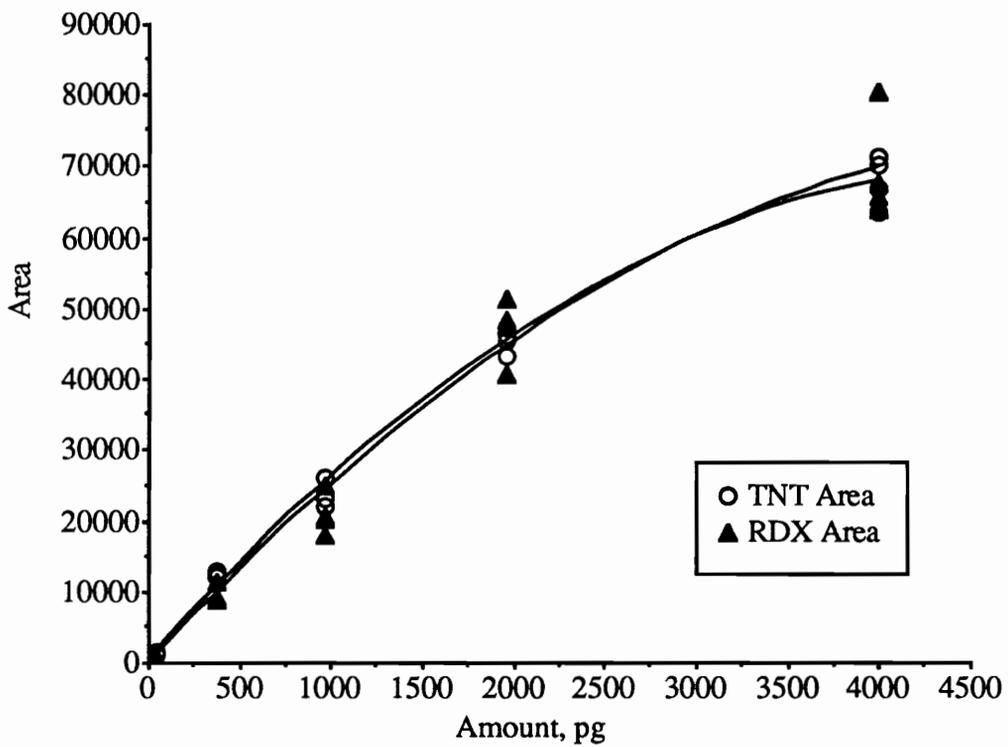


Figure 19. Area vs. Amount for TNT & RDX, Optimized Conditions.

Table 30. LOD and LLD Values for Initial and Optimized Conditions.

Data Set	LOD	LLD
Initial Conditions TNT	7 fg	3.95 pg
Revised Conditions TNT	8 fg	39.5 fg
Initial Conditions RDX	8 fg	39.5 pg
Revised Conditions RDX	11 fg	0.365 pg

Chapter 4. Summary

This dissertation has described the development, characterization, and optimization of an explosive vapor generator based on a capillary gas chromatograph (GC). Significant results obtained from this study are:

- (1) An explosive vapor generator, which produces transient explosive vapors, was built based on a Hewlett Packard model 5890 capillary GC.
- (2) The output of the vapor generator was verified to be chemically equivalent to headspace vapors for 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), by using coupled gas chromatography/mass spectrometry and ion mobility spectrometry.
- (3) The quantitative efficiency of the vapor generator was measured for TNT and RDX by coupled thermal desorption/GC. The efficiency of the vapor generator for TNT was 81%, while for RDX the efficiency was 65%.
- (4) A statistical design employing randomized, blocked, analysis of variance (ANOVA) was developed to permit comparative testing of a series of explosive vapor detectors.

(5) The gas chromatographic conditions for the vapor generator were optimized for TNT and RDX using ANOVA. This optimization resulted in lowering the lowest level detected for TNT and RDX by one to two orders of magnitude, giving values of 39.5 fg for TNT and 0.365 pg for RDX. Limits of detection values of 8 fg for TNT and 11 fg for RDX were obtained with the optimized conditions. When comparing the results of the optimization to literature, the optimized limits of detection are three orders of magnitude lower than previously reported for GC/ECD.

The five results summarized above demonstrate that transient vapor generation of explosive vapors, using a capillary GC based vapor generator, is a viable means for testing and calibration of explosive vapor detectors.

