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Saeed H. Almeer
Old Dominion University

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EXPLOSIVE VAPOR GENERATION AND SAMPLING IN CONJUNCTION WITH ION MOBILITY SPECTROMETRY

by

Saeed H. Almeer
B.S. June 1988, University of Qatar B.S.

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Approved by:

Edward J. Poziomek (Director)

Patricia A. Pleban (Member)

Roy L. Williams (Member)

ABSTRACT

EXPLOSIVE VAPOR GENERATION AND SAMPLING IN CONJUNCTION WITH ION MOBILITY SPECTROMETRY.

Saeed H. Almeer
Old Dominion University, 1998
Director: Dr. Edward J. Poziomek

The primary objective of this research is to develop an inexpensive and reliable method to generate vapor pulses of explosives using 2,4,6-trinitrotoluene (TNT) for proof of concept. A secondary objective is to demonstrate the use of the vapor generator in various applications keeping in mind potential field scenarios involving explosives. A vapor generator/collector system was developed which gives reproducible pulses of TNT vapors at nanogram levels. The use of this technology was demonstrated in evaluating different surfaces for vapor adsorption of TNT in conjunction with ion mobility spectrometry as the primary analytical tool. Of the materials examined, Teflon was by far the best substrate for adsorption, retention, and subsequent recovery of TNT using ion mobility spectrometry for analysis.

To my Mother, Father and all of my family.

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Thanks to Allah for everything. To Him belongs all praise and I ask that He accept this work as an act of worship and forgive me any mistakes.

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CHAPTER I

INTRODUCTION

Objectives

The primary objective of this research is to develop a relatively inexpensive and reliable method to generate vapor pulses of explosives using 2,4,6-trinitrotoluene (TNT) for proof of concept.

A secondary objective is to demonstrate the potential use of the vapor generator in various applications with emphasis on evaluating efficiency of vapor adsorption on surfaces using TNT as the target explosive.

It is a further objective to integrate the technology developed in vapor generation and collection with ion mobility spectrometry (IMS) as the primary analytical tool keeping in mind utility in field scenarios.

Background

Detecting hidden explosives continues to challenge the scientific and engineering community. There are many scenarios and needs. Efficient and rapid detection is required in baggage control areas at airports, in various facilities, and in transportation vehicles with high public access. Another scenario involves detection of land mines and unexploded ordnance hidden in the ground. Bombs may easily be disguised as supposed

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harmless objects of everyday life. In some cases, bombs can be detected by recognition of their typical working parts (timers, detonators, switches, etc.). X-ray imaging can be used to identify nonchemical constituents of bombs. However, positive recognition of bombs by X-ray imaging alone may be impossible in many cases.[1] Several recent reviews on detection and characterization of explosives, explosive residues, and landmines are available[1-3]. A major thrust has been to detect the explosive material itself. Table 1 illustrates structures of common explosives, and Table 2 gives solubilities of several explosives in various solvents.

Explosives can be detected using either vapor-based, aerosol-based or radiation based methods. A classic example of vapor detection (not limited to explosives) is through canine olfaction. Dogs have been used to find people, bombs, land mines, illicit drugs, illegal agricultural products, and chemical and biological warfare agents. In theory, dogs could be trained to find anything that has a discrete odor. Issues involved in the use of dogs to sniff for illegal substances were summarized recently by Rouhi.[6] Canine olfaction represents a technology for which a scientific basis has not been fully established. Unlike a field analytical instrument, dogs do not come with precise specifications. It has been reported that dogs are not supersensitive.[6] Levels of sensitivity in detecting methyl benzoate, a degradation product of cocaine, are thought to be in the low parts-per billion range, levels comparable with most analytical instruments. It seems to be the dog's accurate and discriminating detection abilities that makes their use valuable. The dogs may also be able to detect chemical aerosols as well as vapors. Nevertheless, many questions remain as to what dogs are really responding to in field situations involving, for example, a search for explosives. Many explosives such as

TABLE 1. Structures of common explosives.[3,4]

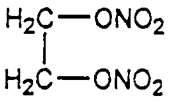
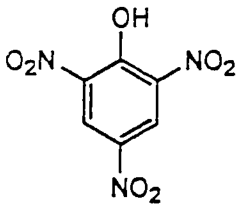
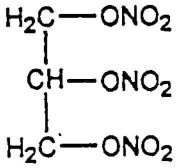
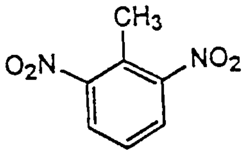
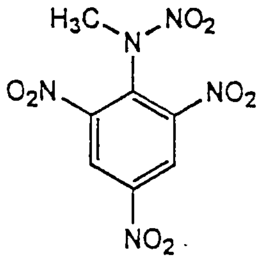
Symbol and name	Structure
EGDN Ethylene glycol dinitrate One of the main components of dynamite. Volatile, making vapor detection easier	 $H_2C{-}ONO_2$ $H_2C{-}ONO_2$
Picric acid Trinitrophenol	
NG Nitroglycerine, glycerol trinitrate	 $H_2C{-}ONO_2$ $CH{-}ONO_2$ $H_2C{-}ONO_2$
DNT Dinitrotoluenes	
Tetryl 2,4,6-Trinitrophenylnitramine Most common military booster	
AN, Ammo-nite Ammonium nitrate Also, commonly used as a fertilizer	NH_4NO_3

TABLE 1. (Continued).

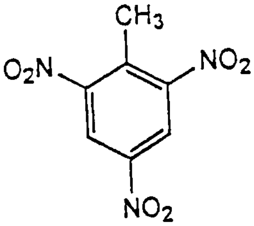
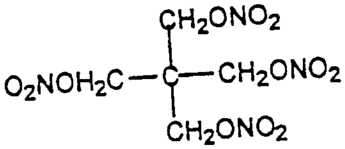
Symbol and name	Structure
TNT Trinitrotoluene, 2,4,6-trinitrotoluene A castable explosive	
RDX Cyclotrimethylenenitramine 1,3,5-Triazacyclohexane Primary ingredient of military plastic explosives known as C-3 and C-4	
PETN Pentaerythritol A plastic explosive material available in bulk form, or with modifications in sheet form under the trade name Detasheet	
Black powder	Mixture of potassium or sodium nitrate, sulfur and charcoal
Dynamite	Various compositions over the years, for example, nitroglycerine, nitrocellulose and sodium nitrate
SEMTEX	A mixture of varying proportions of RDX and PETN together with binder and plasticizer

TABLE 2. Solubility (weight %) of explosives in various solvents at 20 °C.[5]

Explosive	Water	Acetone	Ethanol, 95%	Toluene	Ether	Chloroform	Ethyl acetate
Picric acid	1.17	125.0	6.9	13.0	3.0	2.0	42.0
Tetryl	0.0075	75.0	0.563	8.5	0.418	0.39	40.0
NH_4NO_3	187.0		2.5				
TNT	0.013	109	1.23	55.0		19.0	72.1[a]
RDX	0.005	6.81	0.12	0.02		0.008	2.95[a]
PETN		20.26	0.13	0.23	0.225		10.6

[a] Methyl acetate.

nitroglycerin have low vapor pressures. Vapor pressures of common explosives may vary considerably, and examples are given in Table 3. It seems that nitroglycerine molecules are not what the dogs are responding to. When a type of nitroglycerin-based smokeless powder is presented to a dog, the odor that the dog associates with the material, the odor signature, is composed of acetone, toluene, and limonene and not nitroglycerine.[6] Findings that odor signatures of target materials such as explosives may not include the materials themselves has important implications especially in training detector dogs.

In view of the major differences in vapor pressure among explosives that might be encountered in field scenarios, detection systems should ideally be applicable to both vapors and particles. Detection system choice may be driven by the scenario. For example, Kolla[1] has concluded that detecting bombs in everyday objects requires a combination of radiation-based and vapor-based methods. There may be alternatives but the ideas are important for practitioners to consider in the field. Examples of vapor and

TABLE 3. Vapor pressures of common explosives

Explosive	Relative molecular mass	Vapor pressure[7] ppb[a]	Vapor pressure[5] ppb	°C	Vapor pressure[8] ppb(v/v) 25°C
EGDN	152	63,900			
Picric acid	217		1,300	122	
NG	227	300			580
DNT	182	145	145	20	
			184	25	
Tetryl	287		13	25	
NH_4NO_3	87		26	25	12
			7	24	
TNT	227	6	3	20	9.4
			4	25	
			17	40	
RDX	222	0.0015	0.023	25	0.006
			0.003	25	
			0.001	20	
PETN	316	0.0005	0.004	20	0.018
			7	25	

[a] Temperature not given.

radiation techniques are given in Table 4. This represents relatively expensive equipment. In the case of a bomb threat scenario, the first response usually comes from the local police department. David G. Boyd, director of the Office of Science and Technology of the National Institute of Justice, indicates that local law enforcement

TABLE 4. Examples of vapor and radiation techniques for explosives.[1]

Detection technique	Basis for detection
Vapor based	
Mass spectrometry	Molecular structure
Ion mobility spectrometry	Mobility of ionized molecules
Gas chromatography with electron capture	Chromatographic properties and electron affinity
Gas chromatography with chemiluminescence	Chromatographic properties and presence of nitro groups
Radiation based	
Nuclear magnetic resonance, nuclear quadrupole resonance, and electron spin resonance	Structural fingerprint
X-ray absorption	Heavy metal content, density
X-ray emission	Heavy metal content
X-ray diffraction	Crystalline structure
Gamma-ray absorption	Nitrogen density
Thermal neutron activation	Nitrogen density
Fast neutron activation	Carbon, oxygen, nitrogen densities

"doesn't have anything at all in terms of bomb detection equipment".[6] He explained that most police departments cannot afford any equipment that exceeds the cost of a laptop computer. According to Boyd, the ideal equipment for local bomb squads should cost no more than $10 and be so small it can be worn like a badge or on a belt or stuffed in a pocket. Boyd acknowledges that, "we're not close to where we would like to be".

The most important and time-consuming part of detecting explosives from a total systems perspective is judged to be sampling and sample handling. This is slowly being acknowledged.[1,6] An explosives detector no matter how small or sensitive, requires a threshold amount to operate. Susan F. Hallowell,[6] acting program manager of airport security technology at the Federal Aviation Administration, when questioned on sampling was quoted as saying, " Chemists have been so fixed on detector development, and that's exactly what we've got: very well developed detectors that have no front ends." Long-term goals of the Federal Aviation Administration in vapor/particle detection of explosives were outlined in a 1992 paper by Jankowski, Mecardo, and Hallowell.[7] The overall program was divided into three areas: research, development, and support. Priority research areas included calibrated particle and vapor generators, surface studies, transport mechanisms, and development of simulants for bulk detection.

How to sample explosives presents special challenges because explosives adhere to surfaces. One of the technology barriers in performing research on explosive sampling is the absence of inexpensive equipment and reliable methods to generate explosives vapors/particulates. The technology barrier is addressed as one on the objectives of the present research.

CHAPTER II

DESCRIPTION OF ION MOBILITY SPECTROMETRY (IMS)

Definition and Historical

Ion mobility spectrometry (IMS) refers to the principles, practices, and instrumentation for characterizing chemical substances through gas-phase ion mobilities.[9] IMS can be thought of as an atmospheric ionization source coupled to an ion mobility drift tube.

IMS was introduced by Cohen and Karasek[10] in 1970 as a technique for organic chemical analysis. It was termed plasma chromatography. Many reviews are available.[9,11-16]. Historical perspectives on the birth of IMS are given by Cohen and Karasek as introductory comments to a book by Eiceman and Karpas.[9] By the 1990s, a number of reports had been published on the use of IMS for detection and analysis of a variety of compounds including explosives. Table 5 gives a few examples of the types of

TABLE 5. Examples of chemicals reported to be detected using IMS.[9]

Alkyl amines
Aromatic hydrocarbons
Phthalic Acids
Explosives
Hexachlorobenzene
Nitrobenzaldehyde
Chloroform
Benzene
Organophosphorus esters
Alkyl esters
Narcotics
Ethylcellosolve acetate
Nitrobenzene
SF_6
Bromobenzene
Dicarboxylic acids
Anesthetics
Chloropentafluorobenzene

chemicals that have been detected with IMS. In these cases mass spectrometry was used to identify the ions generated in the ion mobility spectrometer.

