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Title of Dissertation: "Improving Ion Mobility Spectrometry Detection Methods for Trace Forensics and Military Field Applications"

Name of Candidate: LCDR Greg Cook
Doctor of Philosophy Degree
11 October 2006

Dissertation and Abstract Approved:

David Cruess, Ph.D. — 10/27/06 Date
Department of Preventive Medicine & Bimoetrics
Committee Chairperson

CDR Gary Hook — 11 October 06 Date
Department of Preventive Medicine & Bimoetrics
Committee Member

LtCol Peter LaPuma — Oct 11, 06 Date
Department of Preventive Medicine & Bimoetrics
Committee Member

LCDR Gary Morris — Oct 11, 06 Date
Department of Preventive Medicine & Bimoetrics
Committee Member

Steven Durning, M.D. — Oct 11, 2006 Date
Department of Medicine
Committee Member

Brian Eckenrode, Ph.D. — 10/11/06 Date
FBI Counterterrorism & Forensic Science Research Unit
Committee Member

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LCDR Greg W. Cook, MSC, USN
Department of Preventive Medicine and Biometrics
Uniformed Services University of the Health Sciences

Abstract

Title:	Improving Ion Mobility Spectrometry Detection Methods for Trace Forensics and Military Field Applications
	Gregory Wayne Cook, Doctor of Philosophy, Environmental Health Science, 2006
Directed By:	David Cruess, PhD Professor, Department of Preventive Medicine and Biometrics

Ion mobility spectrometry (IMS) is a proven technology for field portable detection of vapor phase explosive compounds due to its high sensitivity and rapid analysis. However, IMS technology is limited in identifying complex samples in the field due to poor resolution and limited dynamic range. Combining gas chromatography (GC) to IMS can overcome some of the limitations by separating the components in a mixture before detection; however, the addition of GC increases system complexity and lengthens analysis times. The performance characteristics of the IMS and GC/IMS operational modes of the GC-IONSCAN® were evaluated to determine if GC/IMS is more reliable than IMS in the detection of explosive compounds amidst interferents. Five explosive compounds (HMTD, PETN, RDX, TATP, and TNT) and four were used.

IMS was more sensitive, provided higher signal response, and offered much higher sample throughput than GC/IMS for analysis of the pure explosive compounds. However, when analyzing the pure interferent substances IMS analysis yielded seven false positives compared to zero false positives with GC/IMS (n=40). When attempting to discern explosive compounds in the presence of the interferent substances, IMS analysis yielded 21 false positive responses compared to one false positive with GC/IMS (n=100). IMS signal response to the explosive compounds was suppressed in 8 of the 20 tests by the interferents when compared to the signal response of the pure explosives; however, signal response suppression with GC/IMS was practically eliminated with signal response suppression occurring in 1 of the 20 tests. For explosive compound field search operations that demand high throughput, these systems could work well together

by deploying IMS for rapid throughput and GC/IMS for confirmation of IMS.

IMPROVING ION MOBILITY SPECTROMETRY DETECTION METHODS FOR TRACE FORENSICS AND MILITARY FIELD APPLICATIONS

By

Gregory Wayne Cook

Thesis submitted to the Faculty of the Graduate School of the
Uniformed Services University of the Health Sciences in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy in
Environmental Health Science

2006

Advisory Committee:
David F. Cruess, PhD (Chair)
Brian A. Eckenrode, PhD
CDR Gary L. Hook, PhD
LtCol Peter T. LaPuma, PhD
Steven J. Durning, MD
LCDR Gary A. Morris, PhD

Dedication

- God. His blessings, love, and goodness abound in my life.
- Sonja. My wonderful wife and best friend. It would be easy to give up military life so we could enjoy some resemblance of 'normalcy'. However, your constant support, understanding, and encouragement make me a better husband, father, and officer while serving our country. Our family's bond will always strengthen and prevail because you put our needs before yours.
- Aubrey & Tia. The reasons for my long hours away from home, not willing to settle for mediocrity, were never apparent to you, though someday you will identify. I thank you for and will never forget your screams, laughter, and hugs at the door.

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- My advisory committee members, Dr. David Cruess, CDR Gary Hook, LtCol Pete LaPuma, Dr. Steve Durning and LCDR Gary Morris, for their mentorship, knowledge, and insight. I look forward to working with each of you at USUHS.Mrs. Kelly Mount and Mr. David McCollam from the FBI Laboratory, Explosives Unit for providing the research study along with many useful discussions explosive compounds and analysis.
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- Ms. Cara Olsen of the Uniformed Services University of the Health Sciences for her assistance with statistical analysis.

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List of Symbols and Abbreviations

AC	Alternating Current
AL	Aluminum
APD	Advanced Portable Detector
ATSA	Aviation and Transportation Security Act
CAM	Chemical Agent Monitor
CFSRU	Counterterrorism and Forensic Science Research Unit
CWA	Chemical Warfare Agent
DC	Direct Current
E	Electric Field
ECD	Electron Capture Detector
EDS	Explosives Detection Systems
ETD	Explosives Trace Detectors
FAIMS	Field Asymmetric Waveform Spectrometry
FBI	Federal Bureau of Investigation
FID	Flame Ionization Detector
GC-ECD	Gas Chromatography-Electron Capture Detection
GC-MS	Gas Chromatography-Mass Spectroscopy
GC-PID	Gas Chromatography-Photoionization Detection
HMTD	Hexamethylene Triperoxide Diamine
ICAM	Improved Chemical Agent Monitor
IMS	Ion Mobility Spectrometry
GC	Gas Chromatography
GC/IMS	Gas Chromatography/Ion Mobility Spectrometry
K	Ion Mobility Constant
K_o	Reduced Ion Mobility Constant
LC-MS	Liquid Chromatography-Mass Spectrometry

l_d	Drift Tube Length
LOD	Limit of Detection
LTM	Low Thermal Mass
ms	Milliseconds
NC	Nitrocellulose
PETN	Pentaerythritol Tetranitrate
PID	Photometric Ionization Detector
ppb_w	Parts Per Billion Weight
ppb_v	Parts Per Billion Weight
ppm_v	Parts Per Million Volume
psi	Pound-force Per Square Inch
RDX	1,3,5-Trinitro-1,3,5-Triazine
RSD	Relative Standard Deviation
SAW	Surface Acoustical Wave
SN	Sodium Nitrate
TATP	Triacetone Triperoxide
TCD	Thermal Conductivity Detector
t_d	Drift Time
Rt	Retention Time
2,4,6 TNT	2,4,6 Trinitrotoluene
TSA	Transportation Security Administration
µg	Microgram
V_d	Drift Velocity
W	Watts

1 Introduction

1.1 Background

An important challenge facing law enforcement and military personnel is the ability to detect, correctly identify, and interdict the illegal possession of explosives intended to initiate terror and harm citizens, both nationally and internationally. Ion mobility spectrometry (IMS) is a proven technology for trace detection of explosives in the field. A well-known limitation of IMS instruments results when analyzing samples that contain mixtures or complex matrices.[1-3] When analyzing mixtures or complex matrices with IMS, some of the compounds are preferentially ionized. Preferential ionization of non-targeted substances can produce interference with trace detection capabilities via analyte masking, which result in false positive or false negative responses. The use of gas chromatography (GC) coupled to IMS can overcome the difficulty of identifying analytes in component matrices by employing a separation step prior to detection. The purpose of this research is to compare IMS and GC/IMS by analyzing five explosive compounds in the presence of four interferents to determine if GC/IMS is more reliable than IMS in the detection of explosive compounds.

1.1.1 Terrorist Events and Sabotages

This research project was initiated in response to a need of the Federal Bureau of Investigation (FBI) to improve commercial airline passenger and baggage screening for the detection, identification, and interdiction of illegal explosives. Over the years,

terrorist incidents and aircraft sabotage using explosives have taken the lives of innocent victims throughout the international community. The bombing of commercial aircraft United Air Lines flight 629 over Denver, Colorado[4], Union des Transports Aereins flight 772 over Niger, Africa[5], Avianca Airlines Flight 203 over Bogota, Colombia[6], Philippines Airlines flight 200 over the Pacific Ocean[7], Pan American flight 103 over Lockerbie, Scotland[8], and the 2004 coordinated Siberia Airlines and Volga-Avia Express flights over Moscow, Russia[9] have caused tragic personal losses, resulted in heightened public concern, and led to accelerated research in the area of explosives detection. The previously mentioned terrorist events coupled with continuing media attention concerning vulnerabilities, lead to the conclusion that threats to civil aviation in the future are not likely to diminish and could possibly increase.

1.1.2 The Need for Field Explosives Detectors

The capability to conduct field detection of explosives is an important need. In response to the terrorist attacks of September 11th President Bush signed the Aviation and Transportation Security Act (ATSA) on November 19, 2001.[10] The ATSA established the Transportation Security Administration (TSA) and directed the federal government to take responsibility for screening all commercial airline passengers and baggage for weapons, explosives, and other hazardous or dangerous items. Prior to ATSA, commercial airlines were responsible for screening passengers and cargo.

Since ATSA's enactment, many aviation security measures have been designed to prevent future acts of terrorism on commercial airlines. For explosives detection, physical inspections, trained detection animals, and sophisticated detection equipment are

currently used. All of the previously mentioned security measures have advantages and limitations with cost being a primary limitation for most methods. TSA currently uses two types of equipment to screen commercial airline passengers and baggage: Explosives Detection Systems (EDS) and Explosives Trace Detectors (ETD).[11] EDSs are large units, similar in size to a small automobile, that use x-ray technology to identify bulk quantities of potentially explosive substances in checked baggage, cargo, and mail. Since this research focuses on trace detection of explosives, EDS are not discussed further. ETDs are much smaller, approximately the size of a large suitcase. The majority use IMS technology to screen personal items or carry-on bags for the presence of explosive compounds. Samples are collected through wipe or vacuum techniques using a cloth sample pad (supplied by the manufacturer) and subsequently analyzed by an ETD for the presence of trace explosive compounds. Since November 2001, TSA has deployed over 1,100 EDS and 7,263 ETD for use in the United States.[10]

1.1.3 Ion Mobility Spectrometry

IMS is one of the most widely used analytical techniques for detecting trace levels of chemical compounds.[12, 13] Conceptually, analytes are identified by the characterization of their gas phase ion mobility in a weak electric field at ambient pressure. A sample is introduced into the IMS through an inlet port; molecules are then ionized and carried into a "drift tube". The ionized molecules are accelerated under an electric field through the drift tube and collide with a collector plate at the opposite end of the tube. The length of time an ionized molecule travels in the drift tube (related to ion mobility) plotted against the ion current detected by the collector plate produces a characteristic "signature" or plasmagram that can be compared to a library of known reduced ion mobilities.[14]

Subsequently, a match of ion mobilities is the basis for identifying chemicals using IMS. The ion mobility of a particular chemical is dependent on the shape, size, cross section, and molecular mass of produced ions. IMS can provide a rapid means for detecting and tentatively identifying chemicals, however IMS is not considered a confirmatory method.[15] While many IMS instruments are used in the field to locate contraband, as with all detection techniques, IMS has limitations.

One limitation with IMS instruments is the poor ability to analyze samples containing mixtures or complex matrices.[1-3] IMS instruments are relatively easy to overload due to the limited number of reactant ions available for ion/analyte reactions. When all reactant ions are depleted, no further increase in product ion concentration is possible.[15-20] Two different ions of similar size and mass may appear to generate a single peak rather than two distinct peaks in an IMS spectrum. When analyzing mixtures or complex matrices with IMS, individual components can be undetected, false positive results can be generated, or interferences can occur with the trace detection capability. One method of addressing these limitations is to separate sample molecules utilizing gas chromatography prior to entering the IMS.

1.1.4 Gas Chromatography/Ion Mobility Spectrometry

GC/IMS is classified as a dual analytical technology that merges two separate techniques to produce a new configuration that takes advantage of their individual capabilities. Coupling compatible GC and IMS analytical methods in tandem has shown improved trace organic chemical detection through improved resolution of chemical species, lower detection limits, improved quantitative response, and higher throughput of complex samples.[21, 22]

In general, GC is an analytical method capable of separating a wide range of complex chemical mixtures by a series of partitions between a moving gas phase and a stationary liquid phase coating bonded to the inner surface of a small diameter fused silica tube (column). As the moving gas phase carries chemical mixtures through the column, the stationary phase interacts more effectively with some molecules than with others. Consequently, a mixture is partitioned into individual components. While two chemicals may have identical IMS ion mobilities, the chemicals almost certainly have different GC retention times, which help resolve the two chemicals prior to entering an IMS.[12]

While GC provides the advantage of separating analyte mixtures into individual components for detection, the addition of GC increases analysis time, system complexity, and power consumption, all of which work against the advantages of IMS.[23] Consequently, if GC is to be added to an IMS detector for field applications, the addition should strive to provide separation in less than one minute, to consume minimal power, to be compact, and to be rugged.