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Appendix A

EVDP Analysis Program

```
' TITLE: EVDP Analysis
' AUTHOR: George A. Reiner
'         Dept. of Chemistry
'         Virginia Tech
'         Blacksburg, VA 24061
'
```

```
' Analyzes limit of detection data obtained as part
'
' of the Explosive Vapor Detection Program at the
'
' Virginia Tech Department of Chemistry.
'
```

Entrysection: 'Determines characteristics of data table

```
INPUT "What level of which explosive was used for this data";explosive$
INPUT "How many detection systems were used";k
INPUT "How many runs were performed";b
fact = 1
FOR count = 1 TO k
  fact = fact * count
NEXT count
permutations = fact^b
PRINT "This combination gives a possibility of "permutations"
permutations."
INPUT "How many random permutations to you wish to
perform";numpermute
IF numpermute > permutations THEN
  PRINT "You can not perform more random permutations than exist."
```

```
GOTO Entrysection
END IF
```

DimensionVariables: 'Dimensions array variables

```
DIM table(k,b)
DIM detectornames$(k)
DIM ti(k)
DIM tj(b)
DIM randnum(k)
DIM permutearray(k,b)
DIM ftable(numpermute)
```

DataEntry: 'Provides for entering data from one level of analysis.

```
FOR i = 1 TO k
  PRINT "What is the name of detection system "i;
  INPUT detectornames$(i)
NEXT i
```

```
FOR i = 1 TO k
  PRINT "For the "detectornames$(i)" detection system:"
  FOR j = 1 TO b
    PRINT "What is the result of run "j;
    INPUT table(i,j)
  NEXT j
NEXT i
```

```
CLS
```

```
FOR i = 1 TO k
  PRINT detectornames$(i),
NEXT i
PRINT
```

```
FOR j = 1 TO b
  FOR i = 1 TO k
```

```
    PRINT table(i,j),
  NEXT i
  PRINT " "
NEXT j
```

```
PRINT:PRINT
```

```
INPUT "Is the data correct <Enter yes or no>";Answer$
IF UCASE$(Answer$) <> "YES" THEN GOTO DataEntry
```

```
PRINT "End of Entry Section..... "
```

AnalyzeData: 'Sends call to subprogram to calculate f statistic.

```
PRINT "Calculating f1.....  please wait."
```

```
CALL fcalc (b,k,table(),ti(),tj())
FofDATA = f1
```

```
PRINT "f1 = "FofDATA
```

PermuteData: 'Randomizes data table and calculates f for each.

```
PRINT "Calculating permutations...  please wait a while."
```

```
FOR i = 1 TO k
  FOR j = 1 TO b
    permutearray(i,j) = table(i,j)
  NEXT j
NEXT i
```

```
RANDOMIZE TIMER
```

```
FOR permutecount = 1 TO numpermute
  FOR j = 1 TO b
    FOR i = 1 TO k
      randnum(i) = RND
```

```

NEXT i
Limit=k
Switch=1
WHILE Switch
  Switch=0
  FOR count = 1 TO (Limit-1)
    IF randnum(count)>randnum(count+1) THEN
      SWAP randnum(count),randnum(count + 1)
      SWAP permutearray(count,j),permutearray(count + 1,j)
      Switch=count
    END IF
  NEXT count
  Limit=Switch
WEND
NEXT j

CALL fcalc (b,k,permutearray(),ti(),tj())
f table(permutecount) = f1
NEXT permutecount

```

SortPermutations: 'Sorts f table created by permutations.

PRINT "Now sorting f table.... please wait"

```

Limit=numpermute
Switch=1
WHILE Switch
  Switch=0
  FOR count = 1 TO (Limit-1)
    IF ftable(count)>ftable(count+1) THEN
      SWAP ftable(count),ftable(count + 1)
      Switch=count
    END IF
  NEXT count
  Limit=Switch
WEND

```

CompileResults: 'Compiles results of f test.

```

count = 0
marker = 0
WHILE marker = 0
    count = count + 1
    IF count = numpermute THEN marker = numpermute
    IF FofDATA = ftable(count) THEN marker = count
WEND
PRINT "the f of the data ranked number "marker" out of"numpermute"."
FOR i = 1 TO 5 : PRINT CHR$(7); : NEXT i
PRINT
PRINT

```

OutputSection: 'Prints data if desired

```

INPUT "Do you want a hard copy (Make sure printer is ready) <Yes or
No>";Answer$
IF UCASE$(Answer$) <> "YES" THEN GOTO ExitSection