Principles of IMS

IMS works under atmospheric pressure conditions. An ion mobility spectrometer consists of a cell in which there exist two regions, the reaction region and the drift region. The IONSCAN® Model 400 spectrometer was used in the current studies. A schematic is shown in Figure 1. Solid and liquid samples are introduced using a desorber inlet. The

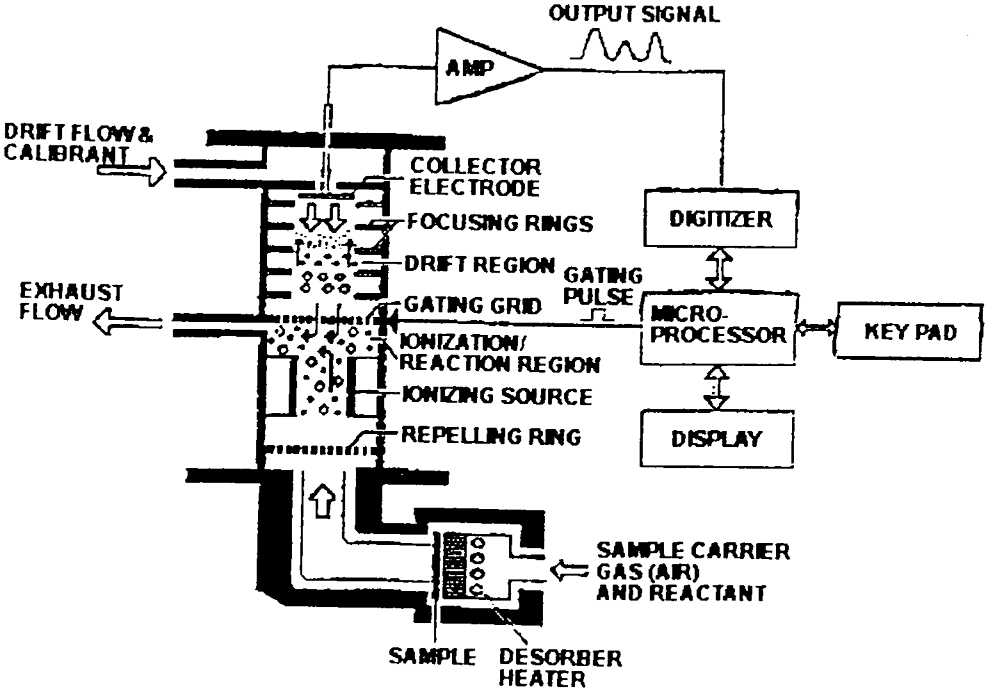


FIG. 1. Schematic of the Barringer IONSCAN® 400 ion mobility spectrometer.[17]

sample is placed on a membrane or filter paper which is then placed into the desorber unit. A Teflon® ticket assembly is available to hold the membrane. A sample carrier gas (typically purified air) carries the sample vapors into the reaction region. A ^{63}Ni source ionizes the carrier gas to produce reactant ions. Reactant ions undergo ion - molecule reactions with the sample molecules to give product ions. The mixture of ions is drawn to a shutter grid under the influence of an electric field where the ions are periodically introduced into the drift region. Once in the drift region, an electric field draws the ions to a collector electrode. The ions are separated into ion mobility peaks. The separation occurs as the result of differences in drift velocities for the different product ions. The drift and carrier gases are ambient air which is dried and purified within the IOSCAN®. No external gas supplies are required. The desorber, inlet, and drift tube are all controlled separately at temperatures that maintain the ions in their vapor state, maintain ion stability, and optimize signal response.

The theoretical relationships for the ion drift velocities are shown below. The drift velocity is proportional to the electric field through a scalar parameter, K, termed mobility (eq. 1). Since the drift velocity is the drift length, L, divided by the drift time, t_d, of the ion to the collector, the mobility is the drift length divided by the drift time and electric field (eq. 2). The mobility is therefore inversely proportional to the drift time of the ion. Mobility can be normalized against temperature and pressure to remove the effects of variable gas density (eq. 3). This is termed reduced mobility (K_o). Larger ions have longer drift times and smaller reduced mobility constants than do smaller ions.

Little molecular fragmentation occurs and the product ions exist commonly as M^+

$$v_d = KE \qquad (1)$$

$$K = L/t_dE \qquad (2)$$

$$K_o = K(273P/760T) \qquad (3)$$

Where:

v_d = ion drift velocity (cm/s)
E = electric field strength (V/cm)
L = length of the ion drift region (cm)
t_d = drift time (s)
P = pressure in mm Hg
T = temperature in °K.
K = ion mobility ($cm^2V^{-1}s^{-1}$)
K_o = reduced ion mobility ($cm^2V^{-1}s^{-1}$)

(charge transfer), MH^+ (proton transfer), M^- (associative electron capture), and $(M-1)^-$ (proton abstraction).[12] Relative proton and electron affinities are important in the ion chemistry. When air is used as both carrier and drift gas, $(H_2O)_xO_2^-$ predominate as the negative ion reactants (negative mode), and $(H_2O)_xH^+$ as the positive ion reactants (positive mode). The reactant ions can be varied by introducing other molecules. For example with nicotinamide, the reactant ion becomes protonated nicotinamide. With a chlorinated alkane, the reactant ion is chloride.

IMS Detection of Explosives

Karasek[18] was the first to report that IMS can be used to detect TNT. Sensitivity was in the picogram range. There have been many citations since then to the use of IMS for the detection of various explosives and related compounds. Much of the work appears in conference/symposium proceedings and government reports which are neither readily available to the public, nor easily retrievable through standard literature search procedures. One such paper by Spangler et al.,[19] describes early work on IMS signatures of head space vapors from explosives. The IMS signature for TNT in purified air showed two peaks, one at 2.57 $cm^2V^{-1}s^{-1}$ for O_2^- reactant ions clustered with water, and the other at 1.54 $cm^2V^{-1}s^{-1}$ for $(TNT\text{-}1)^-$ in which a proton was abstracted (eq. 4). If nitrogen is used as the carrier gas, electron capture occurs to give $(TNT)^-$ (K_o 1.49 $cm^2V^{-1}s^{-1}$) (eq. 5).

$$(H_2O)_xO_2^- + TNT \longrightarrow (TNT\text{-}1)^- + (H_2O)_xO_2H \qquad (4)$$

$$e^- + TNT \longrightarrow (TNT)^- \qquad (5)$$

Atmospheric pressure chemical ionization (APCI) of TNT vapors in air coupled with mass spectrometry led to the identification of $(TNT)^-$, $(TNT\text{-}1)^-$ and $(TNT\text{-}NO)^-$ as major ion products.[20] $(TNT\text{-}NO)^-$ has not been reported in IMS studies of TNT in air. Tanner et al,[20] postulated that $(TNT\text{-}NO)^-$ formation was probably due to nucleophilic substitution of reagent O^- for NO_2.

Barringer Research Limited[21] has compiled IMS signatures of various explosives using an IOSCAN® 250 in the negative mode. Though not specifically stated, it is presumed that the carrier and drift gas is air. The reduced mobility constants obtained for TNT, and several other explosives are given in Table 6. The K_o values may shift depending on the presence of impurities or varying amounts of water.

The negative reactant ion in IMS can be Cl^-. This may arise from trace contaminants of halocarbons in the gas supplied to the drift tube.[9] The level of chlorocarbon contamination may be large enough that Cl^- dominates the spectrum and *de facto*

TABLE 6. Reduced ion mobility constants for several common explosives[21]

Explosive	K_o $cm^2V^{-1}s^{-1}$	Ion mass AMU	Ion description	Sensitivity
TNT	1.4510	227	$(TNT\text{-}H)^-$	300 pg
DNT	1.5665	181	$(DNT\text{-}H)^-$	not given
MNT[a]	1.4727, 1.3840	172, 199	$MNT{\bullet}Cl^-$, $MNT{\bullet}NO_3^-$	not given
RDX	1.3921, 1.3155	257, 284	$RDX{\bullet}Cl^-$, $RDX{\bullet}NO_3^-$	500pg
DMDNB[b]	2.4183	46	NO_2^-	10 ng
NH_4NO_3	1.9325	62	NO_3^-	2 ng

[a]Mononitrotoluene (TNT intermediate and explosive taggant). [b]2,4-Dimethyl-1,3-dinitrobutane (explosive taggant).

becomes the reactant ion. In other instances Cl^- may be desired as a reactant ion. Table 6 shows Cl^- product ions with MNT and RDX. The Barringer IONSCAN® IMS technology has incorporated hexachloroethane as the source of Cl^- and has been utilized in explosives detection as illustrated by eqs. 6-9.[22]

$$R\text{-}Cl + (H_2O)_xO_2^- \longrightarrow Cl^- + R\bullet + x\,H_2O + O_2 \qquad (6)$$

$$Cl^- + M \longrightarrow (M\text{-}1)^- + HCl \qquad \text{(proton loss)} \qquad (7)$$

$$Cl^- + M \longrightarrow M^- + Cl\bullet \qquad \text{(electron capture)} \qquad (8)$$

$$Cl^- + M \longrightarrow (MCl)^- \qquad \text{(chloride attachment)} \qquad (9)$$

The detection of EGDN vapors using Cl^- reactant ions has been discussed in detail by Lawrence and Neudorfl.[23] The addition of dichloromethane to the carrier gas stream was reported to give increased specificity of ionization and the formation of $EGDN{\bullet}Cl^-$ ions.

In the absence of chloride ions in the IMS, autoionization and dissociative electron capture occur with the formation of NO_2^- and NO_3^-. These then act as reactant ions and attach to EGDN to give EGDN•NO_2^- and EGDN•NO_3^-. The minimum detectable quantity for EGDN based on EGDN•NO_3^- (Ko, 1.60 $cm^2V^{-1}s^{-1}$) was found to be 500 pg, as compared to 30 pg for the IMS/Cl^- chemistry.[23]

The K_o values measured for Cl^- (using a BRUKER RAID-1) have been reported to be 2.65 - 2.85 $cm^2V^{-1}s^{-1}$ depending on the humidity of the air stream.[24] Adduct ions of chlorine with negatively charged oxygen have also been observed (K_o, 2.42 $cm^2V^{-1}s^{-1}$).[24] Chloride ion does not participate in TNT ionization chemistry using IMS but RDX does. Also, RDX may appear with attachment of either chloride or nitrate ions (Table 6).

Garofolo et al.,[25] have determined TNT using a Barringer IONSCAN® 250/350 IMS. A linear response between 300 pg and 5000 pg within 0.2-1.0% of the true values was obtained. Dry air carrier gas containing a chlorinated hydrocarbon reactant was used. The K_o for TNT was reported as 1.4541 $cm^2V^{-1}s^{-1}$. Additional information on semiquantitative determination of TNT is given in the results section.

CHAPTER III

VAPOR GENERATION METHODOLOGY

Background

Explosives vapor generation methods are needed, for example, in vapor pressure determination, in the development and testing of detectors, in the development and testing of sample collection and handling methods, and in canine olfaction testing. Generation of explosives vapor is not trivial in view of the low vapor pressure of most explosives (Table 3) and the propensity of the molecules to stick to various surfaces.[25,26] In view of the latter, one might encounter contamination in a vapor generator from a previous test. An example is DNT which is reported to have a vapor pressure of 45 ppb (Table 3) and an equilibrium concentration of 2.27 ± 0.09 μg/L (measured using a 300 L container).[27] Even after a glass vessel (previously exposed to an equilibrium concentration of DNT) had been heated at 70°C for 14.9 hours, 0.7 % of the equilibrium concentration was still present. A continuous vapor generator being used as an olfactometer had been used with a smokeless powder containing DNT.[26] A continuous overnight purge at ambient temperature was not sufficient to remove residual DNT from the generator.[26] (A satisfactory solution with this particular system seemed to be a methanol purge).