The FBI Laboratory Division, Explosives Unit recently expressed interest in GC/IMS technology as a valuable tool for reducing the number of false positive results currently experienced from interferents in the field. A new GC/IMS instrument, that permits pre-separation of complex samples prior to detection, has emerged that warrants evaluation. Understanding the potential to reduce interferences, using this instrument, will help ensure that new technologies are optimized for field operational units. The evaluation will assess the instrument's strengths and weaknesses in regards to sensitivity,

accuracy, and precision to five explosive compounds amidst four chemical matrix interferents.

1.1.5 Military Relevance

IMS has been widely used in the military and other government organizations to detect explosive compounds and chemical warfare agents (CWA) in wartime, treaty verification, stockpile reductions, and to monitor building air quality and base perimeters.[24, 25] To date more than 50,000 handheld IMS detectors have been deployed for use by Armed Forces from Britain, Canada, and the United States. [26] IMS instrumentation currently used by military establishments include the: M-8A1 detector system, Chemical Agent Monitor (CAM), Improved Chemical Agent Monitor (ICAM), Advanced Portable Detector (APD 2000), M90 Chemical Agent System, and M-22 Automatic Chemical Agent Detector Alarm (ACADA) continuous air monitoring systems. Potential use of IMS technology can be expanded to include monitoring for emission control, environmental protection, air quality control for workplace safety, and for the detection of narcotics and other controlled substances.

1.2 Research Question and Specific Aims

Research Question: Does the addition of GC to an IMS improve current detection capabilities for trace organic explosive compounds in the presence of interferents?

Specific Aims:

1. Compare Cotton and Teflon® sample materials for the field portable IMS (IONSCAN®) and GC/IMS (GC-IONSCAN®) systems.

2. Establish baseline performance of a field portable IMS (IONSCAN®) and GC/IMS (GC-IONSCAN®) system in terms of detection limit, upper saturation limit, sample throughput rate, and precision using five explosive compounds.
3. Assess the detection capabilities of the field portable IMS (IONSCAN®) and GC/IMS (GC-IONSCAN®) systems amidst four chemical matrix interferents in terms of accuracy.Assess the detection capabilities of five explosive compounds amidst four chemical matrix interferents with the field portable IMS (IONSCAN®) and GC/IMS (GC-IONSCAN®) systems in terms of accuracy, signal response, and precision.

2 Literature Review

This research tested the capabilities of IMS and GC technologies to enhance field sampling and analysis capabilities of explosive compounds. Field-portable IMS technology development programs have existed since the early 1960's.[17] IMS use for analytical field sampling and military preparedness has been well established and successfully used for environmental pollutants, herbicides, pesticides, petroleum products narcotics, CWAs, and explosives detection.[1, 12, 15, 25, 27-33] GC is a separation technique that was pioneered in the 1950s and has continued to be further developed for accurate, rapid, field analysis methods. Current research in improving GC focuses on the development of faster chromatography with lower power consumption while retaining separation efficiency. The sections below provide insight into proven successes of IMS and GC technologies, as well as promising potential future developments. The motivation for combining GC and IMS analytical techniques in this research is also discussed.

2.1 Detection Instrumentation

Many instruments are available for chemical detection. Today, trace detection technologies are maturing on a variety of fronts and an expanding array of instrumentation is available. Some systems are large, complicated, and expensive, while others are smaller, easier to use, and less expensive; however, the latter tend to be less effective. Competing trace detection technologies available for explosive compounds include surface acoustical wave (SAW) sensors, Raman and infrared spectroscopy, and

hyphenated chromatographic techniques such as gas chromatography-electron capture detection (GC-ECD), gas chromatography-photoionization detection (GC-PID), gas chromatography-mass spectroscopy (GC-MS), and liquid chromatography-mass spectrometry (LC-MS).

Surface acoustic wave (SAW) detection is based on piezoelectric crystals that resonate at a specific, measurable frequency.[12] Molecules bind to the surface of the crystal and the resonant frequency shifts in proportion to the mass and other properties of the material being deposited. While SAW devices are small and low-powered (battery operation capability), major limitations of their use include cross-sensitivity and poor selectivity.[15]

Raman and infrared spectroscopy techniques analyze molecules by irradiating analytes with light and measuring the inelastically scattered (Raman), emitted, or absorbed (infrared) wavelengths.[12] Because molecules have different electronic, vibrational and rotational energies, resulting data can provide reliable identification of relatively pure unknown materials. Limitations with spectroscopic instrumentation include: limited analysis of mixtures, sensitivity (dependant on weather conditions), and potential decomposition or deflagration of unstable explosives when imparting energy during analysis.[34]

High-quality, sensitive detectors such as GC-ECD, GC-PID, GC-MS and LC-MS have been used for many years to detect and identify trace materials.[35] However, with the exception of GC-MS and LC-MS, the other techniques cannot easily identify compounds. While the portability of such instruments is improving, combining GC or LC with a sensitive and selective mass spectrometer detector for the field requires

considerable operating expertise and still presents significant design and performance challenges for high-quality, high-speed, field-portable GC-MS or LC-MS.[36, 35] Recently, Smith, *et al.* explored new sampling techniques and column heating approaches to expand and improve GC-MS for unknown chemical detection and identification in field settings.[37]

This research focuses only on a field application of IMS and GC/IMS chemical detection technologies. The advantages of IMS include high sensitivity, analytical flexibility, near-real time monitoring, and comparatively low cost. The coupling of GC to IMS has proven to be a good match in enabling IMS to overcome two vulnerabilities: ease of overloading resulting in incomplete separations and susceptibility to interferences that suppress ionization efficiency and sensitivity. By moderating the amount of analyte introduced into the detector, the dynamic range can potentially be increased and selectivity improved by separating complex matrixes into individual components.

Few specific studies of IMS performance with chemical interferents have been reported.[3, 19] Matz*, et al*. focused on air contaminant compounds with trinitrotoluene (TNT) using a laboratory constructed instrument. Fytche*, et. al*. tested substances for spectral interference with drugs of abuse; however, a close look at the substances indicates these would not typically be found in an airport setting. To date, no detailed studies of comparing IMS and GC/IMS detection methods of explosive compounds with chemical interferents have been published.

2.2 Ion Mobility Spectrometry

2.2.1 Theory

IMS instrumentation was introduced as an analytical technique in 1970.[38, 39] Originally known as plasma chromatography, IMS technology characterizes chemicals on the basis of velocity of gas-phase ions in a weak electric field. The principle of operation for an IMS is shown in Figure 2-1.

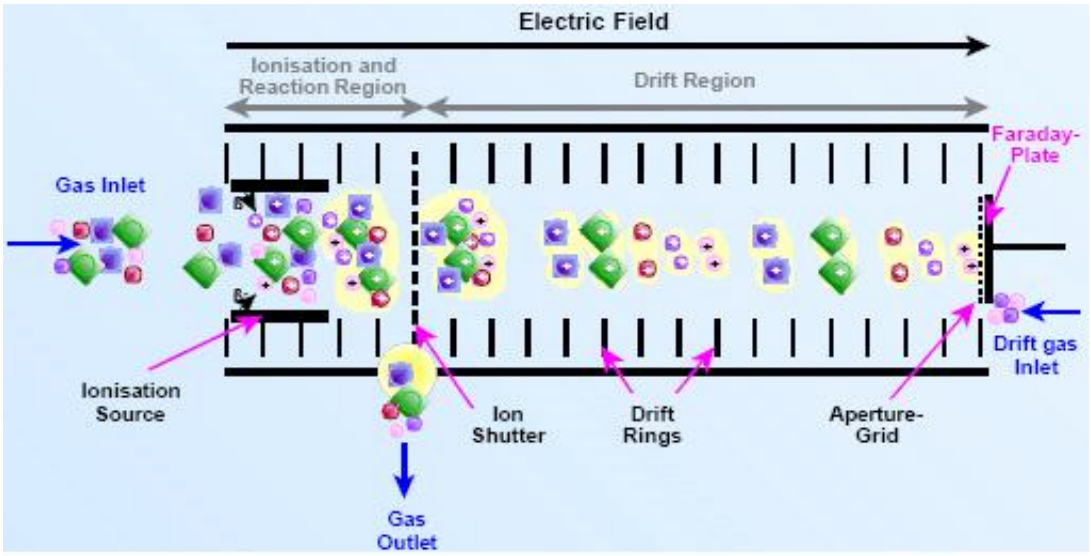


Figure 2-1: Schematic of an ion mobility spectrometer (IMS).

Molecules are carried in a stream of dried, filtered, ambient air or carrier gas from the instrument's inlet into the ionization region where high-energy electrons and reactant ions create ionized sample molecules. A variety of energy sources can be used to produce the high-energy electrons used for ionization. Energy sources used include ultraviolet lamps, lasers, corona discharge, electrospray, or the radioactive material ^{63}Ni, which is the most common.[15, 40] Ionic species, referred to as reactant ions, are generated from the interaction of the energy source with ambient air and water molecules.

Hydrated protons ($(H_2O)_nH^+$) dominate as the positive reactive ions and hydrated oxygen molecules ($(H_2O)_nO_2^-$) dominate as the negative reactant ions.[39] The composition of reactant ions can be altered by introducing a chemical ionization agent or "dopant". A dopant aids in the ionization process by suppressing background interferences, concentrating the reservoir of charge into one or a few preferred ions, and simplifying the plasmagram.[12] Various chlorocarbons are used as dopants to produce chloride ions to selectively ionize explosive compounds and increase the sensitivity for detection.[16, 17]

Through a series of complex ion/molecule reactions between the entering sample vapors and the reactant ions, product ions (positively or negatively charged) are formed by proton transfer ($RH^+ + P \rightarrow R + PH^+$), charge transfer ($R^+ + P \rightarrow R + P^+$), electron capture ($e^- + P \rightarrow P^-$), charge transfer ($R^- + P \rightarrow R + P^-$), dissociative electron capture ($R^- + AP \rightarrow R + A^* + P^-$), or proton abstraction ($R^- + HP \rightarrow RH + P^-$) processes.[39] A repeller grid moves the product ions of a selected polarity toward an ion gate grid. Through a series of pulses from the gate grid (fabricated from thin parallel wires) the product ions are transferred into the drift region where they are accelerated against a counterflow of purified ambient air drift gas. Inside the drift region, consisting of a series of electrically charged metal guard rings, the product ions move under the influence of a constant electric field (~200-400 V/cm) toward a metal collector electrode. Due to collisions between ions and ambient air drift gas, separation takes place depending on the individual mobility of a molecule.[14] The degree of separation is based primarily on the ion's charge, molecular mass, and cross-sectional area.[40] Most ions have a drift time between 10 and 40 milliseconds with lighter ions having higher mobility values than heavier ions.[41, 42] Though all drift tubes share common electrical features, there are no commercial

standards on construction materials (commonly stainless steel) or dimensions (typically 4-20 centimeters in length).[15]

The collector electrode (Faraday plate) detects ions after they traverse the drift region and generates an electromagnetic pulse. In low linear electric fields (<1000V/cm), ions acquire a reproducible average velocity, or drift velocity, determined by the number of collisions they make with other molecules in the drift region and the counterflow of the drift gas (used to clear the drift region of molecules after sample analysis is complete).[14] The drift velocity, V_d, (cm/s), of the ions is equal to the drift tube length, l_d, (cm) divided by the drift time, t_d, (sec) as shown in Equation 2-1.[43]

$$V_d = \frac{l_d}{t_d} \qquad \textbf{Equation (2-1)}$$

The drift velocity is directly proportional to the strength of the electric field, E, (V/cm) expressed by Equation 2-2, where the ion mobility, K, is constant, usually computed in $cm^2/V\text{-}s$.

$$V_d = KE \qquad \textbf{Equation (2-2)}$$

The standard procedure to determine an ion's mobility is to measure an ion's drift time (t_d), through a specified drift length (l_d) under a known electric field (E). Ion mobility is expressed by Equation 2-3.[44]

$$K = \frac{l_d}{t_d} E \qquad \textbf{Equation (2-3)}$$

Since IMS instruments operate at ambient temperature and pressure, ion mobility is normalized to correct for variations in gas density and is referred to as the reduced mobility value (K_o).[14]

K_o is calculated using to Equation 2-4.[44]

$$K_o = K\left(\frac{273}{T}\right)\left(\frac{P}{760}\right) \qquad \textbf{Equation (2-4)}$$

In some applications, a reference ion is used to calculate K_o as shown in Equation 2-5.[43]

$$\text{sample } K_o = \left(\frac{\text{reference } t_d \times \text{reference } K_o}{\text{sample } t_d}\right) \qquad \textbf{Equation (2-5)}$$

It is important to point out that the K_o of a particular chemical is a characteristic of that chemical and not a unique identifier.[14]

Using a computer, the output of an IMS instrument can be displayed as an XY graph, also known as a plasmagram to provide information contained in the ion mobility measurement of a chemical. The plasmagram visually displays drift time, peak shape, and fragmentation of a chemical from which the mobility coefficient can be determined. A plasmagram from RDX at 71° F and 773.16 Torr is shown in Figure 2-2. The cumulative signal intensity, digital units (du), is plotted against drift time (milliseconds (ms)). The resulting drift time for RDX is 13.269 ms with a K_o of 1.4502 using nitrobenzonitrile as the reference ion.