```

```

LPRINT CHR$(12);
LPRINT
LPRINT
LPRINT explosive$

```

```

LPRINT,

```

```

FOR i = 1 TO k
    LPRINT detectornames$(i),
NEXT i
LPRINT
LPRINT
FOR j = 1 TO b
    LPRINT "Run "j,
    FOR i = 1 TO k
        LPRINT table(i,j),
    NEXT i
    LPRINT " "
NEXT j

```

```

LPRINT:LPRINT:LPRINT

```

```

LPRINT numpermute" permutations performed out of a possible
"permutations"."
LPRINT
LPRINT "f1 = "FofDATA
LPRINT
LPRINT "the f of the data ranked number "marker" out of"numpermute"."

```

```

ExitSection:           'Terminates Program.
END

```

```

SUB fcalc (b,k,table(2),ti(1),tj(1)) STATIC      'Subprogram to analyze
data.
SHARED f1

```

```

FOR i = 1 TO k : ti(i)=0 : NEXT i          ' Zero all variables
FOR j = 1 TO b : tj(j)=0 : NEXT j
TT = 0
sumYIIsquare = 0
sumTIsquare = 0
sumTJsquare = 0
SST = 0
SSA = 0
SSB = 0
SSE = 0
s1square = 0
ssquare = 0

```

```

FOR i = 1 TO k                               ' Calculate all totals
  FOR j = 1 TO b
    ti(i) = ti(i) + table(i,j)
  NEXT j
NEXT i
FOR j = 1 TO b
  FOR i = 1 TO k
    tj(j) = tj(j) + table(i,j)
    TT = TT + table(i,j)
  
```

```

    NEXT i
NEXT j

commonpart = TT^2/(b*k)           ' Calculate all sum squares &
F

FOR i = 1 TO k
    FOR j = 1 TO b
        sumYIJsquare = sumYIJsquare + table(i,j)^2
    NEXT j
NEXT i
SST = sumYIJsquare - commonpart

FOR i = 1 TO k
    sumTIsquare = sumTIsquare + ti(i)^2
NEXT i
SSA = sumTIsquare/b - commonpart

FOR j = 1 TO b
    sumTJsquare = sumTJsquare + tj(j)^2
NEXT j
SSB = sumTJsquare/k - commonpart

SSE = SST - SSA - SSB

s1square = SSA/(k-1)
ssquare = SSE/((b-1)*(k-1))

IF ssquare = 0 THEN
    f1 = 3.42083D+38
    EXIT SUB
END IF

f1 = s1square/ssquare

END SUB

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Vita

George Allen Reiner, son of John H. and Emma B. Reiner, was born on October 9, 1964 in Lebanon, PA. He attended Lebanon High School in Lebanon, PA, from September 1978 until June 1982 where in order to get out of incredibly boring study halls, he worked as a chemistry prep. assistant to Mr. Irwin Stucky and Mrs. Yvonne Jones. He graduated from Lebanon High School in June of 1982. His undergraduate work was performed at Lebanon Valley College from August 1982 until May 1986. While attending Lebanon Valley College, he performed research in several area including: using ^{32}P to develop an assay for the activity of polyphosphate kinase, interfacing techniques between a PE 900 GC and a HP 2100S computer, studying the mechanism of elimination reactions using ^3H , and work on automating a spectrophotometric method for the determination of protein diffusion coefficients. This research at LVC was performed in the laboratories of Dr. Owen Moe and Dr. Donald Dahlberg. He graduated from LVC Cum Laude with chemistry department honors in May 1986 earning a "BS in Chem" degree.

George began graduate work in chemistry at Virginia Tech in September 1986. From September 1986 until May 1988 he was a chemistry teaching assistant under Professor Glanville. From May 1988 until August 1988 he was an intern under Nelson Risser in the GC/MS

volatiles laboratory at Lancaster Laboratories Inc. in Lancaster, PA. From August 1988 until December 1990, he was a graduate research assistant under Dr. Harold M. McNair, performing research on the generation and detection of explosive vapors. He completed the requirements for the PhD degree in November of 1990.

George has accepted employment with Exxon Research and Engineering Company in Clinton, NJ.

A handwritten signature in cursive script that reads "George A. Reiner". The signature is written in black ink and is positioned to the right of the text block above it.