Specialized vapor generators have been reported in meeting specific needs. The difficulties involved can be illustrated through an example in which a vapor generator was built to deliver odorants to canines. It was discovered that RDX, the explosive compound, could not be found in the system except for the generator reservoir itself.[26] It was found that cyclohexanone, a solvent used in purification of the explosive material, and straight chain hydrocarbons, were the primary chemicals in the system. The results suggested that performance of vapor generators needs to be validated by appropriate analytical techniques.

The present research deals with the explosive TNT. Reported methods of TNT vapor generation can be categorized as using either closed systems, continuous streams or pulses. Examples follow.

Closed systems

Nieuwenhuizen et al.,[28] estimated the vapor concentration of TNT above buried landmines under simulated conditions utilizing methyl ^{14}C-labelled TNT. The experiments included use of TNT covered with polyvinylchloride (PVC) with and without a layer of soil covering the PVC. Control experiments were also performed to generate and measure vapors from TNT alone in the test equipment. The experimental system consisted of a glass vessel equipped with a glass stirring device to allow mixing of the atmosphere. A Geiger-Mueller counting tube was mounted in the upper part of the vessel. A perforated Teflon or stainless steel shield was used to prevent direct radiation to come from the TNT sample contained in the cup. Gas inlet and outlet connections were used for taking air samples through sampling devices utilizing a vacuum pump. It was found that even with equilibration times of over 200 hours, the signals failed to become constant. Problems included sorption of ^{14}C-labelled TNT vapors on the counter window. Measurements at 20°C were not reproducible. The average of nine runs gave a TNT vapor concentration of 11 ± 8 ppb.

Bender et al.,[29] studied diffusion of TNT vapors to various surfaces utilizing 10 L glass dessicator jars that contained about 150 mg of TNT particles. Test surfaces remained in the jars from 20 to 90 days at ambient temperature before removal for analysis. It was assumed that the amount of TNT vapor generated under these conditions was equivalent to that of TNT vapor pressure.

Continuous streams

The work by Dionne et al.,[8] is widely cited for vapor pressures of the explosives TNT, RDX, PETN, NG and NH_4NO_3. The publication also contains a comprehensive listing of literature reports on the vapor pressure measurements of explosives prior to 1986. The vapor generator reported by Dionne et al.,[8] contains a small amount of explosive in equilibrium with a carrier gas. The effluent was collected in a cold trap and analyzed using GC. A schematic of the system is given in Figure 2. Nitrogen gas was passed through a Drierite/molecular sieve filter, a mass flow controller, and through Teflon® tubing to a glass impinger containing the explosive. The generator glassware was immersed in a heated sand bath which allowed the temperature to be controlled to within 0.1°C. The gas containing the explosive vapor was allowed to exit through a temperature-controlled glass-transfer line. Separate generator systems were assembled for each explosive. In the case of TNT, about 200 mg were used. The system was operated with carrier gas flowing, for a minimum of a week, to allow equilibration before use.

The continuous vapor generator used as an olfactometer and mentioned above[26] is

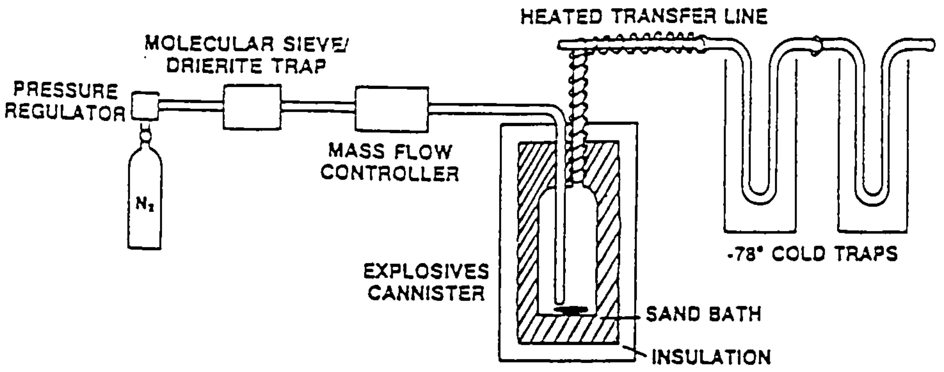


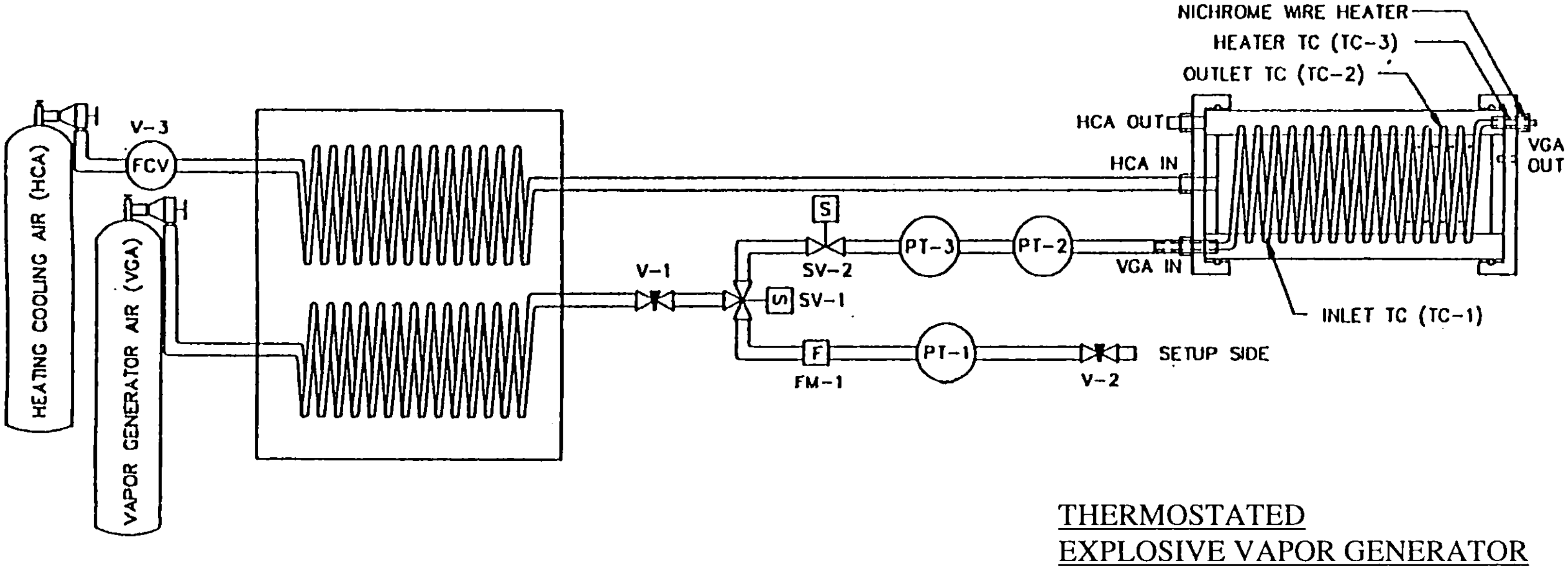
FIG. 2. Continuous vapor-stream generator for explosives.[3]

worth describing in more detail. The system involves a five-stage dilution capability. The explosives source is placed in a glass vessel submerged in a heated water bath. A stream of air through the vessel results in a vapor of explosive that is then cooled to ambient temperature using a coiled condensation column. The vapor is then diluted by consecutive additions of known quantities of air through one to five 100 or 1000 fold dilution steps. The net range of dilution factors is 10^{-2} to 10^{-15}. It was assumed that a saturated head space of vapor exists above the explosives sample and that there is no loss of mass during the dilution process. The system did not achieve the desired performance.[26]

Pulses

Davies, et al.,[30] reviewed designs for pulsed explosives vapor generators reported prior to 1993. One system involved injecting an explosives standard into a modified GC resulting in vapor emission at the exit of the capillary column.[31] Another system utilized a heated syringe containing a reservoir of the explosive in the syringe barrel.[32] Significant variability in the output from the GC generator, and the lack of controls in the syringe method led Davies and coworkers[30,33] to construct a generator based on a modification of a continuous-flow design by Carter et al.[34] The explosives were deposited on quartz beads which were then loaded into a stainless steel tube. The tube was coiled and placed inside a temperature-controlled chamber. Ultrapure air was passed through the coil to carry the vapors of the specific explosive. The generator is capable of delivering a pulse of varying mass through the control of coil temperature, airflow rate, and pulse width. The system is computer controlled. Vapor pulse output has been calibrated in the picogram to nanogram range using IMS. A diagram of the system illustrating the various control points is given in Figure 3. The computer data acquisition/control system is not shown.

Vapor pulse generators based on the above design were built for TNT, RDX, and PETN to support an independent validation and verification facility for explosives detection systems for the Federal Aviation Administration.[30] The purpose is to use the generators as quantitative vapor standards to establish the lower limits of explosives detection systems. Use of the vapor generator to characterize performance of a mass spectrometer for RDX and PETN was described by Scott et al.[35] Five second vapor pulses were presented to the mass spectrometer ionization region at approximately 100-



THERMOSTATED
EXPLOSIVE VAPOR GENERATOR

THERMOSTATED AIR SUPPLY
HCA: Compressed air
VGA: Zero air
V-3: Flow control valve

FLOW CONTROL MANIFOLD
V-1, V-2: Micrometer control valve
SV-1, SV-2: Solonoid valves
PT-1, PT-2, PT-3: Pressure transducer

FIG. 3. Schematic of a vapor generation system for explosives adapted from reference 33.

150°C through a special sampler interface. The vapor generator oven temperatures were set to allow a range of 200 to 5000 pg of explosive to be injected. The flow rate through the generator was varied between 40 and 240 mL/min. The little adsorption in the sampling train was attributed to the use of high flow velocity and high temperature.

Relevance of Reported Technologies to the Present Research

A simple and relatively inexpensive vapor generator was needed in the present research to deliver reproducible amounts of TNT vapor pulses for applications such as evaluating efficiency of vapor adsorption on surfaces. A review, as outlined above, did not identify a system which met our needs. One of the important requirements was that the system be compatible with the Barringer IONSCAN® 400 IMS.

There have been various reports on explosive vapors and solids introduction techniques in conjunction with IMS, This often involves some modification of the IMS inlet for direct injection of vapors. There are also probes that have been used with solids. Some of the possibilities were described by Spangler, et al.,[19] in early applications of IMS for the detection of explosives.

The vapor generator/collector system described in the present research is based on thermal desorption and uses the IONSCAN® 400 IMS sample holder as part of the collector.

CHAPTER IV

EXPERIMENTAL

Materials and Chemicals

Solvents and reagents were used as received. Acetonitrile (Baxter), and methanol (Fisher) were HPLC grade. Toluene, A.C.S. reagent grade (Spectrum) and Sylon-CT, Cat. No. 3-3065 (Supelco, Inc.) were used in silanization of quartz membranes (QMA). The explosives (TNT, RDX, tetryl) were obtained as standard solutions (1 mg/mL in acetonitrile) from Radian International. Ammonium nitrate was A.C.S. reagent grade (Fisher). Nitric Acid was 16 M, analytical grade (Mallinckrodt).

The adsorbents included: Teflon® membranes (Barringer); QMA quartz fiber filters (Whatman); solid-phase extraction membranes (C-18, 3-M) (Fisher); paper towels (Preference®) Fort Howard Corp., Green Bay, WI; filter paper No. 404, Lot No. B952, Schleicher & Schuell (S&S); cotton cloth from gloves (40456900, United Kingdom); and nylon membranes, Nylaflo® P/N S66608, 0.45 µm, (Gelman Sciences). Organophilic zeolite - Teflon membranes (1A; TZ25, 22-25% zeolite; TZ42, 23-42% zeolite) were experimental materials fabricated by FluoroTechniques using organophilic zeolite from Aldrich. The adsorbents were cleaned immediately prior to use by passing them through at least one IMS desorption cycle. This also served to provide background IMS signatures.