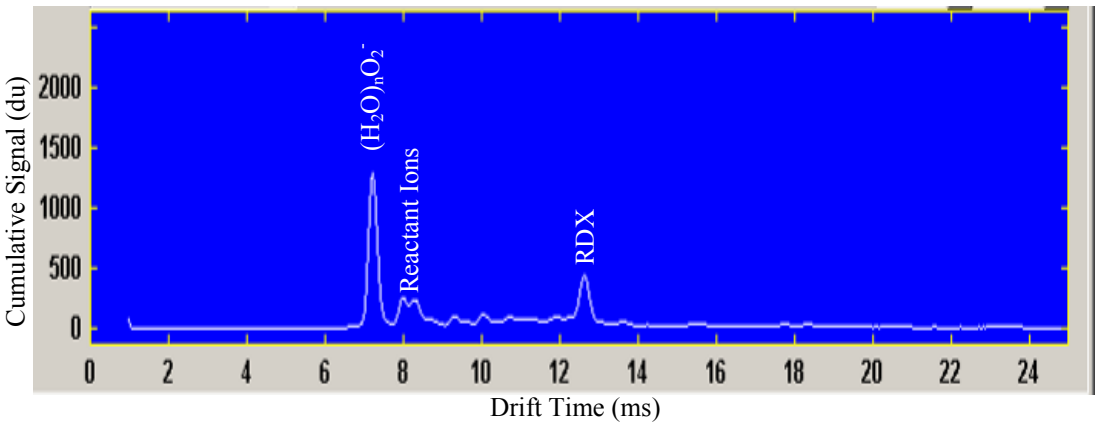


Figure 2-2: RDX plasmagram plotting ion current against drift time. (negative ion mode)

In an IMS, reactant ions are continuously produced and extracted by the electric field into the drift region. Reactant ions pass through the drift region and exhibit a distinct spectrum. In the absence of other chemicals, a reactant ion peak will form the largest peak in an IMS spectrum because the reactant ions are the only analyte, and thus charge carriers present in the system. When molecules enter the detector the reactant ion peak decreases in intensity as charge transfer reactions occur. The reactant ion peak re-intensifies as molecules pass through the system and charge transfer reactions complete.

The product ion peak (RDX in Figure 2-2) represents the output of ionized molecules, in a positive or negative ion mode depending on the polarity of the applied electric field. A single or series of product ion peaks form a characteristic "signature" of a compound. The height of the product ion peak(s) corresponds to the intensity of the electromagnetic signal generated when ions strike the collector electrode. For an IMS to identify a chemical, a product ion peak(s) must conform to parameters found in detection algorithms and the onboard library of known reduced mobilities.[14] Actual outputs from an IMS are more complex than displayed in Figure 2-2 because field samples do not normally consist of a single pure substance. As a consequence, IMS lacks the ability to definitively identify individual components in sample mixtures or complex matrices.

2.2.2 History

During the 1970's, researchers gathered basic information about the technology.[38, 39] Reactant ions were identified, ion mobility constants for many organic compounds (alcohols, nitrosamines, nitroaromatics) were measured, temperature effects were evaluated and ion mass-to-mobility correlations were made.[16] Early drift tube designs were not fully enclosed and allowed molecules to diffuse into the drift cell creating

complex ion flow patterns, ion source overload, and erroneous concentration/mobility coefficient correlations.[17] These circumstances negatively affected the acceptance of IMS and by 1980 the number of published scientific journal articles had declined to zero. In the early 1980s, Baim designed an enclosed IMS drift cell with unidirectional gas flow that could also be tuned to perform selective drift time mobility monitoring.[43] Baim's design eliminated the complicating early analytical designs, resulting in the ability to obtain more reproducible and sensitive measurements. Subsequently, the introduction of dopants (ammonia[45], acetone[30], and chloride ions[46]) increased the specificity of IMS detection capabilities. Additional work, pioneered in the 1980s, included the introduction of new ionization sources: laser, photoionization, and electrospray.[30]

In the early 1990s, researchers from Russia developed what has become known as field asymmetric waveform ion mobility spectrometry (FAIMS).[47, 48] Different terms have been used to describe this principle: differential mobility spectrometry (DMS), field ion spectrometry (FIS), and radio-frequency ion mobility spectrometry (RFIMS). Figure 2-3 illustrates the operation of FAIMS.

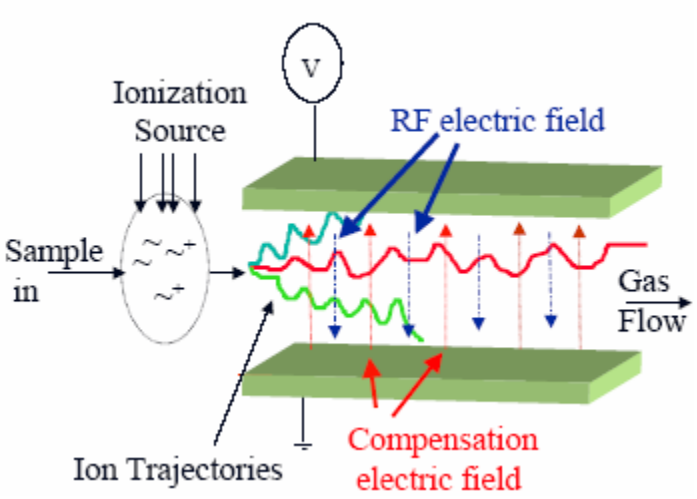


Figure 2-3: Operation principle for field asymmetric waveform ion mobility spectrometry (FAIMS)

In traditional IMS instruments, the K_o for an ion is constant at low electric fields (100-400 V/cm).[14] If two ions have the same mobility in the low electric field they cannot be separated. In the late 1980s, researchers discovered that at electric fields above 1000 V/cm, ion drift velocity is no longer proportional to the electric field, but nonlinear and dependent on the strength of the electric field.[47] In FAIMS, like traditional IMS, ionized molecules are created using reactant ions and high-energy electrons. Ionized molecules are separated based on their change of mobility. The difference between FAIMS and traditional IMS exists within the strength of the electric field. Ionized molecules enter the FAIMS drift region (see Figure 2-3) that contains two parallel plate electrodes rather than a series of guard rings. One electrode is maintained at ground potential, while an oscillating high voltage AC (~1,000-10,000 V/cm) is applied to the other.[48] Sample components are separated as voltage is scanned and the differences in ion mobilities exploited. As ions traverse the drift tube, the asymmetric electric field causes ion trajectories to deflect toward one of the plates. A compensating low voltage direct current (DC) field is applied to the plate in opposition to the drift caused by the asymmetric alternating current (AC) field, preventing ions from reaching the plate and being deflected into the drift tube wall. Thus, selected ions can pass through to the collector electrode while all other ions are deflected into one of the plate electrodes. Unlike traditional IMS, FAIMS does not have an ion gate and ions are continuously introduced into the drift region. While FAIMS has shown some success, the principle limitation has been poor separation due to ion space charge repulsion effects and the extremely fast movement of ions (<10 ms) through the drift region.[48, 49]

2.2.2.1 Explosive Compound Detection

The application of IMS to detect explosives is second only to its extensive use as chemical warfare agent detectors.[17] The strong electron affinity exhibited by explosive compounds translates to a high efficiency for creating negative ions and allows part-per billion (ppb_w) or sub-nanogram detection limits with IMS.[50] Karasak was the first to report that IMS could be used to detect explosives; reporting detection of TNT at ppb_w levels in 1974.[51] Spangler subsequently published manuscripts on the detection of TNT and 1,3,5-Trinitro-1,3,5-Triazine (RDX) with IMS.[1, 52] Fetterolf later showed detection for common explosive compounds at levels as low as 200 picograms.[44] The very low vapor pressure of TNT, RDX, and Pentaerythritol Tetranitrate (PETN) makes it difficult to detect explosive compounds by vapor methods alone.[53] Explosive analytes must be collected onto a sample media and thermally desorbed to facilitate transportation to the ionization region. Carr was the first to successfully analyze explosive compounds with low volatility using thermal desorption.[41] The vapor generator/collector system described herein is based on thermal desorption. There are many additional citations of IMS use for detecting various explosive compounds over the last three decades; however the work appears in conference/ symposium proceedings and government reports not readily available to the public.

Commercial instruments for explosive compound detection were not fielded until after the Pan Am flight 103 explosion over Lockerbie, Scotland in 1988.[50] Subsequent experiments showed successful implementation of IMS in this field application.[44] Ion Track developed the first field portable explosive vapor detector based on IMS technology, the VaporTracer®, in 1997.[50] In 1999, Barringer introduced a handheld IMS,

the SABRE®, that could operate in an explosive particle or vapor detecting mode.[50] More recently, due to fears of terrorism in commercial aviation, IMS has been more widely implemented as a rapid, non-invasive screening tool for passengers and carry-on items.[17] Currently, the IONSCAN® [54] and ITEMISER® are the most commonly used field portable IMS instruments for explosives detection, [55] with more than 15,000 analyzers in the field colectively.[17]

2.2.3 Advantages

When viewed in the context of other analytical instruments, IMS offers several appealing features that have increased the use of IMS in detecting chemicals in field settings. The main advantages of IMS include:

1) excellent detection method for single component samples,
2) fast analysis time (provides output data in seconds),
3) sensitive technique (picogram detection limits),
4) does not require sample pretreatment,
5) operates at atmospheric pressure (mass spectrometers, which operate under a vacuum, make field use difficult),
6) selectively detects chemicals based on gas phase ion mobility (other simple ionization instruments, flame ionization detector (FID) photometric ionization detector (PID), electron capture detector (ECD) and thermal conductivity detector (TCD), provide only a record of gas phase effluents that is not compound specific),
7) loss of volatile samples does not occur (as with electrospray techniques),

8) polarity of the electric field can be altered so both positive and negative ions can be detected,
9) solid samples as well as analytes in solution (with some preparation) can be analyzed,
10) can be miniaturized and operated by battery power,
11) when compared to other technologies that are capable of identifying chemicals, IMS is relatively inexpensive to purchase and operate.[15, 26, 42, 56-59]

2.2.4 Limitations

While IMS technology has demonstrated many positive characteristics, some limitations are exhibited:

1) Chemical mixtures are not analyzed without problems due to complex interactions that produce incomplete separation and obscure ion peaks, leading to uncertain detection and identification. IMS instruments are prone to inaccurate detection and false positive/false negative response when chemical interferents are present in samples.
2) IMS signal response is strongly dependent on analyte concentration, vapor pressure, and proton/electron affinity.
3) IMS signal response is influenced by atmospheric temperature and pressure because IMS does not operate in a vacuum.
4) IMS instruments are relatively easy to saturate. Linear response is often limited to two orders of magnitude of sample mass. IMS saturation is primarily due to the limited number of reactant ions available for ion/analyte reactions. When all reactant ions are depleted, no further increase in product ion concentration is

possible. Thus sample size must be carefully controlled at the instrument's entrance to prevent saturation or non-linear response due to the depletion of reactant ions.[15-20]

If these limitations can be mitigated, IMS can be a better detector. One way to overcome IMS limitations is by coupling GC to the front of the IMS detector.[43] The addition of GC can improve selectivity and specificity by controlling sample volume and separating individual chemicals entering the detector, preventing detector saturation, and increasing IMS dynamic range.

2.2.5 Field Applications

When sampling in the field it is impractical to assume that the conditions will be the same as in the laboratory. Collected samples can potentially contain non-targeted substances that create complex matrices (background composition of little analytical interest) that interfere with analyses. Interference can occur primarily in two ways: (1) ionization of the background composition at the expense of targeted ions inside the IMS reaction region or (2) interferent compounds having similar drift times. While complete suppression of targeted analyte signals can result in failure to detect (i.e. false negative) similar drift times can result in an innocuous substance being identified as a targeted substance (i.e. false positive). Matz, *et al*.[19] investigated 17 different air contaminant compounds as chemical interferents in IMS analysis of TNT using a laboratory constructed instrument. Ten of the suspected interferents did not show IMS response and one (4,6 dinitro-o-cresol) of the other seven had a similar ion mobility, which resulted in ion peak overlap. Even with this interferent, TNT could be differentiated. Using IMS,

Fytche*, et al.* tested 139 substances of which 6 caused a false positive for heroin; however the substances evaluated would not typically be found in an airport setting.

2.3 Gas Chromatography

2.3.1 Theory

GC has been a widely used separation technique for detecting and identifying many kinds of chemicals over the last 50 years.[60] Additionally, GC has become a mainstay in research, industry, and government for analyzing air, water, and soil for numerous chemicals. GC is a method capable of separating a wide range of complex chemical mixtures by a series of partitions between a moving gas phase and a stationary phase held in a small diameter tubular column. A volume of sample is carried down the column by a flow of carrier gas and separated into individual components when interactions occur with the stationary phase coating. The stationary phase coating interacts with some molecules more than others; consequently, partitioning a sample mixture into individual components.[60] The speed at which analysis takes place is dependent on several factors including the type, length, and temperature of the column and the velocity of the carrier gas. In general, total analysis times are in minutes to hours. Figure 2-3 illustrates the GC separation process.

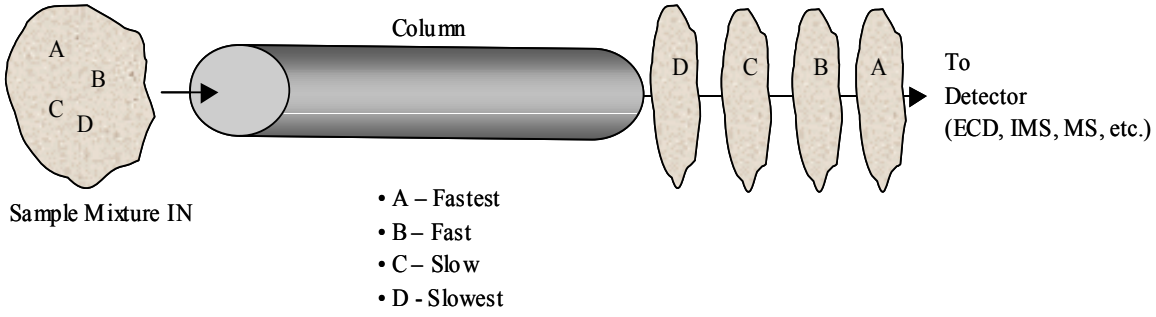


Figure 2-4: Graphic representation of the gas chromatography (GC) process.

2.3.2 History

The invention of GC is generally attributed to Martin and James, in 1952, who demonstrated the ability to separate volatile fatty acids using two glass columns with a silicone-based stationary phase and nitrogen carrier gas.[61] The technique became popular in the petroleum industry and biochemistry fields throughout the 1950s, as researchers used 1-5 meter columns packed with liquid phase coated particles to analyze petroleum products and amino acids.[60] In 1957, Golay produced the first inner wall-coated capillary column, a 1 m, 0.8 mm inner diameter glass tube with polyethylene glycol stationary phase.[62] The inner wall-coated capillary column provided much better analyte resolution due to the removal of the airflow resistance generated in packed columns. In the early development of capillary GC columns, researchers experimented with a variety of materials (nylon, copper, nickel, and stainless steel) because difficulties were experienced with analyte absorption into some column materials.[60] In 1961, Desty fabricated a coiled capillary column made from glass tubing that overcame the difficulties experienced with analyte absorption into metal columns.[63] Unfortunately, patent law restricted advances of glass capillary columns until the late 1970's so researchers focused efforts to improving packed column designs and temperature programming.[64] Glass capillary columns were predominantly used until superseded by Dandeneau and Zerenner design of a fused silica capillary column design in 1979.[65] Fused silica columns proved more durable than glass columns. Chemically inert fused silica columns also overcame recurring issues of polar analyte absorption with glass columns.[60] Today, manufacturers offer a wide range of highly developed fused silica column lengths and diameters with stationary phases and film thickness for achieving desired separations.

Originally, separations of analytes were achieved by holding column temperature constant. In 1952, published work by Griffiths demonstrated the peak spread for late eluting compounds could be minimized by increasing column temperature during the run.[60] In 1957, Dal Nogare further explored temperature programming by applying current through a stainless steel column wrapped with insulation.[62] This work demonstrated that by applying a linear increase of temperature during a GC run, mixtures could be more rapidly separated.

Most GC instruments still use an air circulation oven to heat a column. GC's with air circulation ovens are not easily portable or efficient with power. These systems also limit sample throughput due to a narrow range of temperature heating rates and lengthy cooling rates.[66] Modern air circulation GC ovens can achieve temperature heating rates of 75°C/min, but above 175°C the ramp rate is limited to approximately 30°C/min.[66]

2.4 Gas Chromatography/Ion Mobility Spectrometry

2.4.1 GC/IMS Theory

The principle of operation of GC/IMS is shown in Figure 2-5. In addition to the individual GC and IMS components shown, GC/IMS systems require peripheral equipment such as a carrier gas supply and a computer data system.

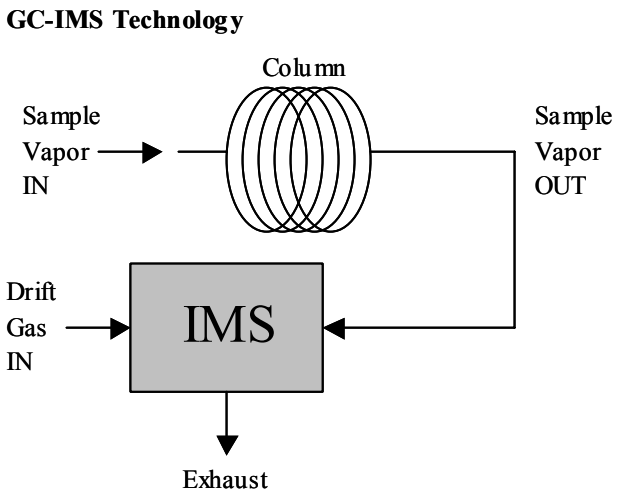


Figure 2-5: Graphic representation of gas chromatograph/ion mobility spectrometry (GC/IMS).

In a GC/IMS instrument, column effluent is introduced into the IMS ionization region over a period of minutes. Multiple IMS scans (on the order of 40-50 per second) of the column effluent are performed. The pre-separation provided by the GC simplifies the chemistry within the ionization region. By minimizing the number of constituents present at any one time, product ions can be formed without competitive ionization interferences. Figure 2-6 shows a characteristic three-axis graph (GC/IMS chromatogram) from a GC/IMS. In the GC/IMS chromatogram of RDX, the white line on the z-axis denotes a GC retention time (123 s), the x-axis denotes an IMS drift time (13.269 ms) and the y-axis IMS denotes signal intensity (1100 du). IMS scans have been compiled from front to back.

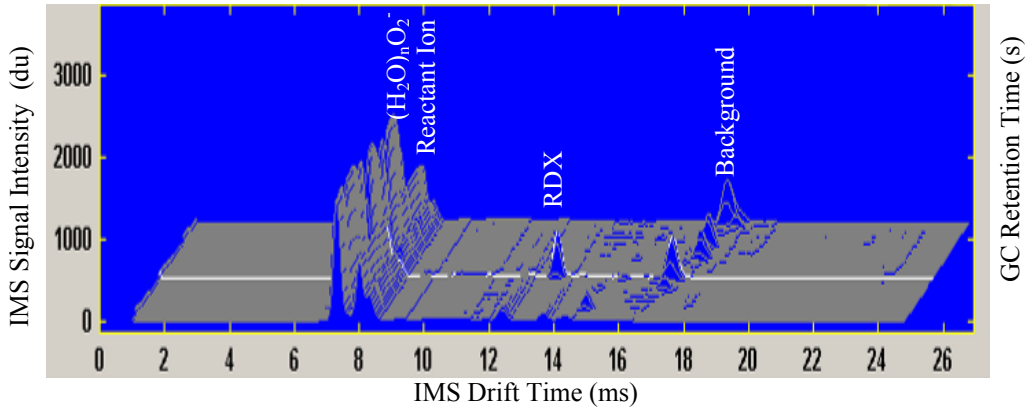


Figure 2-6: GC/IMS chromatogram of RDX. (t_d 13.269 ms, Rt 123 s.)

2.4.2 History

IMS was first coupled with a GC system, by Karasek and Keller in 1972 using a conventional packed column.[58] A number of researchers followed Karasek and Keller's work, demonstrating successful separation of analytes from complex liquid and vapor mixtures.[67-69] Though advances were realized throughout the 70's, two technical problems limited widespread use. First, the sensitivity of IMS instruments was compromised when GC was added due to residual solvents, unresolved analytes, column bleed, and carrier gas contamination from glass and metal packed columns. The factors altered ionization region chemistry and affected the response and reliability of the IMS detector. Secondly, the large volumes of IMS ionization cells (~7mL) caused loss of reproducibility, sensitivity, and chromatographic resolution due to diffusion and adsorption effects.[43]

GC/IMS shortcomings prompted the development of a new generation of IMS systems. Baim introduced the first new IMS design in 1982.[43] Baim's design introduced unidirectional gas flow with an enclosed and reduced drift tube volume. The design

decreased residence time of ions in the drift region and improved resolution, reproducibility, and sensitivity. Also in the 1980s, research with packed columns became superseded by capillary columns.[43, 59] In the 1990s, detection capabilities of trace organic chemicals improved with better resolution of chemical matrices with GC/IMS. The improved resolution provided by GC has resulted in lower detection limits, improved quantitative response and higher sample throughput for IMS.[21, 40, 70] In 1996, NASA selected GC/IMS technology, in the form of an instrument called a Volatile Organic Analyzer, to monitor for volatile organic compounds onboard the International Space Station, where it remains to date.[26]

2.4.2.1 Explosive Compound Detection

While many commercial trace explosives detection systems are in use today, very few use GC/IMS. One of the first commercial GC/IMS instruments developed for detecting explosive compounds was the Orion® in 1997.[50] Designed by Intelligent Detection Systems, the large unit can be configured to screen personnel or vehicles. Smiths Detection (formerly Barringer) began selling the GC-IONSCAN® in 1999 though the instrument was not designed for high speed separation.[50, 71] Varian Products introduced the CP-4900, a micro-machined narrow-bore GC column with FAIMS, in 2003.[72] However, the CP-4900 does not feature a temperature programmable oven and is targeted toward analyzing hydrocarbons, chlorofluorocarbons, and halogenated anesthetics.[17] In 2005, Thermo Electron Corporation presented the EGIS Defender®.[73] Advertised as a high-speed explosives detector, the instrument contains a 1-meter GC with FAIMS.

2.4.3 Limitations

GC separation has offered the advantage of separating analyte mixtures into individual components for improved detection. However, the addition of GC increases system complexity, power consumption, and analysis time, slowing the measurement from seconds to tens of minutes or more, all of which work against the advantages of IMS.[23]

Within the last few years, new GC/IMS designs that offer improved speed and portability have been developed. One way to overcome lengthy analysis times is to use short (17 cm - 3 m) columns.[74] [22] While short GC methods can pre-separate analytes, the specificity that can be obtained is limited because separation of analytes is not as efficient as with longer columns.[75] A second technique has been to use high speed or multicapillary GC with FAIMS though the cost is high and commercial availability is poor.[76] While in some cases, improved pre-separation can be achieved by using GC, some compounds may co-elute and interfere with the detection of compounds.[77]

2.5 Specific Explosive Compounds for Analysis

The detection of explosives is a very complicated task because they are typically comprised of many chemicals, each with different properties. Secondly, some explosive compounds typically have low vapor pressures. A technique must be used to collect low volatile analytes or only a minimal amount of a sample can be measured in detection.[53] A third factor that must be considered is that some chemicals that are major components in explosives (i.e. nitrogen) have legitimate commercial uses. Thus the detection of a particular chemical does not necessarily indicate the presence of an explosive material.