TNT solutions containing 0.5, 1.0, 5.0, 7.5, 10, 15, 20, and 25 ng/µL were prepared by placing 0.5, 1.0, 5.0, 7.5, 10, 15, 20, and 25 µL, respectively, of the standard stock solution into a vial. Acetonitrile solvent was added using Eppendorf pipettes in appropriate amounts to give solutions with final volumes of 1.0 mL.

Equipment

Ion Mobility Spectrometer. The IMS used in this study was a Barringer IONSCAN® 400. Purified room air was used as the carrier and drift gas in the IMS. Operational parameters included: drift tube temperature, 105 °C; inlet temperature, 240 °C; desorber temperature 250 °C; drift tube flow rate, 351 cc/min; sample flow rate, 300 cc/min; and analysis time, 6.00 s. The diffusion tube containing hexachloroethane as a Cl^- reactant ion source had been removed. However, residual hexachloroethane remained in the system. The IMS signatures are presented in digital units (du) for the maximum amplitude of an ion peak.

Vapor Generator and Collector. The vapor generator/collector system designed as part of the present research is illustrated in Figure 4. The desorption chamber consists of a screw-on cap assembly to hold the QMA membrane. A nichrome electrical heating element controlled by a DC power supply (not shown) (PS-1830D, Instek) is centered above the QMA. An O-ring provides a tight seal. The explosive vapor passes through a short column connected to an aluminum collector designed to hold a Barringer IONSCAN® sample holder. The assembly is hinged which allows facile placement and removal of the sample holder. Though not shown in the schematic, there is also an O-ring to provide a seal between the sample holder and the collector. There is no O-ring in the hinged cover. The vapor passes over the test adsorbent and out along the collector

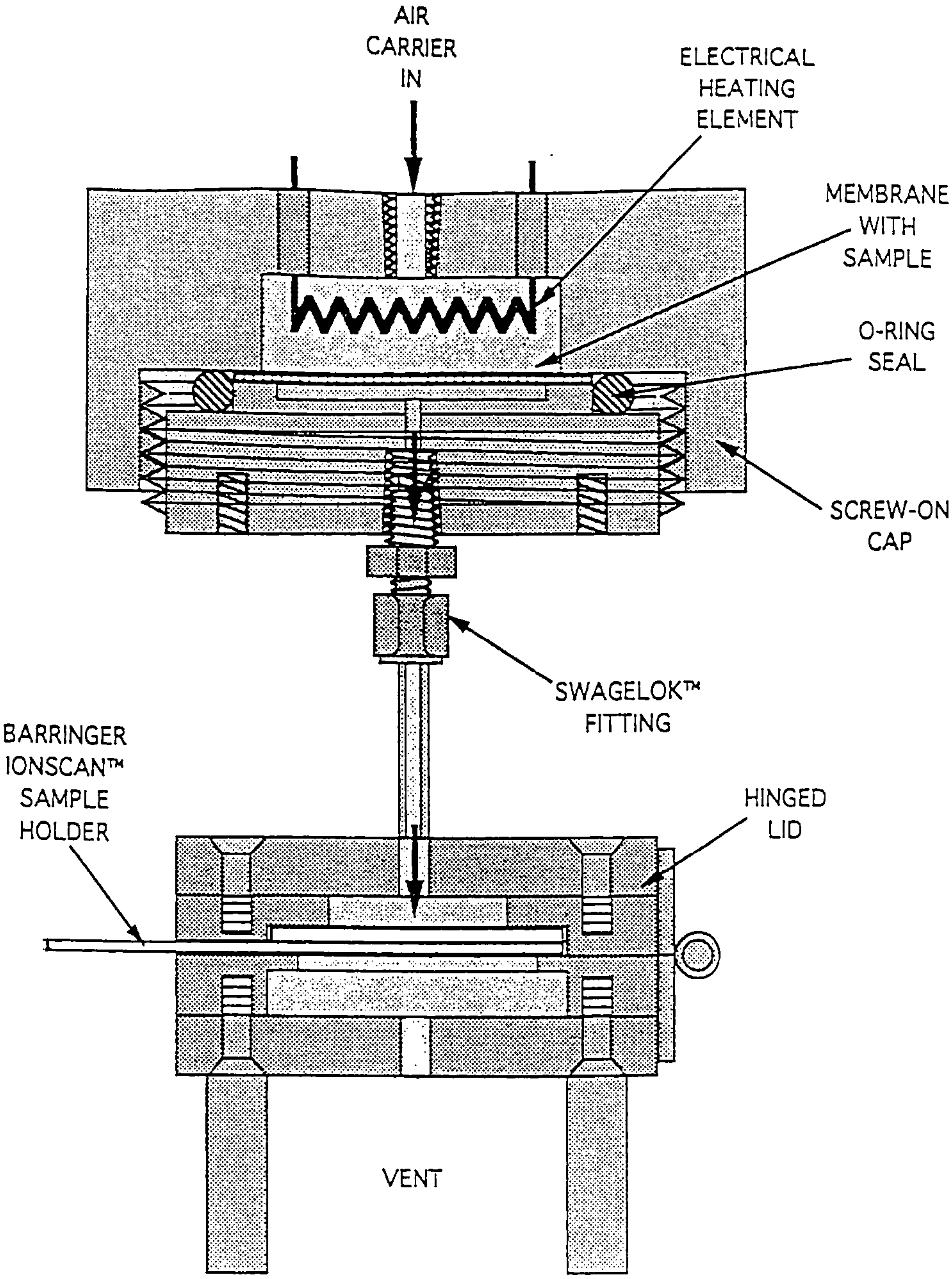


FIG. 4. A cross-section view of the vapor generator/collector assembly.

sides just above the sample holder. Air does not pass through the adsorbent as confirmed by a flowmeter connected to the vent. The exit of air along the collector sides was confirmed visually by the use of smoke generated using diesel oil in the thermal desorber.

Typical IMS Sample Run

Purified air from the IONSCAN® 400 is passed into the system at a flow rate of 20.5 ± 0.2 cc/min controlled by a needle valve and checked with a digital flowmeter (Humonics). (The flow rate at the Swagelok® fitting outlet of the generator with a QMA membrane in place was 19.2 ± 0.2 cc/min.) The settings on the power supply are 15 on volts and 3 on amperes. The QMA and test adsorbent (e.g., Teflon® membrane) are cleaned using the IMS, and their background signatures recorded. The adsorbent material (already in an IONSCAN® sample holder) is placed into the collector. Twenty-five µL of the TNT solution is applied to the center of the QMA membrane using a 25 µL syringe (Hamilton). The QMA membrane is positioned in the brass sample holder (containing the heating elements), and the plug is screwed into it. (Tweezers are always used in handling the QMA and adsorbent materials.) The desorber is connected to the collector through the Swagelok® fitting. The power supply is turned on, and the outside temperature of the screw cap is monitored using a thermocouple taped to the surface until a temperature of 40 °C is reached. This normally takes close to 2 minutes, and reflects an inside temperature of 235-250 °C. The power supply is turned off. The IONSCAN® sample holder is immediately removed from the collector and analyzed using IMS. The QMA membrane from the desorber is also analyzed. The different parts of the generator/collector assembly are cleaned with small amounts of acetonitrile, i.e., 50 - 100 μL depending on the part. Tubes and connections are rinsed once, and surfaces are wiped using Kimwipes®. The system is reassembled and checked for TNT with the IMS using fresh membranes. If TNT is found, the cleaning process is repeated. One cleaning is normally sufficient to remove TNT to undetectable levels.

Quality Assurance/Quality Control (QA/QC)

Meaningful procedures related to detection and analysis of explosives must include elements of a quality assurance program. The work with IMS followed a QA/QC procedure specifically written by Homstead and Poziomek[36] for the Barringer IONSCAN® 400 spectrometer.

The protocol employs TNT as the reference standard using IMS in the negative mode. A five point calibration curve was used to determine concentration levels suitable for QC check solutions. Peak amplitudes and K_o values were established for QC check solutions that must be met each day before proceeding with analyses. Any deviation from these criteria requires assessment of the problem and corrective action. The procedure was found helpful in maintaining data quality, and in providing an early indication of potential problems. A similar procedure were developed for IMS work in the positive mode except that cocaine hydrochloride was chosen as the reference standard.

It is a common practice to report K_o values to five significant figures. This is also done in the present report. However, it has been found through our QA/QC checks that K_o values may vary in day-to-day measurements apparently due to changes in dessicant/charcoal and pressure transducer performance. Three significant figures may be more realistic for reporting K_o values; in most situations this is of no concern unless an interference has an ion peak with its K_o very close to that of the target analyte.

Preparation of Silanized Quartz Membranes

The QMA membranes are placed in the bottom of a beaker and covered with Sylon-CT solution. The membranes are allowed to stand for three minutes, and excess solution is poured off into a waste container. The membranes are covered with toluene and allowed to stand for another three minutes. The excess toluene is poured off, and the membranes are rinsed with methanol until the solution is clear. The membranes are allowed to air dry then placed in an oven at 110°C overnight. This procedure sufficed for the present screening work but in some cases, the silanization did not appear complete. The technique needs to be examined more closely especially taking caution that the membranes do not cover each other thus ensuring that diffusion of the Sylon CT solution is not impeded.

CHAPTER V

RESULTS AND DISCUSSION

Semiquantitative Analysis of TNT

IMS calibration information and curves for TNT have been reported in the last five years by several investigators, e.g., Davies, et al., (1993),[30] Garofolo, et al., (1996),[25] Rodacy, et al, (1997),[37] and Parmeter, et al., (1997)[38]. IMS spectrometers and experimental conditions differ. Linear responses were reported between 5-1000 pg,[30] 300-5000 pg,[25] and 85-2000 pg/sec (continuous flow mass loss mode in conjunction with a vapor generator).[38] Figure 5 illustrates the relationship between peak height and TNT concentration plotted from data published by Garofolo, et al.[25] The relationship reported by Rodacy et al.,[37] appears quadratic with considerable scatter of points (Figure 6). IMS typically has two orders of magnitude in sample mass over which the response is linear.[39]

Our work using standard solutions of TNT, Teflon® membranes, and the IMS operational parameters listed above, gave two linear regions 50-500 pg, and 500-15,000 pg before saturation became evident (Table 7, Figure 7). The calibration curve within the linear ranges was used to estimate the amounts of TNT sorbed on Teflon membranes in the vapor generator/collector system.

Generation of TNT Vapor Pulses

A plot of IMS peak amplitude of TNT adsorbed on Teflon® in the collector vs. different TNT starting amounts in the generator appears in Figure 8. The data are given in Table 8. Comparing the amplitudes to those in the TNT IMS calibration curve, it is

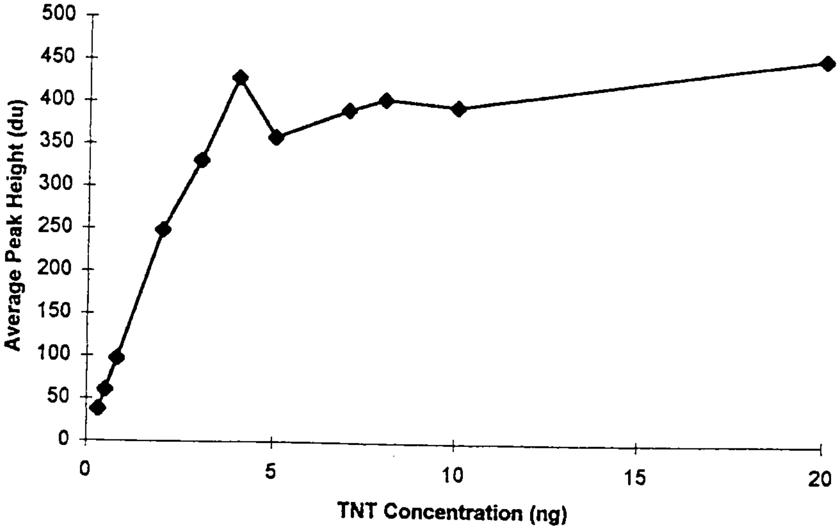


FIG. 5. Plot of IMS peak amplitude vs. TNT amounts adapted from reference 25.