Furton and Myers [78] compiled two representative, but not exhaustive tables listing the properties of explosives. Table 2-1 provides the typical mixtures of common military and industrial high explosives.

Commonly Used Explosives	Main Compositions
C-2	RDX+TNT+DNT+NC+MNT
C-3	RDX+TNT+DNT+Tetryl+NC
C-4	RDX+Polyisobutylene+Fuel oil
Cyclotol	RDX+TNT
DBX	TNT+RDX+AN+AL
HTA-3	HMX+TNT+AL
Pentolite	PETN+TNT
PTX-1	RDX+TNT+Tetryl
PTX-2	RDX+TNT+PETN
Tetryol	TNT+Tetryl
Dynamite	NG+NC+SN
Red Diamond	NG+EGDN+SN+AN+Chalk+NaCl

Table 2-1: Main compositional mixtures of common military and industrial high explosives [78]

Table 2-2 provides the major chemical compound classes found in common military and industrial high explosives.

Compound Class	Example	Symbol	Commonly found/used in the following
Aliphatic Nitro	Nitromethane	n/a	Liquid fuel additive
	Hydrazine	n/a	Rocket fuel and liquid component of two-part explosive
Aromatic nitro (C-NO2)	Nitrobenzene	NB	Manufacturing process to produce aniline
	Nitrotoluene	NT	Synthesis of explosives
	Dinitrobenzene	DNB	Synthetic substance used in explosives
	Dinitrotoluene	DNT	Air bags of automobiles
	amino-dinitrotoluene	A-DNT	Synthetic substance used in explosives
	Trinitrobenzene	TNB	Synthetic substance used in explosives
	2,4,6-trinitrotoluene	TNT	Composition B with equal part RDX, Pentolite with equal part PETN
	2,4-dinitrotoluene	DNT	gelatinizing and waterproofing agent in explosives
	picric acid	n/a	Priming charge
Nitrate ester (C-O-NO2)	Methyl nitrate	n/a	Synthetic substance used in explosives
	Nitroglycerin	NG	Certain dynamites, pharmaceutical
	Ethyl glycol dinitrate	EGDN	Some dynamites
	Diethylene glycol dinitrate	DEGDN, MTN	Synthetic substance used in explosives
	Pentaerythitrol tetranitrate	PETN	Detonating cord, Detasheet (Flex-X military name), Semtex with RDX
	Nitrocellulose	NC	'Guncotton' main component of single-based smokeless powder
	Nitrocellulose and NG	NC, NG	Double-based smokeless powder
	Nitrocellulose, NG and nitroguanidine	NC, NG	Triple-based smokeless powder
Nitramines (C-N-NO2)	Methylamine nitrate	n/a	Propellant
	Tetranitro-N-methyaniline	Tetryl	Booster explosive
	Trinitro-triazacylohexane (cyclonite)	RDX	C-4, tetrytol-military dynamite w/TNT
	Tetranitro-tetracylooctane (octogen)	HMX	Her Majesty's Explosive
Acid salts ($NH4^+$)	Ammonium nitrate	AN	ANFO with fuel oil, nitro-carbo-nitrates (NCN) w/oil
	Ammonium perchlorate	n/a	Rocket fuel
	Potassium nitrate	PN	Black powder with charcoal and sulfur
Primary Explosives	Lead azide	n/a	Detonating fuses
	Lead styphnate	n/a	Blasting caps; component in primers
	Mercury fulminate	n/a	Initiating explosive
	Tetramino nitrate	n/a	Initiating explosive
	Hexamethylene triperoxide diamine	HMTD	Amateurs in detonators
	Triacetone triperoxide	TATP	Amateurs in detonators

Table 2-2: Major chemical components of common military and industrial high explosives [78]

Table 2-2 also illustrates the many chemicals that constitute high explosive materials. Complex mixtures of the chemicals as well as impurities found with explosive materials can have major implications on an instrument's ability to correctly identify trace concentrations of contraband. Even when complex mixtures can be separated, preferentially ionized compounds can further complicate detection. In today's world, many explosive compounds can be obtained from rogue military sources or individuals can discover recipes to synthesize explosives by searching the Internet.[79, 80]

After consulting with representatives from the FBI Explosives Unit of the Laboratory Division, five explosive compounds, listed in Table 2-3, were selected for evaluation.

Explosive Compound	Symbol
Hexamethylene Triperoxide Diamine	HMTD
Pentaerythritol Tetranitrate	PETN
1,3,5-Trinitro-1,3,5-Triazine	RDX
Triacetone Triperoxide	TATP
2,4,6 Trinitrotoluene	2,4,6 TNT

Table 2-3: Explosive compounds evaluated in current study.

Selection of the explosives used in this research was based on several factors:

1) representative of the organic explosives compound classes (nitramines, nitro-esters, nitro aromatics, and peroxides),
2) frequency of use in global occurrences,
3) ease of availability,
4) military relevance,
5) highly energetic,
6) ease of synthesis (i.e. peroxides).

Particularly, in the last factor, information and raw materials to make peroxide explosives can be easily be obtained by a non-chemist.[80-82] All five compounds are defined by the Bureau of Alcohol, Tobacco and Firearms (ATF) as explosive materials and are subject to United States (U.S.) regulations.[82]

Early manuscripts document IMS detection of nitrosamines with limits of 100ng/µl (ethanol) and nitroaromatics with limits of .001mg/m^3 in air.[51, 52] Most explosives possess relatively high electronegativities and will be best observed in negative ion mode; however, TATP is an exception to this rule. TATP is best observed in positive ion mode by most IMS instruments because the explosive contains no nitro groups.[83]

2.5.1 Hexamethylene triperoxide diamine (HMTD)

HMTD is a non-commercial, primary, organic peroxide high explosive that has been previously used in detonators by terrorists groups and amateurs.[84] A significant concern is that the recipe for HMTD can easily be found on Internet web pages with detailed descriptions on how to make the explosive compound from hexamine, hydrogen peroxide, and citric acid.[85] The Algerian terrorist, arrested upon entry to the US from Canada prior to the millennium celebration, was found to possess HMTD.[35] Presently, there is no reported application of HMTD as a commercial or military explosive.[86]

Unlike most conventional explosive compounds, HMTD contains no nitro groups or metallic elements, making detection by standard methods quite difficult. HMTD has no significant UV, visible or fluorescence spectra with detection limited to IR/Raman spectroscopy and LC/MS.[86] Currently, no sensitive method for quantitative trace analysis of HMTD is available.

2.5.2 Pentaerythritol tetranitrate (PETN)

PETN is a white crystalline explosive compound used widely as a priming composition in detonators, a base charge in blasting caps of small caliber ammunition, and the explosive core in detonating cords.[87] The recipe for PETN can easily be found on Internet web pages with comprehensive methods on how to synthesize the compound from, nitric acid, urea, sodium carbonate, and acetone.[80] PETN has been routinely detected at nanogram levels using IMS.

2.5.3 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX)

RDX, also known as Royal Demolition Explosive or hexogen, is a nitramine compound, second in strength (8.7 km/s) to nitroglycerin among common explosive compounds.[88] RDX is often used in mixtures with other explosives, oils, waxes and plasticizers to make C-4 or with PETN to make the most common explosive, Semtex.[87] RDX has a high degree of stability in storage and is considered the most powerful military high explosive. RDX is used as a base charge in detonators and in blasting caps. The International Security and Arms Control reports that RDX is the most serious threat in aircraft sabotage because it can be easily molded for concealment, remains stable, and in small amounts can destroy a large airplane in flight.[89] The Algerian terrorist, arrested upon entry to the U.S. from Canada prior to the millennium celebration, was found to possess RDX in addition to HMTD.[35] IMS is an established method of choice for detecting RDX.[90]

2.5.4 Triacetone triperoxide (TATP)

TATP is a sensitive and relatively easily produced home-made high explosive that has been used in acts of terror and sabotage in the United States, Israel, and the United Kingdom.[35] Specific examples of TATP use include the explosion onboard Philippine Airlines flight 200 in 1994 [91] and the 2003 "shoe-bomber" incident where Richard Reid's hiking boots were found to be packed with TATP combined with PETN.[7, 91, 92] In 2003, a sixteen-year-old was arrested in Washington state for making TATP in his house.[81] TATP can be prepared using the readily available commercial products, acetone, hydrogen peroxide, and a strong acid (hydrochloric or sulfuric).[93]

Unlike most explosive compounds, TATP does not contain nitro groups or metallic elements, making detection of concealed product difficult.[83] Detection of TATP by IMS was first reported by Buttigieg, *et al*. in 2003.[83] A key finding in Buttigieg's study revealed that IMS detects TATP in positive mode, differing from most explosive compounds that are identified in negative ion mode, because the explosive contains no nitro groups. TATP is not used in military or commercial applications because of its low chemical stability and high sensitivity to mechanical shock.[94]

2.5.5 2,4,6 Trinitrotoluene (2,4,6 TNT)

TNT was first used on a wide scale during World War I and is still used today by the military and in civilian mining and quarrying activities.[95] TNT is classified as a secondary explosive because it is less susceptible to initiation and requires a primary or initiating explosive to ignite. TNT can be used as a booster or as a bursting charge for high-explosive shells and bombs. TNT may be mixed with other explosives such as

RDX and is a constituent of many other explosives, such as amatol, pentolite, tetrytol, torpex, tritonal, picratol, and ednatol. TNT has been used under such names as Triton, Trotyl, Trilite, Trinol, and Tritolo. Chemical names for TNT are trinitrotoluene and trinitrotol. The advantages of TNT include low cost, safety in handling, high explosive power, good chemical and thermal stability, and compatibility with other explosives.[87] Karasek *et al*. was the first to report using IMS to detect TNT, obtaining a negative ion response.[96]

Table 2-4, provides diagrams of the chemical structures and physical properties for the five explosive compounds selected for evaluation.

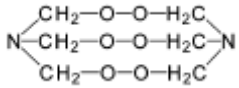
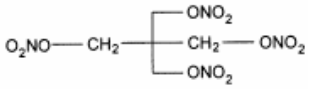
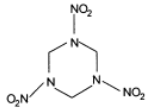
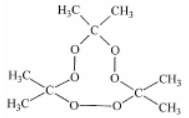
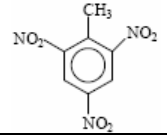
Explosive Compound	Structure	Molecular Formula	Class	Type of Explosive	Detonation Rate (m/s)	Vapor pressure (Torr) at 25°C	Molecular Weight	Color	Detection Mode	K_o (ms)
HMTD		$C_6H_{12}N_2O_6$	Peroxide	Primary	4511		208.1	White	Negative	$(M+Cl)^-$ 1.7304
PETN		$C_5H_8N_4O_{12}$	Nitrate ester	Primary	8260	$1.4x10^{-8}$ (18ppt)	316.2	White	Negative	$(M+Cl)^-$ 1.1479 $(M+NO_3)^-$ 1.0985
RDX		$C_3H_6N_6O_6$	Nitramine	Secondary	8750	$4.6x10^{-9}$ (6ppt)	222.6	White	Negative	$(M+Cl)^-$ 1.3880 $(M+NO_3)^-$ 1.3105
TATP		$C_9H_{18}O_6$	Peroxide	Primary	5300		222.2	White	Positive	MH^+ 1.665
TNT		$C_7H_5N_3O_6$	Aromatic nitro	Secondary	6930	$5.8x10^{-6}$ (7ppb)	227.2	Colorless/light yellow	Negative	$(M-H)^-$ 1.451

Table 2-4: Structure and properties of explosive compounds evaluated in current study.

3 Methodology

This chapter describes the methods used to answer the research question discussed in Chapter 1. The primary objective was to determine if IMS chemical detection methods could be improved for trace forensics and military field applications. A test plan was developed to compare the performance characteristics of the IMS and GC/IMS operational modes of the GC-IONSCAN®. Known liquid concentrations of HMTD, PETN, RDX, TATP, and TNT were analyzed to determine instrument response (mean sum of the product ion(s) maximum peak amplitude), detection limits, sensitivity, and precision. In addition, compound specificity and resolution of four chemical interferent products without and amidst the five explosive compounds was assessed with the IMS and GC/IMS operational modes of the GC-IONSCAN®.

3.1 GC-IONSCAN®

The instrument used in this research, a GC-IONSCAN® manufactured by Smiths Detection (Warren, NJ), weighs approximately 70 lbs., (see Figure 3-1) and was introduced in 1999 as a transportable field-screening instrument for explosive or narcotics detection. The instrument can be operated in two settings: explosives (negative ion detection) or narcotics (positive ion detection). The GC-IONSCAN® can provide semi-quantitative analysis of compounds based on ion mobility, retention time, characteristic chemical ionization peaks (analyte product ions), drift time, and amplitude of the response.