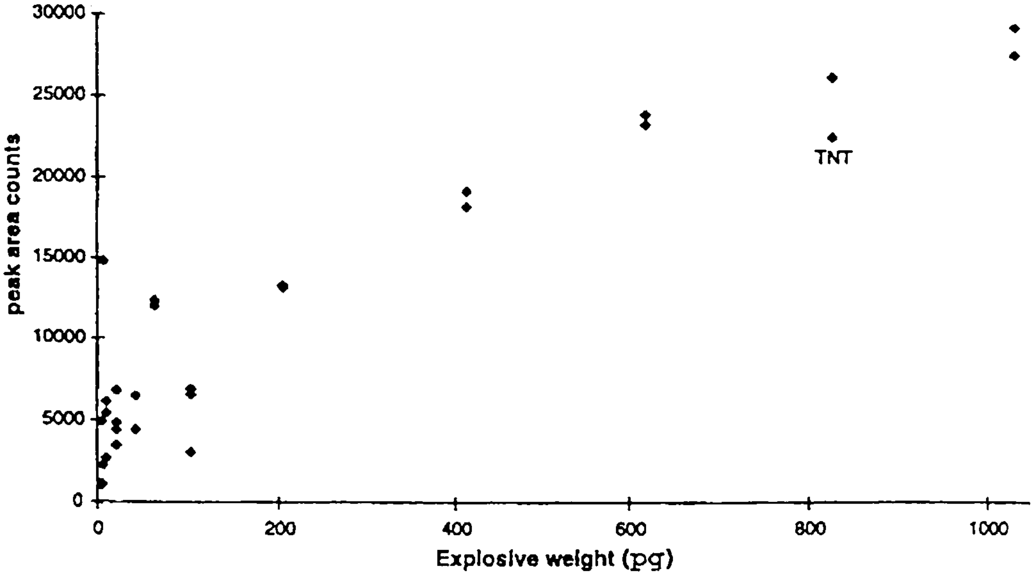


FIG. 6. Plot of IMS peak area vs. TNT amounts adapted from reference 37.

TABLE 7. IMS calibration data for TNT.

Amount ng	Amplitude du	Amplitude Average du	Standard Deviation du	%RSD
0.05	26 28 33	29	3.6	14
0.1	215 194 254	221	31	14
0.5	384 402 403	396	11	3
5	547 540 517	535	16	3
10	738 753 732	741	11	1
15	841 859 871	857	15	2
20	870 830 901	867	36	4

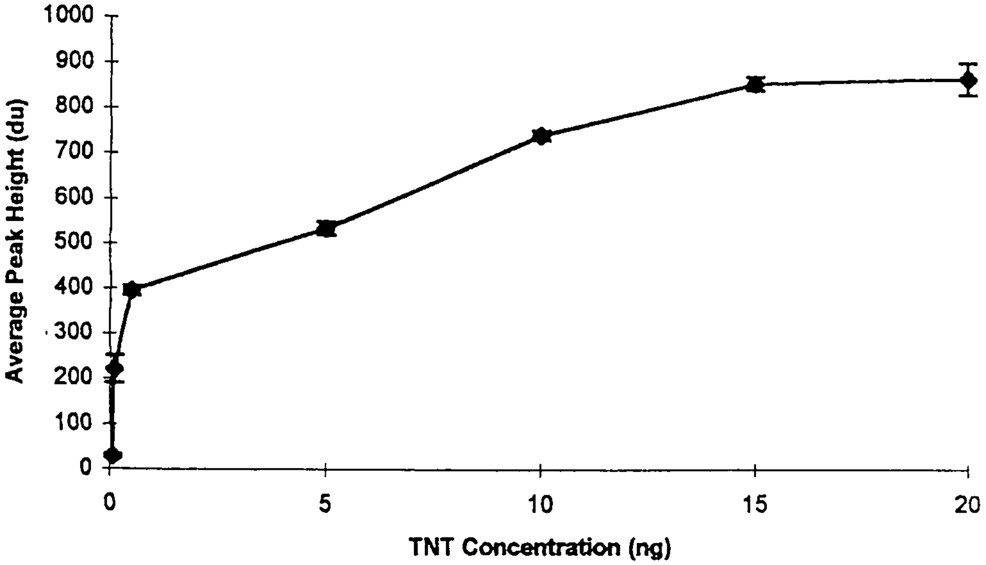


FIG. 7. Plot of IMS peak amplitude vs. TNT amounts.

TABLE 8. IMS data for TNT adsorbed on Teflon® in the collector relative to starting amounts of TNT in the generator.

Initial TNT Amount ng	Amplitude du	Amplitude Average du	Standard Deviation du	%RSD
25	24 28 39	30	7.8	26
125	187 198 179	187	9.5	5.1
188	373 331 300	335	37	11
250	616 603 616	594	27	4.6
375	722 644 751	706	55	7.8
625	782 782 778	781	2.3	0.3

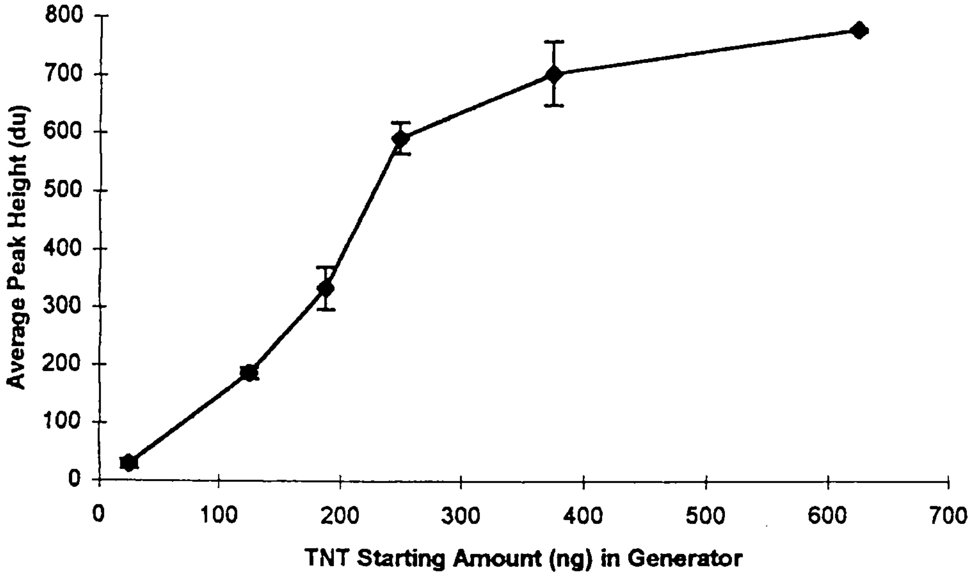


FIG. 8. Plot of IMS Peak Amplitude of TNT Adsorbed on Teflon® in the Collector vs. Different TNT Starting Amounts in the Generator.

clear that about 2-3 % of the original amount in the generator is adsorbed. This is the baseline data to be used in judging performance of other surfaces. The results do not give an indication of how efficient Teflon® is in adsorbing the TNT vapor pulse. TNT is lost through adsorption on the walls of the system before vapors reach the Teflon®. Also, decomposition occurs as a result of heating TNT on QMA. It is not an objective of the present research to achieve efficiency in transfer of TNT vapors from the generator to the collector. The primary objective is to develop an inexpensive and reliable method to generate vapor pulses of TNT. Based on the results shown in Table 8 and Figure 8, this has been accomplished.

It is important however, to understand the relative adsorption of TNT vapors within the vapor generator/collector system. Such information will be useful for any redesign considerations in the future. An experiment was performed using 250 ng of TNT in the generator, and analyzing rinse solutions (acetonitrile) from different parts of the generator/collector system. The acetonitrile was allowed to evaporate on Teflon successively depositing 25 µL portions. The membranes were then analyzed using IMS. Results are given in Table 9 for three runs. The areas in the system where the TNT is accumulating are in the Swagelok® fitting, the short column between the generator and the collector, and on the inside surface of the hinged collector lid. Though cleaning the system between runs is not a lengthy task, it is likely that cleaning is not necessary to achieve a set pulse concentration. This was not investigated but presents an attractive option in situations where only one concentration is required, for example in screening experiments.

Table 9. Relative adsorption of TNT within the vapor generator/collector system.

Generator/collector system part	IMS peak amplitude of TNT residue (du)
Inside of screw-on cover	206
	63
	141
QMA membrane	145
	321
	163
Plate below QMA membrane	1350
	1390
	1300
Inside of Swagelok® fitting	1270
	1391
	1303
Column connecting generator to collector	1475
	1389
	1654
Top inside of hinged collector lid	644
	112
	0
Teflon® adsorbent membrane	672
	581
	585
O-Ring and sample holder plate below the Teflon®	0
	0
	0

Comparison of Various Materials in the Adsorption and Retention of TNT Vapors

The list of materials investigated in the adsorption of TNT vapors is given in Table 10. Each was examined for retention of TNT by depositing 10 ng of TNT in acetonitrile on the surface followed by IMS analysis. The resulting amplitudes for the TNT ion peak are given in a bar chart in descending order of intensity (Figure 9). An experimental Teflon®-zeolite membrane (1A) releases the TNT most readily in the IMS thermal desorption chamber, while no TNT was found to desorb from the C18 solid phase extraction material. It is possible that TNT is decomposing on a particular surface. However, decomposition was not evident through the appearance of anomalous ion peaks. Figure 10 gives IMS results with the surfaces being allowed to sorb TNT from a vapor pulse using 250 ng TNT in the vapor generator/collector system. It is clear that use

TABLE 10. Materials examined in the adsorption of TNT vapors.

Adsorbent material[a]	Symbol
Teflon membrane, Barringer	T
Teflon - organophilic zeolite membrane	1A
Teflon - 22-25% organophilic zeolite membrane	TZ25
Teflon - 23-42% organophilic zeolite membrane	TZ42
Filter paper, Schleicher & Schuell	S&S
Quartz fiber filter	QMA
Cotton cloth	JR7
Paper towel	PT
Solid phase extraction membrane,	C-18
Nylon membrane	NM

[a] See the experimental section for more details.

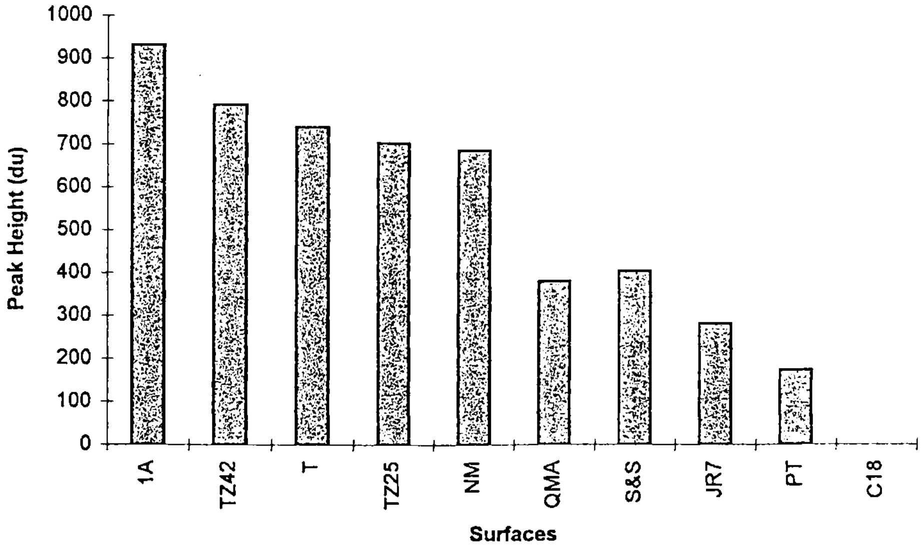


FIG. 9. IMS analysis of 10 ng TNT deposited on various surfaces from acetonitrile.