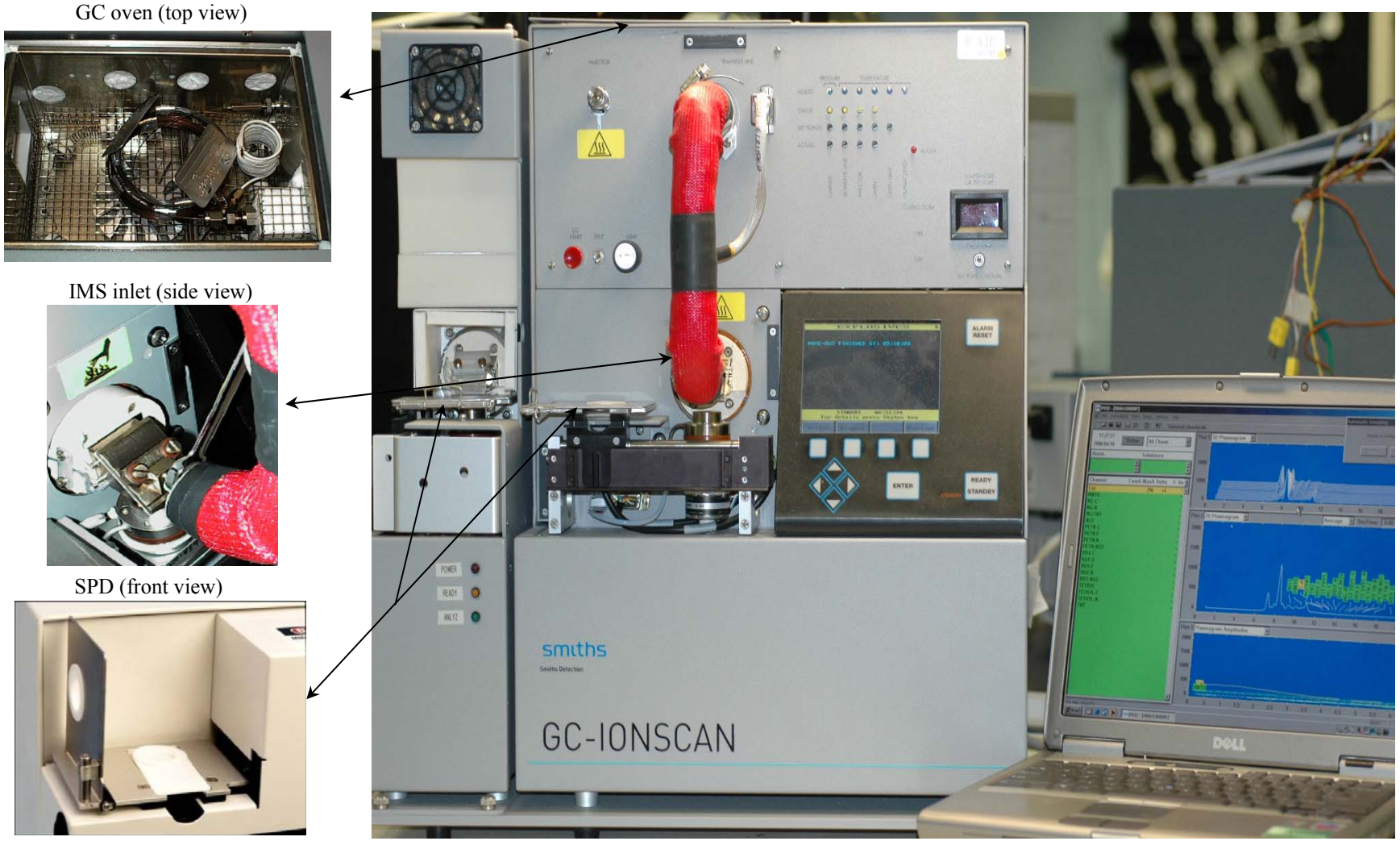


Figure 3-1: Smiths Detection GC-IONSCAN® instrument

The instrument can also be operated in two modes: IMS only and GC/IMS (which combines GC and IMS). A flow schematic of the GC-IONSCAN® is shown in Figure 3-2.

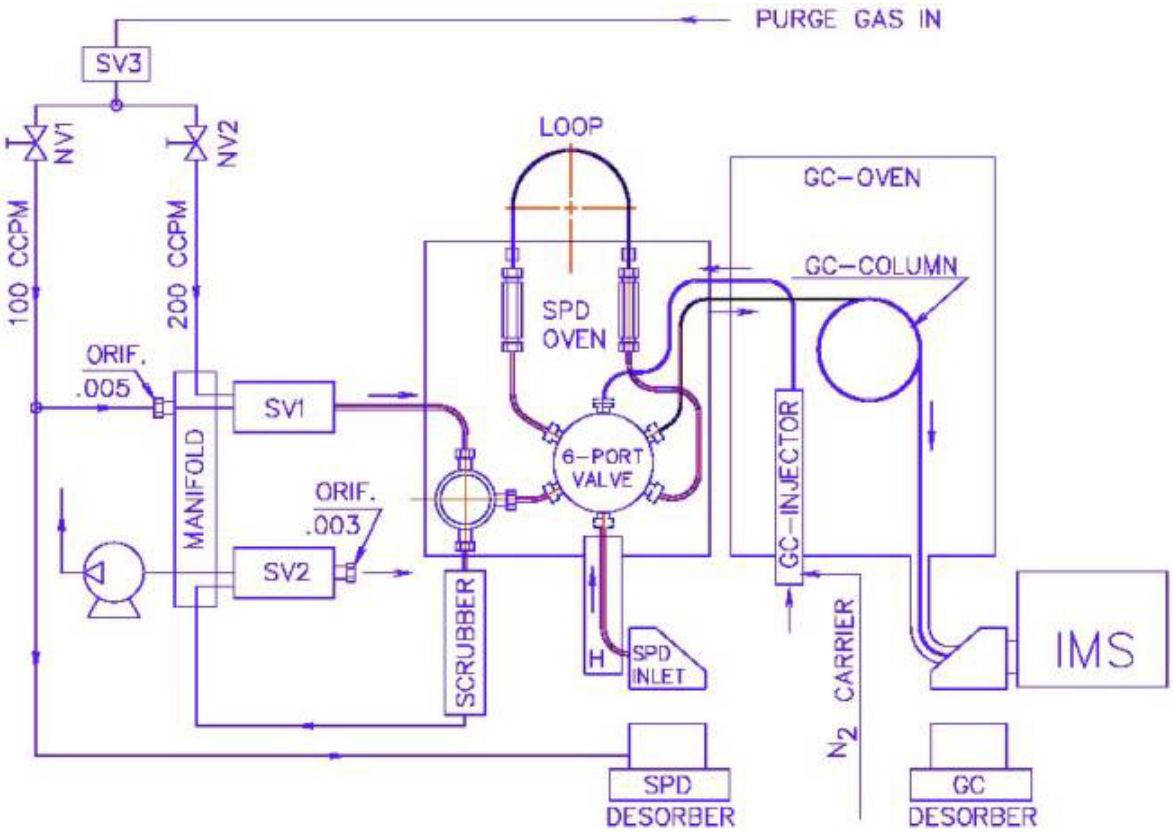


Figure 3-2: Schematic of the GC-IONSCAN®

Samples are obtained by wiping or deposition onto a Teflon® or cotton "swab". In the IMS mode, analytes are thermally desorbed in a solid phase desorber (SPD) and combined with makeup gas (air filtered with charcoal and Drierite™). The GC column is bypassed permitting quick and direct analysis of thermally desorbed molecules in seconds. In the GC/IMS mode, solvent extracts can be directly injected onto the GC column or solvents and solid particles can be thermally desorbed from a swab via an SPD. When thermally desorbed, analyte enters a sample loop (10cm MXT-1; 0.53mm internal diameter; 7.0µm film thickness) via a six-port valve. After desorption is

complete, the six-port valve switches, the sample loop (i.e sample trap) is heated, and sample vapors are carried into the column.

In the positive setting, a trace amount of nicotinamide is automatically added into the ionization region as a chemical ionization dopant and an internal calibrant. In the negative setting, a trace amount hexachloroethane is automatically added as a chemical ionization dopant. A trace amount of 4-nitro-benzylnitrile is automatically added as an internal calibrant. The reagents are housed within the instrument as solids in permeation tubes that are heated during operation. To ensure calibration of the instrument, the software continuously monitors the drift times of the ions produced from the internal calibrants. The software uses the internal calibrant drift time to calculate expected reduced ion mobilities (K_o) for targeted compounds. The drift time of the calibrant ions is compared to a reference value and the difference is reported as a "delta" value on the instrument display. The calibrant position is monitored whenever the instrument is idle, resulting in a continuous calibration process. The operating conditions of the GC-IONSCAN® can be fully controlled from the instrument's front panel or via an external computer via the GC-IONSCAN® software. The instrument requires either 110 or 220V AC power (1400W max) for operation.[71]

3.2 Instrument Setup

The GC-IONSCAN® instrument was used in accordance with the user manual and manufacturer recommendations. In-house optimizations of the operating parameters were not performed prior to data collection to maintain consistency with factory default settings and following the recommendations provided by the manufacturer. Data acquisition parameters are listed in Table 3-1.

Data Acquisition Parameters					
	HMTD*	PETN	RDX	TATP*	TNT
	IMS Experimental Conditions				
Operating mode	Negative	Negative	Negative	Positive	Negative
Sampling time (s)	10	10	10	10	10
Desorber temperature (°C)	225	227	227	220	227
Inlet temperature (°C)	240	242	242	225	242
Drift tube temperature (°C)	105	112	112	150	112
Shutter gate width (ms)	0.02				
IMS scan period (ms)	25				
Segments per analysis	30				
Scans added per segment	20				
Analysis duration (s)	15				
Electric field gradient (v/cm)	200	200	200	175	200
Product ion drift time variability (µs)	50	45	45	50	45
Product ion detection threshold (du)	$(M+Cl)^-$ (2)	$(M+Cl)^-$ (25) $(M+NO_3)^-$ (50)	$(M+Cl)^-$ (25) $(M)_2Cl^-$ (40) $(M+NO_3)^-$ (50)	$M+H^+$ (50)	$(M-H)^-$ (5)
	GC/IMS Experimental Conditions				
Loop cycle program (s)	sample (10); heat (3); purge (15); cool (15)				
Loop temperature (°C)	220	220	220	240	220
Valve temperature (°C)	200	200	200	220	200
GC column	15-m MXT-1; 0.53mm internal diameter; 1.0µm film thickness				
Oven initial temperature (°C) Oven initial hold (s) Oven ramp rate (ºC/min) Oven final temperature (°C) Final hold (s)	120 20 40 240 20	120 20 40 240 20	120 20 40 240 20	80 120	120 20 40 240 20
Transfer line temperature (°C)	180	220	220	240	220
Analysis duration (s)	220				
Segments per analysis	300				
Scans added per segment	20 (for the first 80s) 40 (for the last 140s)				
Product ion retention time (variability) (s)	90 (±5)	114 (±5)	117 (±5)	71 (±5)	100 (±5)

Table 3-1: GC-IONSCAN® data acquisition parameters
***TATP and HMTD were not part of the original onboard library. Analysis was performed using parameters obtained from Smiths Detection.**

When the GC-IONSCAN® was operated in IMS only mode, drift gas and carrier gas were purified ambient air. The air was purified with activated charcoal and a desiccant by drawing the air through the instrument purification unit. When operated in GC/IMS mode, drift and carrier gas were BIP® helium (Airgas, Salem, NH) with less

than 10 ppb_v oxygen, 20 ppb_v water, 100 ppb_v total hydrocarbons and 3 ppm_v nitrogen. Carrier gas pressure was set at 15 psi. The drift gas flow was set at 350 cc/min. HMTD and TATP were not part of the original onboard library for the GC-IONSCAN®; however, they were added using parameters obtained from the manufacturer.

3.2.1 Data Acquisition and Processing

All methods and data were analyzed and processed using the manufacturer's GC-IONSCAN® software (Instrument Manager version 5.114). Data was transferred via an RS-232 cable linked to a remote 1.4 GHz Pentium notebook computer (Dell, LATITUDE D600) for processing, display, and storage. MATLAB® (version R2006a) was used to graphically display data.