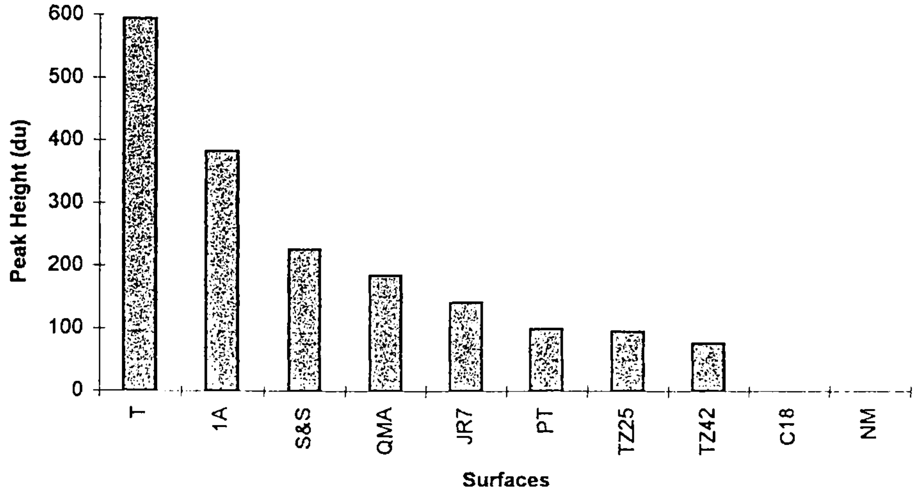


FIG. 10. IMS analysis of TNT adsorbed on various surfaces from the vapor state using 250 ng TNT in the vapor generator/collector system.

of Teflon® leads to the greatest amount of TNT being adsorbed and subsequently desorbed using IMS. It does not necessarily reflect the efficiency of TNT adsorption from the the vapor state under the conditions in the vapor generator/collector system. Most likely the C18 solid phase extraction material is the most efficient collector; however, it also binds TNT most efficiently under the IMS thermal desorption conditions. Analysis for TNT would require techniques such as solvent extraction. Practitioners who are considering use of IMS analysis in conjunction with passive sampling would use Figure 10 and choose Teflon® which clearly gives the best overall performance.

An IMS peak for NO_3^- was noted when utilizing the vapor generator/collector system with several of the adsorbents. However, NO_3^- was not noted when TNT was deposited on any of the substrates and analyzed directly using IMS. This indicates TNT decomposition under the vapor generator conditions. TNT is undoubtedly the source of the NO_3^- , but it is not clear what is adsorbing on the substrates to cause appearance of NO_3^- in the IMS plasmagrams. Cotton cloth and paper towel showed the strongest NO_3^- peaks followed by S&S paper and then the TZ42 and TZ25 zeolites. Nitrate was not observed with Teflon®. The decomposition of TNT on QMA will be discussed in detail later.

Performance of Silanized vs. Unsilanized Quartz Membranes

Commercially available quartz membranes (QMA) were routinely used to hold samples in the oven portion of the generator. Quartz was chosen since it does not decompose under high temperatures. Other glass fiber materials are available and may be suitable, but these were not examined. We thought it would be interesting to compare the performance of unsilanized and silanized QMA both in the generation and collection of TNT vapors. Initially the matrices were compared using the IONSCAN® 400 IMS in a normal fashion by allowing a solution of know TNT concentration to evaporate on the membranes followed by IMS analysis. The IMS background of the silanized membrane was found to be cleaner than commercial QMA that had been heated through several IMS cycles. With 10 ng of TNT, the amplitude of the resulting TNT peak using commercial QMA was somewhat higher in comparison to that from the silanized membrane. In some cases an additional peak at K_o 1.4386 $cm^2V^{-1}s^{-1}$ (low intensity) was obtained with unsilanized QMA. This is probably due to QMA background. However, no advantage was noted in using silanized QMA over unsilanized material in the normal IMS mode with TNT.

A series of experiments were performed in which silanized and unsilanized QMA were compared in the vapor generator/collector both as sample matrices in the desorber and as adsorbers for vapor. The most interesting observation was with the combination unsilanized QMA (contained in the desorber) and silanized QMA (contained in the collector). No TNT vapor adsorption was evident on silanized QMA, however, a very strong NO_3^- peak appeared (Fig. 11).

It is conjectured that TNT decomposed on the QMA, with one of the products, NO_3^- probably as HNO_3, being adsorbed readily by the silanized QMA. There also appears to be a difference between unsilanized QMA and silanized QMA for affinity of TNT vapors and TNT decomposition products from QMA. When unsilanized QMA is used in both the oven and the collector, the presence of the TNT peak is clear. However, no NO_3^- peak appeared above the background. This was confirmed with several runs. With

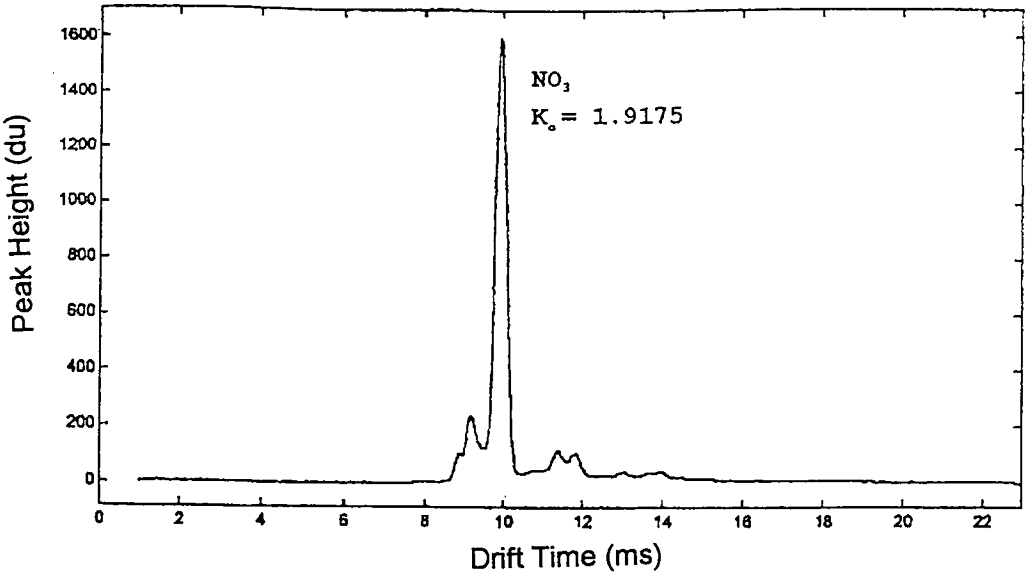


FIG. 11. IMS signature using TNT in the vapor generator/collector with unsilanized QMA as the desorber material and silanized QMA as the adsorbent.

silanized QMA as the adsorbent, NO_3^- was evident but not TNT (Figure 11). With partially silanized QMA as the adsorbent, both TNT and NO_3^- were found. If silanized QMA is used in the oven, decomposition of TNT is very clear using either silanized or unsilanized QMA as the collector. In both cases, NO_3^- and TNT are present but not in the same ratios. When silanized QMA is used both as a desorber and collector, a greater number of peaks were observed in comparison to all other combinations.

It was also interesting to note that under similar temperature conditions, a brown spot of reasonable intensity appeared on the side of the QMA closest to the nicrome heater-wire. (The sample is deposited on the side away from the heater.) This confirms sample decomposition but may involve the silanized matrix as well. In no other case, (all of the sample matrices examined in this research) was color observed. This may be exploitable as a new color test for TNT but needs to be checked with a number of other organic compounds to allow an appreciation of selectivity.

In summary, considering the nature of the studies reported here, use of silanized QMA offers no advantages over commercial QMA as the sample matrix in the heater portion of the vapor generator. The experiments did confirm that TNT decomposes when heated on either unsilanized or silanized QMA. The decomposition mechanism, product yields, and product ratios may vary, but this was not examined further. It represents an interesting area for future research.

Use of Tetryl and NH_4NO_3 in the Vapor Generator/Collector

TNT, tetryl and NH_4NO_3 have approximately the same reported vapor pressures (Table 3). We wanted to determine whether the conditions used in the vapor generator/collector for TNT would apply to tetryl and NH_4NO_3 as well.

IMS signatures of tetryl and NH_4NO_3 are reported (e.g., ref. 21). Tetryl was reported to show several IMS peaks: (tetryl•tetryl - H)$^-$ (K_o, 0.9613 $cm^2V^{-1}s^{-1}$); tetryl•NO_3^- (K_o, 1.1839 $cm^2V^{-1}s^{-1}$); tetryl•Cl^- (K_o, 1.2205 $cm^2V^{-1}s^{-1}$); (tetryl - NO_2)$^-$ (K_o 1.3973 $cm^2V^{-1}s^{-1}$); and [tetryl - 2(NO_2)]$^-$ K_o, 1.5513 $cm^2V^{-1}s^{-1}$.[21] Karpas[40] reported Ko values of 1.45 and 1.62 $cm^2V^{-1}s^{-1}$ for the major ions of tetryl at 250°C using air for the carrier and drift gases. Under the conditions described in the Experimental section we found one major ion peak with K_o 1.3660 $cm^2V^{-1}s^{-1}$ for tetryl on Teflon (Figure 12A). The reasons for the variations between investigators are not clear but may be due to differences in reactant ion chemistry. In the present work, air was used as both the carrier and drift gases.

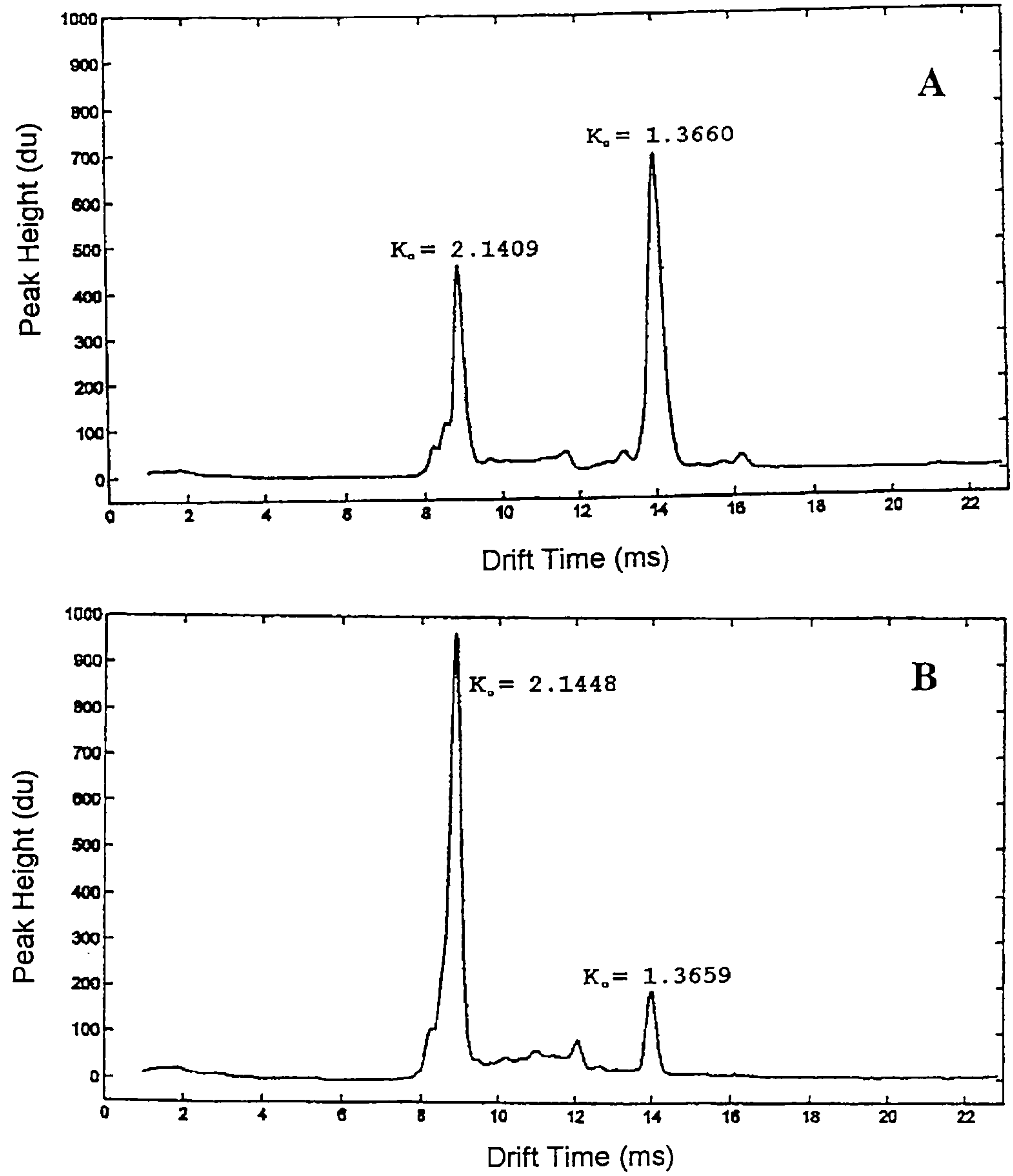


FIG. 12. IMS signatures of 10 ng tetryl on Teflon® (A), and tetryl adsorbed on Teflon® from 250 ng of tetryl heated on QMA in the vapor generator(B).

Traces of hexachloroethane were present as a source of chloride ion for reactant ion chemistry. However, the source of hexachloroethane had been removed.

Use of tetryl with the vapor generator/collector and Teflon as the adsorbent gave the expected ion peak for tetryl (based on the results with tetryl placed directly on Teflon) with little if any decomposition being evident (Figure 12B).

The reported IMS plasmagram for NH_4NO_3 shows one peak, NO_3^- with K_o 1.9325 $cm^2V^{-1}s^{-1}$.[21] AMMONAL, a mixture of NH_4NO_3 and Al powder gave the same peak. Figure 13A shows the IMS signature of 10 ng NH_4NO_3 on Teflon (from a methanol solution) with a prominent ion peak being evident for NO_3^-. However, no nitrate peak was found when a solution of 10 ng NH_4NO_3 was allowed to evaporate on either QMA, paper towel, cotton glove, or S&S filter paper materials and then analyzed using IMS. In repeat runs with QMA, some NO_3^- was noted but not consistently. The IMS plasmagram of Teflon which had been exposed to vapors from 250ng NH_4NO_3 heated in the vapor generator is shown in Figure 13B. No NO_3^- peak is noted. Also, no NO_3^- was found using QMA, paper towel, cotton glove, and S&S filter paper materials in the collector.

It is concluded that under the conditions of heating and air flow in the generator, the NH_4NO_3 decomposes on QMA. Under the IMS conditions described, 10 ng of NH_4NO_3 on Teflon gives an ion peak for NO_3^- but appears to decompose when using either QMA, paper towel, cotton glove, or S&S filter paper as sample matrices.

Thermal decomposition of NH_4NO_3 occurs predominantly by an ionic mechanism in the temperature range 200°C to 300°C. The first step is a dissociation equilibrium between NH_4NO_3, NH_3 and HNO_3 (eq. 10).[41,42]

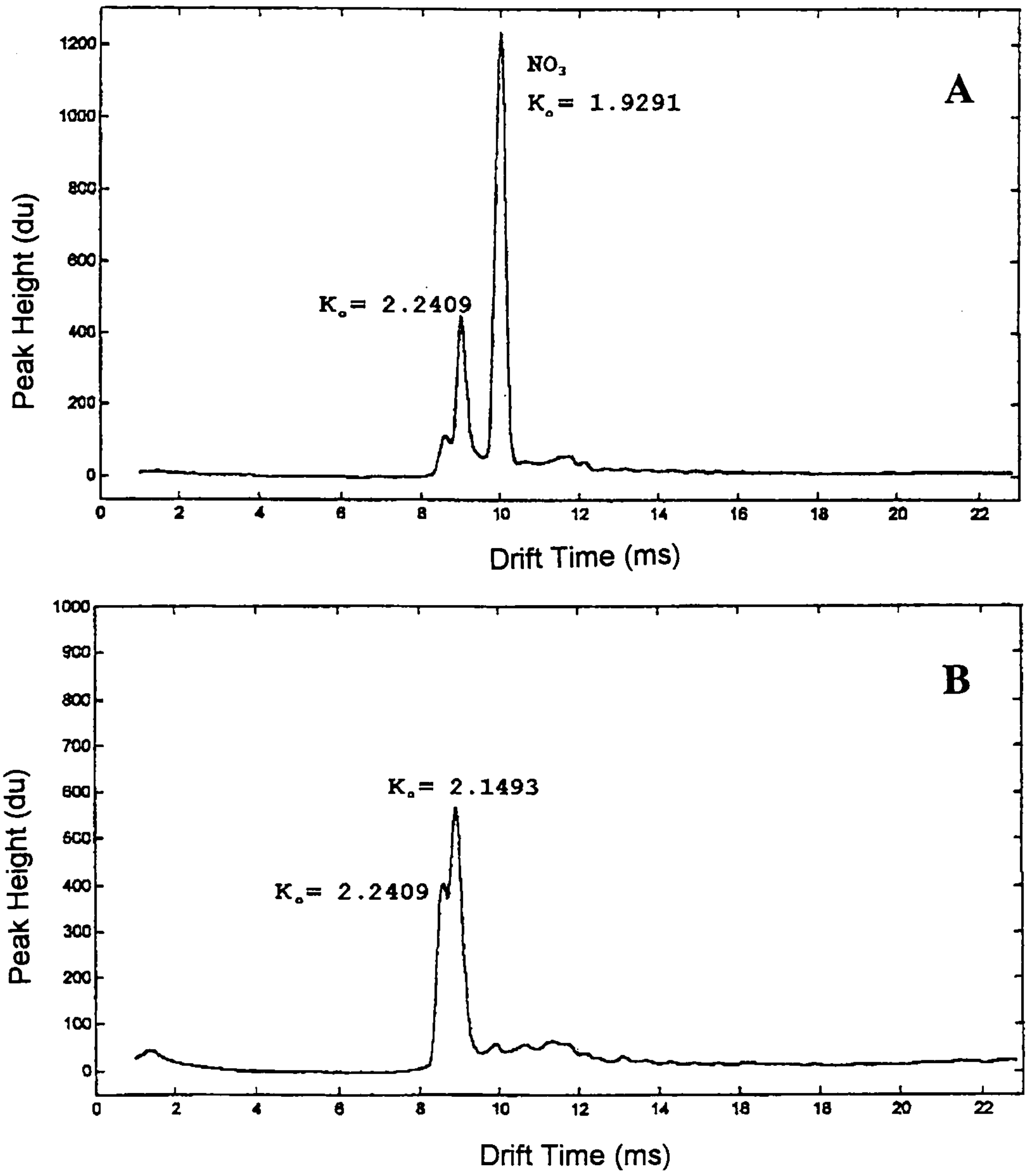


FIG. 13. IMS signature of 10 ng NH_4NO_3 on Teflon® (A) and the IMS plasmagram of Teflon® which had been exposed to vapors from 250 ng of NH_4NO_3 heated on QMA in the vapor generator (B).

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 \qquad (10)$$

This dissociation equilibrium may be responsible for the vapor pressure of NH_4NO_3 and HNO_3 may be the compound entering the IMS reaction chamber when NH_4NO_3 is being analyzed. Formation of nitronium ion has been found to be rate determining in the decomposition of NH_4NO_3 . This is acid catalyzed with NH_4^+, H_3O^+ or NH_4^+ being possible sources of H^+ (eq. 11). The nitronium ion then reacts with NH_3 to give N_2O (eq. 12).[42]

$$HNO_3 + H^+ \rightleftharpoons H_2ONO_2^+ \rightleftharpoons NO_2^+ + H_2O \qquad (11)$$

$$NO_2^+ + NH_3 \longrightarrow N_2O + H_3O^+ \qquad (12)$$

In the present work the QMA may be serving as an acid thus catalyzing the thermal decomposition of NH_4NO_3 under the conditions in the reactor. The same or other mechanisms may be operating in the IMS desorption chamber. A variety of materials may accelerate the decomposition of NH_4NO_3.[41] Water and ammonia inhibit the decomposition but HNO_3 serves as a catalyst.

Use of HNO_3 in the Vapor Generator/Collector

In view of the observation that NO_3^- was found in IMS plasmagrams using several adsorbent materials from the vapor generator/collector with TNT, but not found using NH_4NO_3, lead us to examine HNO_3 under similar conditions. Methanolic solutions were prepared by diluting concentrated HNO_3. Solutions were also tested in which initial dilution was with water followed by acetonitrile. It was noted that the presence of water has a retarding effect on IMS measurements. Water may also be involved in decomposition of HNO_3. This leads to complications in attempting to understand the role of HNO_3 in the various reactions mentioned above by using IMS. It is clear that under our conditions, the IMS sensitivity to HNO_3 is less than to NH_4NO_3. No NO_3^- ion peak was observed with 10 ng of HNO_3. A peak was observed at 50 ng (Figure 14A). No NO_3^- was noted using Teflon as an adsorbent in the collector chamber from an experimental run with 250 ng HNO_3 on QMA in the vapor generator (Figure 14B). In view of the difficulties in working with HNO_3 using IMS, no further work was performed.

Decomposition of TNT on QMA

It has been reported that the early thermal decomposition reactions of polyaromatic compounds undoubtedly involves simple homolysis of the C-NO_2 bond to form an NO_2 radical and an aromatic radical. However, there may be alternate decomposition pathways. For nitroarenes there is another common decomposition path, i.e., hydrogen transfer to the nitro group and susequent loss of HONO.[43] An extensive review on the kinetics and mechanisms of thermal decomposition of nitroaromatic explosives has been written by Brill and James.[44] It was established recently using Fourier transform - ion cyclotron resonance - mass spectrometry (FT-IC-MS) that the initial step in the thermolysis of RDX and PETN is N-NO_2 (nitramine) and O-NO_2 (nitrate ester) bond homolysis, respectively.[45]