3.3 Sample Preparation

Known masses of HMTD, PETN, RDX, TATP, and 2,4,6 TNT (all 99% or greater in purity) were obtained from the FBI Explosives Unit of the Laboratory Division (Quantico, VA). A stock solution of 100 ng/µL HMTD was prepared by dissolving the solid compound in acetone (Optima, Fisher Scientific, Fair Lawn, NJ). Stock solution standards of 100 ng/µL PETN, RDX, TATP, and TNT each were prepared by dissolving the solid compounds in methanol (HPLC Grade, Fisher Scientific, Fair Lawn, NJ). The stock solutions were used to make 100 ng/µL, 50 ng/µL, 10 ng/µL, 5 ng/µL, 1 ng/µL, and 0.1 ng/µL standards for the experiments. All standards were mixed in a vortex mixer (Vortex-Genie 2, Scientific Industries, Bohemia, NY) for 30 seconds. All standards were kept in amber glass vials with Teflon® lined screw caps (Supelco, Bellefonte, PA) and refrigerated (8°C) when not in use.

3.4 Methods

The instrument was allowed to warm up for at least 30 minutes before analysis began. Once the instrument was warm, the device parameters, listed in Table 3-1, were verified and an instrument blank sample was collected prior to sample analysis. Second, a swab blank was collected to record background generated by the swab. Third, a swab/solvent blank was collected to record any background generated by the solvent. To minimize any internal or external changes, the time between the blank samples and the start of analyses was held to less than one minute. A new swab was used for each analysis and an instrument blank was collected between analyses to ensure the samples were not cross contaminated.

Samples were prepared by unscrewing the standard's vial cap, collecting a 1µL extraction with a 10µL (micro-liter) syringe (Hamilton, Reno, NV), and depositing directly onto the swab, one explosive compound per sample. An air plug was used to ensure the entire 1µL was forced out of the syringe. The solvent was allowed to evaporate (approximately 5 s) before the swab was placed into the thermal desorption unit. The desorption unit automatically vaporized the sample and subsequently introduced the sample into the IMS or GC/IMS. Experiments with HMTD, PETN, RDX, and TNT were performed in the negative setting. Experiments with TATP were performed in the positive setting. The sum of the analytes ion(s) maximum peak amplitudes were recorded and used for comparisons. For each sample, the result was considered a positive identification if both of the following criteria were met:

1) Ion peaks in the IMS plasmagram or GC/IMS chromatogram could be attributed to the analyte through ion mobility interpretation.

2) The analyte peaks of the IMS plasmagram or GC/IMS chromatogram were more than three times the background noise.

3.4.1 Evaluation of Sample Swabs

Currently, the Transportation Security Administration (TSA) collects samples in the field using rectangular (55mm x 75mm) cotton swabs (Smiths Detection, Warren, NJ). Teflon® swabs (30mm diameter x 0.25mm) are also available (Smiths Detection, Warren, NJ). A preliminary study was conducted to determine the swab material for optimal adsorption, retention, and desorption of the selected analytes in this experiment. To select the optimal swab, a clean background was established, 10 ng of an individual explosive compound was deposited onto cotton and Teflon® swabs, and analyzed. Five replicates of each explosive compound were collected for reproducibility. The sum of the analyte ion(s) maximum peak amplitude was recorded after the analysis.

3.4.2 Evaluation with Explosive Compounds

After determining the optimal swab for all five explosive compounds, the IMS and GC/IMS operational modes of the instrument were compared by analyzing the five selected explosive compounds at concentrations ranging from 0.1 to 100 ng/μL. The sensitivity of the operational modes was determined for each explosive compound by stepping down the concentration of each to determine the lowest detectable quantity of analyte loaded onto a swab. Five replicates at each analyte concentration were measured for reproducibility.

3.4.3 Evaluation with Interferents

In the third experiment, four commercial products commonly found in airport settings and identified as potential interferents by the FBI Counterterrorism & Forensic Science Research Unit (CFSRU), (Quantico, VA) were analyzed as pure compounds by both operational modes of the instrument to test the effect of chemical interferents on analysis. For security purposes, the interferents will not be disclosed by name. The interferents will be referred to as Interferent #1, Interferent #2, Interferent #3, and Interferent #4. Interferents #1 and #2 were deposited onto sample swabs in 5 µL aliquots and allowed to dry. The dry mass of Interferent #1 deposited on a sample swab was approximately 700µg and the dry mass of Interferent #2 deposited on a sample swab was approximately 420µg. A 100 mg droplet of Interferent #3 was placed on a 10 square inch clean pane of glass and spread as evenly as possible using a gloved finger. One-centimeter swab wipes were collected from the glass pane. The mass of Interferent #3 collected on a sample swab was approximately 500µg. For Interferent #4, 25mg of dry particles were placed inside a 0.5-liter plastic bag and shaken. One-centimeter swab wipes were collected from the bag interior. The dry mass of Interferent #4 collected on a sample swab was approximately 450µg. Care was taken not to over-sample the interferents by avoiding collection of visible particles on a swab. The approximate weight was determined by weighing five of each interferent containing swab and calculating the mean. For reproducibility, five replicates, one interferent per sample, were analyzed by the IMS and GC/IMS operational modes of the instrument.

3.4.4 Evaluation with Interferents and Explosive Compound Mixtures

In the fourth experiment, the operational modes of the instrument were assessed to determine the ability to discern a single target explosive compound (HMTD, PETN, RDX, TATP, and TNT) in the presence of each of the four interferents (one at a time). Sample swabs were prepared with the four interferents, with the same quantity as previously described, and then spiked with the explosive compound (at least one order of magnitude higher than the LOD). Five replicates of each single interferent/single explosive combination sample were analyzed by the IMS and GC/IMS operational modes of the instrument for reproducibility.

3.5 Statistical Methods for Data Analysis

The sum of the analytes product ion(s) maximum peak amplitude was recorded after analyzing samples and the mean was computed for each set. Each set was compared for reproducibility by determining the relative standard deviation (RSD) for the five replicates in each sample set.

4 Experimental Results

4.1 Instrument Output

The instrument used in this research provides chemical analysis information through output that is displayed as a plasmagram. A plasmagram of an 'instrument blank' collected in the IMS mode, negative setting is displayed in Figure 4-1. Signal intensity is plotted against drift time and analysis duration. The resulting ion peaks in Figure 4-1 are the reactant ions, hydrated oxygen molecules $(H_2O)_nO_2^-$ from ambient air and chloride ions $(H_2O)_nCl^-$ from a dopant, hexachloroethane. In the absence of other chemicals, reactant ion peak(s) form the largest peak(s) in a plasmagram because they are the only charge carriers present in the detector.

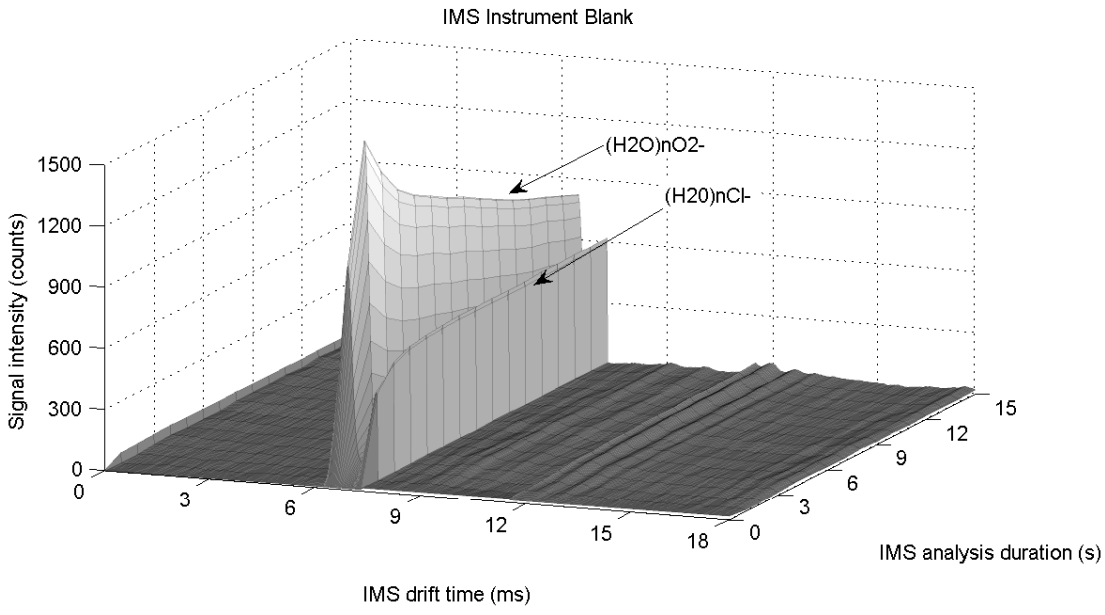


Figure 4-1: Plasmagram from an IMS 'instrument blank'.

A plasmagram from IMS analysis of a 10ng TNT sample is presented in Figure 4-2. This plasmagram graphically illustrates the IMS drift time and peak shape of TNT as $(TNT\text{-}H)^-$. The resulting drift time for TNT was 12.637ms with a calculated ion mobility (K_o) of 1.4502cm^2/V-s using nitrobenzonitrile as the reference ion (Equation 2-5). When TNT was analyzed, the reactant ion(s) [$(H_2O)_nO_2^-$ and Cl^-] decreased in intensity as the TNT ions increased in intensity. The reactant ion(s) re-intensified as the TNT analyte passed through the drift region and charge transfer reactions completed. Ions formed from components in the Teflon® swab and background composition of little analytical interest were observed in the plasmagram; however, these ions were much lower in abundance and formed at times that did not interfere with the targeted analytes. For IMS to identify a chemical, a product ion peak [$(TNT\text{-}H)^-$ in Figure 4-2] must conform to detection algorithm parameters and the known K_o value in the onboard library.

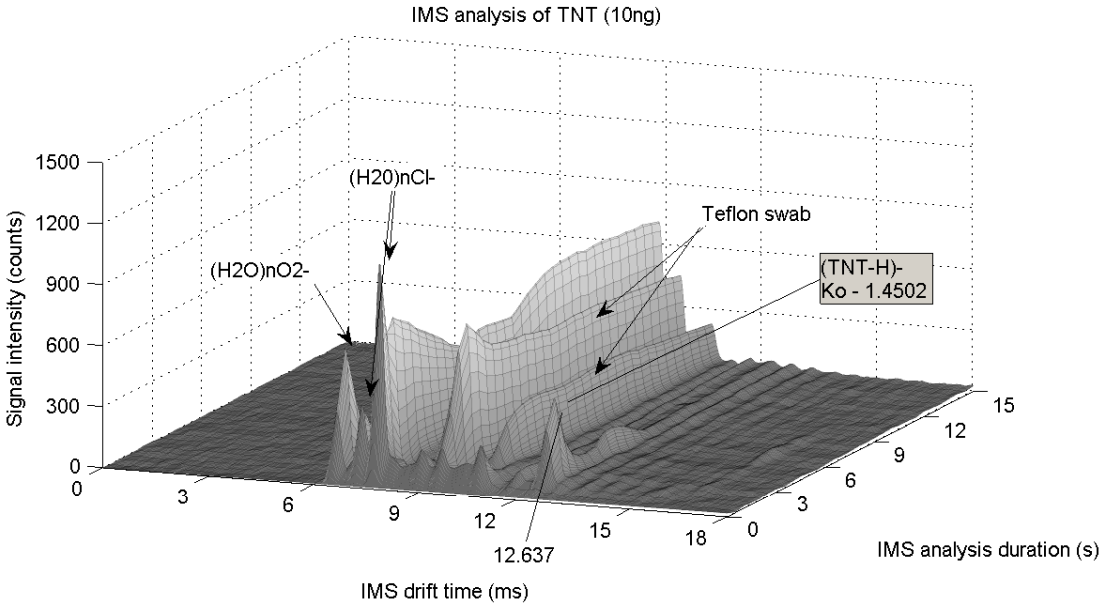


Figure 4-2: Plasmagram from a 10ng TNT sample on a Teflon swab by IMS analysis.

A GC/IMS chromatogram of an 'instrument blank' collected in the negative setting is displayed in Figure 4-3. Signal intensity is plotted against IMS drift time and GC retention time. In the GC/IMS mode, column effluent is introduced into the IMS ionization region. Forty IMS scans per second of the GC column effluent were collected. The resulting peaks in Figure 4-3 are the reactant ions, hydrated oxygen molecules $(H_2O)_nO_2^-$ from ambient air and hydrated chloride ions $(H_2O)_nCl^-$ from a chemical ionization dopant, hexachloroethane. IMS scans have been compiled starting from front to back on the z-axis.