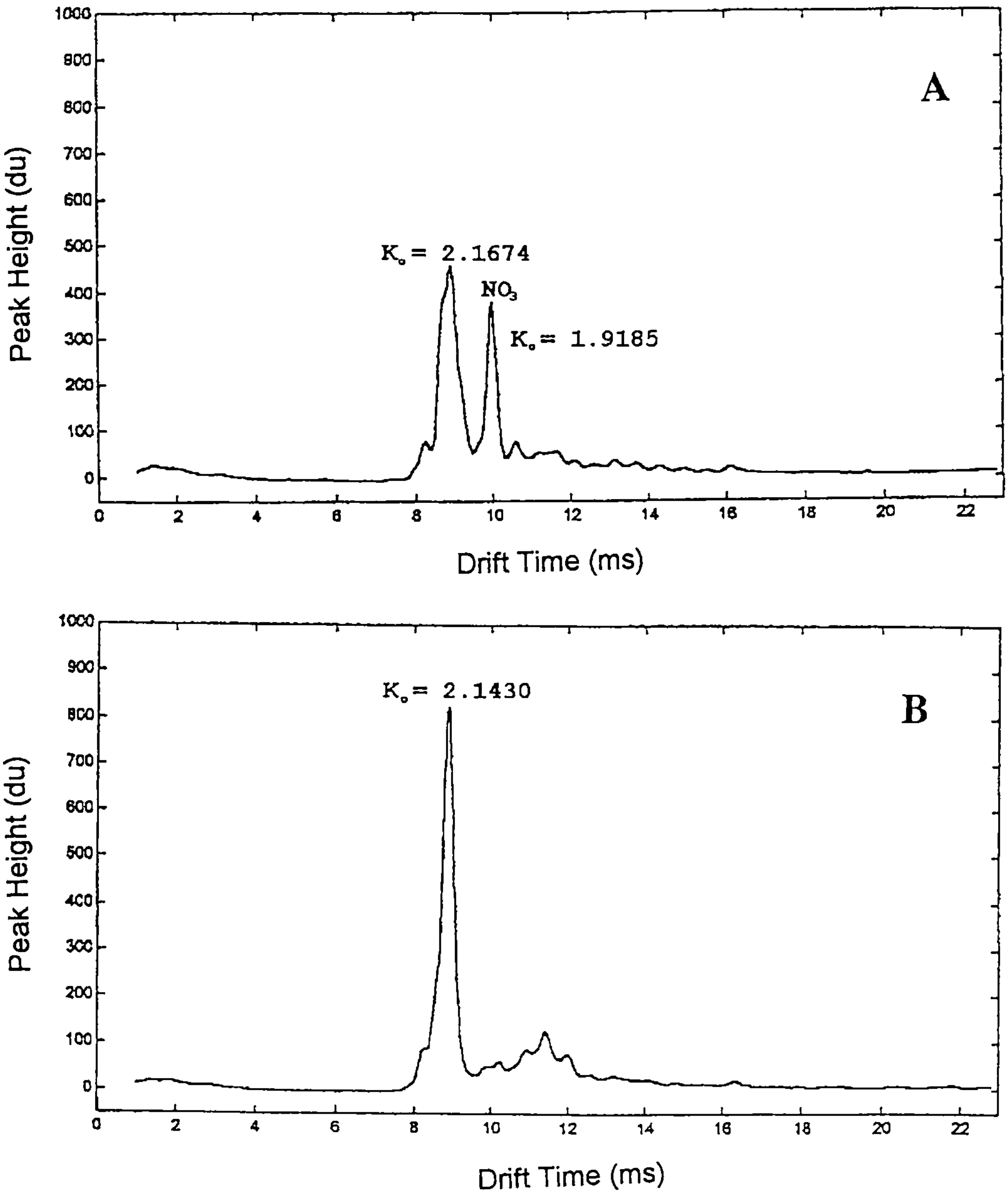


FIG. 14. IMS signatures of 50 ng HNO_3 on Teflon® (A), and Teflon® from 250 ng of HNO_3 heated on QMA in the vapor generator (B).

It is clear from the appearance of NO_3^- on several of the adsorbents used in the vapor generator/collector that TNT decomposes on heating. The QMA substrate may be involved in the decomposition reactions. Many compounds including essentially any source of H• or other radicals have been reported to accelerate the rate of decomposition of TNT which itself produces radicals at the 10^{-4} M level when heated below 300°C. Catalysis rather than intermolecular association of TNT may be responsible for the faster rate of decomposition on TNT in the solid phase in comparison to the vapor phase.

The influence of catalysis by the walls of reactors (including glass) and the supporting surfaces of TNT samples has been mentioned by many authors as a potential factor in the reaction rate, but does not seem to have been systematically investigated. It is difficult to separate the role of catalysis by the decomposition products from the role of surface catalysis.

Any NO_2 formed from TNT on QMA, would be swept away to the collector adsorbent. Nitrogen dioxide in the gas state is in equilibrium with dinitrogen tetroxide (N_2O_4). At room temperature, there is about 33% by volume of NO_2 in the gas at equilibrium. The chemical properties of NO_2 and N_2O_4 differ somewhat but both are reactive. Both are reducing agents. Many reactions ascribed to N_2O_4 have been reported to give NO_3^-. Reaction with water gives HNO_3 (eq. 13).[46]

$$N_2O_4 \quad + \quad H_2O \quad \longrightarrow \quad HNO_3 \quad + \quad HNO_2 \qquad (13)$$

Both NO_3^- and NO_2^- can be detected using IMS (Table 6). In the case of NO_2^-, it was observed as an IMS reaction product from 2,4-dimethyl 1,3-dinitrobutane (DMDNB).

It is logical to expect N_2O_4 to react with traces of water on adsorbents in the collector to form HNO_3. The HNO_3 formed this way would not have appreciable water in the vicinity and should not be subject to water retardation effects with the IMS as noted with samples diluted from concentrated HNO_3. (See the discussion above on use of HNO3 in the vapor generator/collector. The adsorbents likely to hold water molecules more readily (cotton cloth, and S&S filter paper) also exhibited the highest intensity ion peaks for NO_3^-. The source of NO_3^- observed in the IMS signature with adsorbents used in the vapor generator/collector may be NO_2 formed from TNT. Another possibility may be nitration of the adsorbent to form an unstable nitrate which decomposes upon heating in the IMS desorption chamber to form NO_2 which may lead to NO_3^- in the reaction chamber (eqs 14-15). However, more definitive research is needed to elucidate the actual

$$N_2O_4 + \text{sorbent-OH} \longrightarrow \text{sorbent-ONO}_2 + HNO_2 \qquad (14)$$

$$\text{sorbent-ONO}_2 + \text{IMS heat} \longrightarrow NO_2 + \text{IMS chemistry} \longrightarrow NO_3^- \quad (15)$$

mechanism(s).

Use of RDX in the Vapor Generator/Collector

Based on the results reported above, it was predicted that the explosive RDX would decompose in the vapor generator/collector. That was found to be the case. The IMS of RDX on Teflon shows one major ion peak (K_o, 1.3591) (Figure 15A). RDX adsorbed on

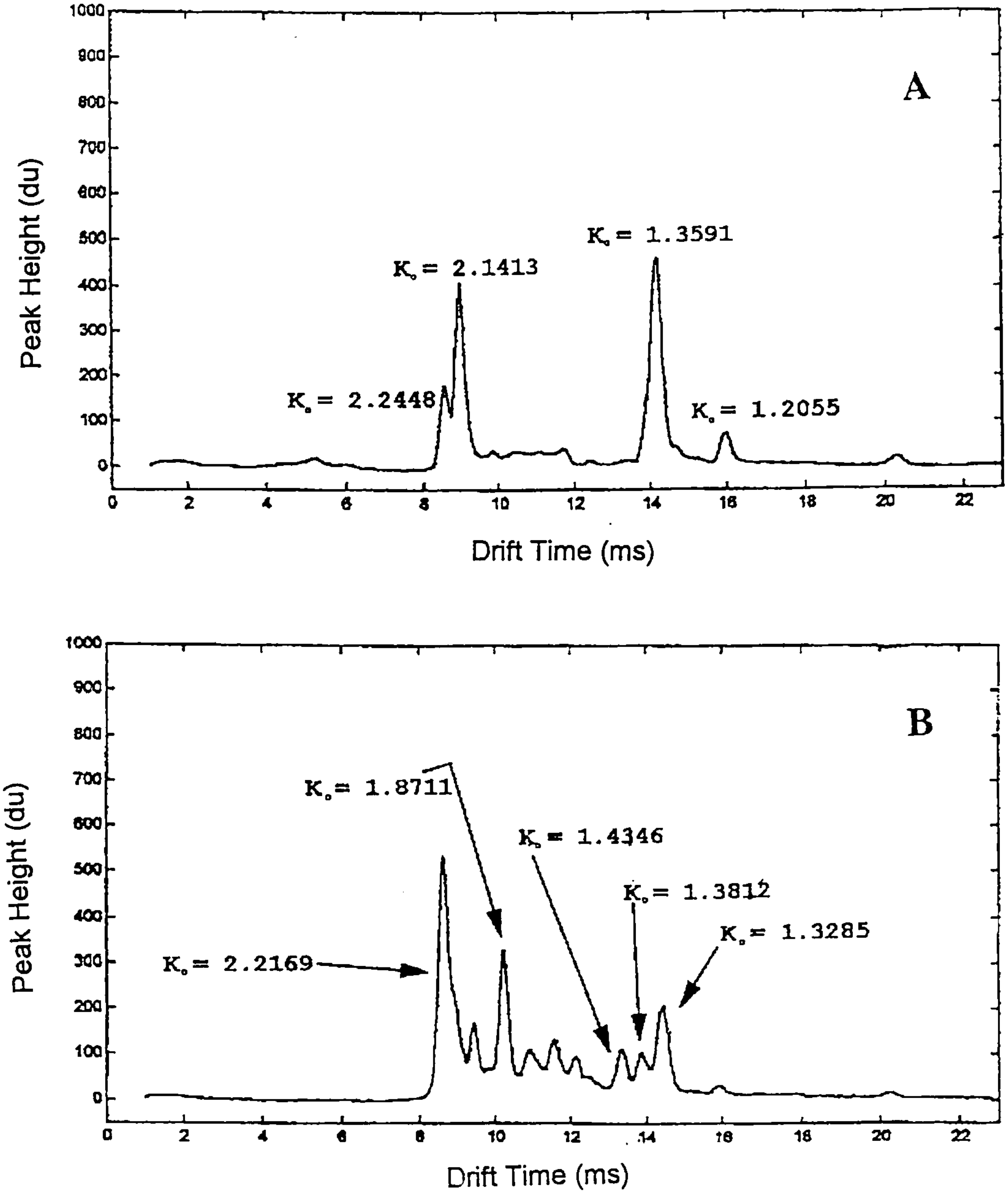


FIG. 15. IMS signatures of 10 ng RDX on Teflon® (A), and RDX decomposition products adsorbed on Teflon® from 250 ng of RDX heated on QMA in the vapor generator (B).

Teflon from 250 ng of RDX heated on QMA in the vapor generator gives many ion peaks (Figure 15B). Increasing the airflow and decreasing the temperature will most likely be necessary to avoid the decomposition.

CHAPTER VI

CONCLUSIONS

A relatively simple vapor generator/collector system has been developed to generate pulses of explosive vapors for studies of sampling in conjunction with ion mobility spectrometry as the analytical tool. The system gives reproducible results in generating TNT vapors at low nanogram levels. With some modification, such as changes in desorber temperature and air flow, the system should be able to be used with explosives of vastly different vapor pressures.

The use of the technology was demonstrated in evaluating different surfaces for adsorption of TNT vapors from a low air flow. Of the ten materials examined, Teflon® by far was found to be the best substrate for adsorption, retention, and subsequent recovery of TNT using ion mobility spectrometry for analysis.

The present work has also illustrated that TNT is bound more strongly on some surfaces than others. It has also shown that decomposition of small amounts of TNT on quartz fiber membranes occurs rapidly in the temperature range 235-250 °C as evidenced by the collection and determination of NO_3^- away from the surface.

The experimental apparatus developed for generation of vapor pulses can be used to study the decomposition of small amounts of explosives as a function of surface, and temperature in the presence and absence of air, and in a static environment or in a flowing gas stream. Applications are envisioned in studies in which surfaces are being optimized for vapor adsorption of compounds other than explosives. This would most likely apply to environmental situations involving target analytes with low vapor pressures.

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VITA

Saeed H. Almeer
Department of Chemistry and Biochemistry
Old Dominion University
Norfolk, Virginia 23529-0126

Education

M.S in Chemistry, Old Dominion University, Norfolk, VA May 1998.
B.S in Chemistry, University of Qatar, Doha, Qatar, June 1988.

Academic Experience

Teaching, University of Qatar, January 1989 - June 1994.
Laboratory Work, University of Qatar, January 1990 - June 1994.

Scholarship

M.S and Ph.D scholarship in Analytical Chemistry from the University of Qatar, May 1994.

Presentations (indicates presenter)*

- ◊ Use of Solid Phase Extraction Techniques in Sampling: Contraband Drugs and Explosives, *E.J. Poziomek, S. Almeer, M.C. Galicia, and G.E. Orzechowska, Invited Presentation, Gordon Research Conference, Queen's College, Oxford, UK. August 1997.
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- ◊ Research on Generation and Adsorption of Explosive Vapors (Poster), S.H. Almeer, E.J. Poziomek, Multi-Discipline Student Research Poster Session, Sponsored by Sigma Xi, The Scientific Research Society, Tidewater Chapter and the American Chemical Society, Hampton Roads Section, Norfolk, VA. April 1998.