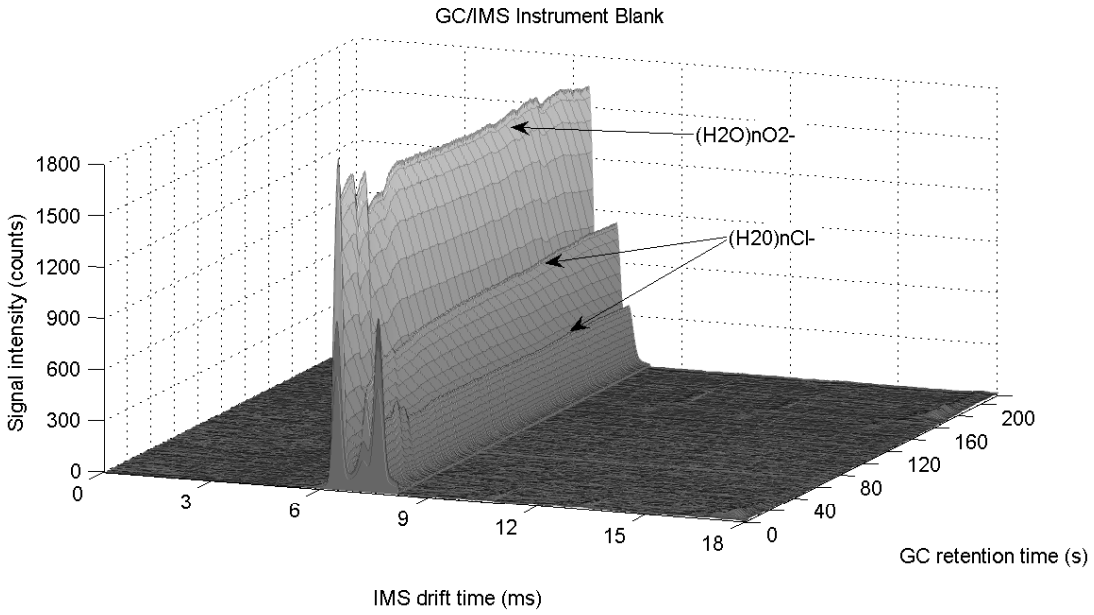


Figure 4-3: GC/IMS chromatogram from an 'instrument blank'.

A GC/IMS chromatogram from analysis of a 10ng TNT sample is presented in Figure 4-4. This GC/IMS chromatogram graphically illustrates the 3-dimensional analysis of GC/IMS; IMS drift time and GC retention time plotted against signal intensity. The pre-separation provided by the GC simplifies the chemistry within the ionization region. By minimizing the number of constituents present at any one time, analyte ions can be formed without competitive ionization interferences. In Figure 4-4,

the z-axis denotes the GC retention time (104s), the x-axis denotes the IMS drift time (12.737ms) and the y-axis denotes the signal intensity (765 counts) for the TNT peak. The calculated ion mobility (K_o) of TNT was 1.4507cm^2/V-s using nitrobenzonitrile as the reference ion. Decrease of the reactant ions $(H_2O)_nO_2^-$ and $(H_2O)_nCl^-$ from charge transfer reactions can be observed in Figure 4-4. For GC/IMS to identify a chemical, a product ion peak [$(TNT-H)^-$ in Figure 4-4] must conform to detection algorithm parameters, the onboard library of known K_o, and the retention time (see Table 3-1).

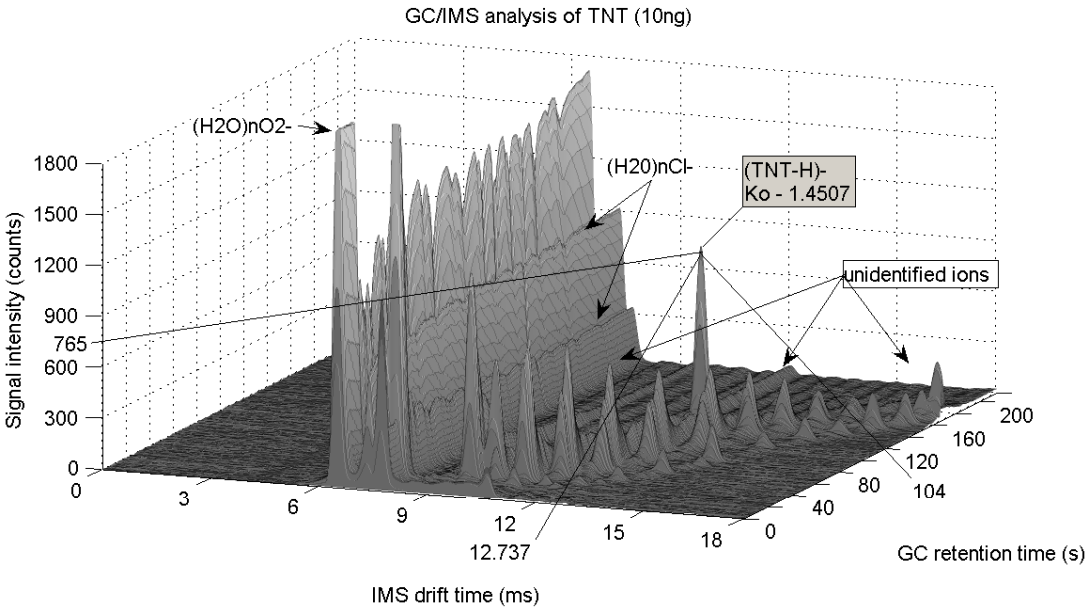


Figure 4-4: GC/IMS chromatogram of 10ng TNT.

4.2 Sample Swab Analysis

Cotton and Teflon® swabs (Smiths Detection, Warren, NJ) were evaluated to determine the optimal swab for adsorption, retention, and desorption. Ten ng of either (HMTD, PETN, RDX, TATP, or TNT) was deposited on the swab surface, followed by

IMS analysis (n=5). The sum of each analyte's product ion(s) maximum peak amplitude (peak amplitude) was used for comparison. The results are shown in Figure 4-5.

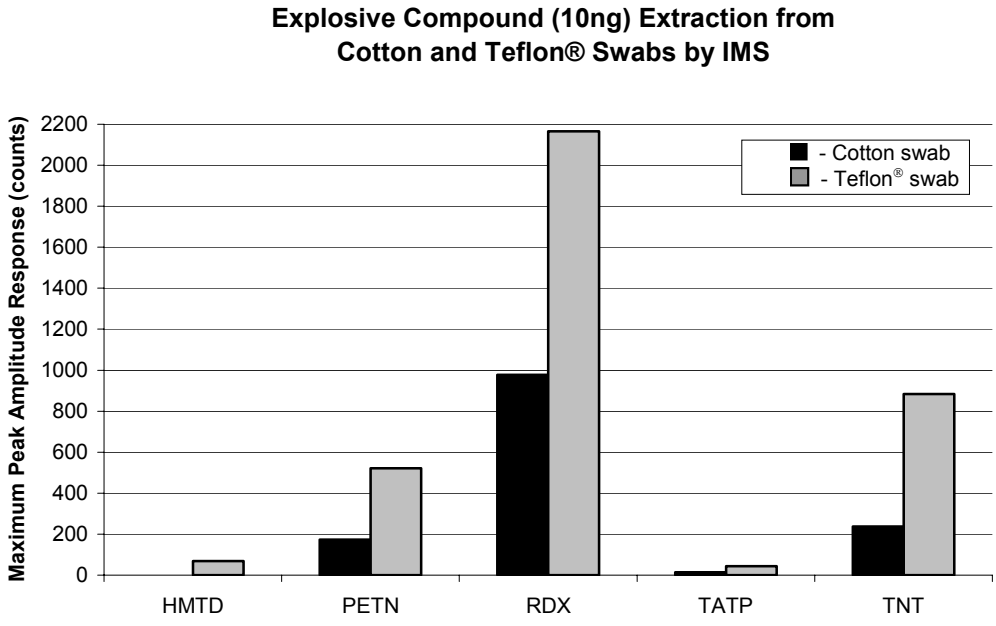


Figure 4-5: IMS maximum peak response. ■ cotton swab □ Teflon® swab

In all cases, a larger amount of explosive compound was extracted with the Teflon® swab. Ten nanograms of HMTD was not detected using a cotton swab. Based on the low reactivity of Teflon® and the larger response for all five explosive compounds, only Teflon® swabs were used through the remainder of this research. The use of cotton swabs was discontinued. A related study, in which a larger mass of TNT was desorbed from Teflon® versus cotton agrees with these findings.[97]

4.3 Sample Throughput Rate

The IMS and GC/IMS operational modes of the GC-IONSCAN® were evaluated to determine the sample throughput rate. The sample throughput rate was defined as the length of time from the start of swab thermal desorption to restoration of the original

reactant ion intensity. This time included instrument analysis, computer processing, results display, and stabilization for subsequent sample analysis. IMS and GC/IMS were evaluated by analyzing 10ng extractions of RDX liquid standard on a Teflon® swab (n=10). In-house adjustments of the desorbing and analyzing parameters were not made from the factory default settings. The average throughput rate for IMS was one sample every 21 seconds. The average throughput rate for GC/IMS was one sample every 6 minutes 13 seconds.

Using the factory default settings, analysis times for GC/IMS and even IMS were longer than desired for high-demand field use applications. The sample throughput rate for both modes can be reduced through shorter SPD heating and/or analysis duration. One observation with GC/IMS throughput rate was the lengthy cooling time of the air circulation oven. The average cooling time of the air circulation oven from 200°C to 100°C was 1 minute 51 seconds (n=10). GC systems that employ an air circulation oven to heat the column not only limit sample throughput through lengthy cooling rates, but also tend to have a narrow range of temperature heating rates. Furthermore, air circulation ovens are neither easily portable nor power efficient. The air circulation oven in the GC-IONSCAN® has a maximum temperature heating rate of 40°C/min and contributes to the weight and power requirements of the system. While the most modern air circulation GC ovens can achieve temperature heating rates of 75°C/min, above 175°C the ramp rate is limited to approximately 30°C/min.[66]

An alternative to heating a GC column by an air circulation oven is to heat the column directly. Resistive heating of capillary GC columns was first demonstrated in 1989.[98] Since that time, several resistive heating designs have become commercially

available. Resistively heated column designs can attain temperature programming rates much faster than the conventional air circulation ovens with temperature program rates of 200°C/min possible.[99] The chromatography obtained using resistively heated columns has also shown to be equivalent to that obtained with standard GC air circulation laboratory instruments.[66] Additional benefits of resistively heated columns, particularly for field equipment, are the lower power requirements (battery operable), miniature size (3 inch diameter x ½ inch thick coil), lightweight construction (less than 16 ounces), and rapid cooling rates, which can provide faster analysis cycles and increased sample throughput.[99] Replacing the GC-IONSCAN® air circulation oven with a resistively heated column may provide faster analysis cycles and increase sample throughput for chemical analysis in the GC/IMS mode.

4.4 Explosive Compounds Analysis

4.4.1 Detection Limits

To determine the Limit of Detection (LOD) for each explosive, 1 μL liquid standards were deposited on Teflon® swabs and analyzed by IMS and GC/IMS (n=5). The LOD is defined as the mass of target analyte required to produce an alarm at the given detection algorithm. Using the instrument parameters described in Table 3-1, the LODs for the five explosive compounds are listed in Table 4-1 and Figure 4-6. The results show IMS and GC/IMS had the same LOD for RDX and TNT; however, the LOD for GC/IMS was higher than IMS for PETN, TATP, and HMTD. Several factors may have attributed to the higher GC/IMS LODs, such as sub-optimal SPD, loop, column or detection algorithm parameters. A lower GC/IMS LOD for PETN (10ng) and HMTD

(50ng) was observed after lowering the SPD, oven, and transfer line temperatures; however, for the purposes of this study and to maintain consistency, parameters for the research herein were not altered from the factory settings. LODs, similar to those presented in Table 4-1, have been observed.[44]

	IMS	GC/IMS	Ion Peaks Observed
RDX	0.1 ng	0.1 ng	$(M+Cl)^-$ $(M)_2Cl^-$ $(M+N0_3)^-$
2,4,6 TNT	1 ng	1 ng	$(M-H)^-$
PETN	1 ng	50 ng	$(M+Cl)^-$ $(M+N0_3)^-$
TATP	5 ng	50 ng	$(M+H)^+$
HMTD	5 ng	100 ng	$(M+Cl)^-$

Table 4-1: Limit of Detection for the GC-IONSCAN®.

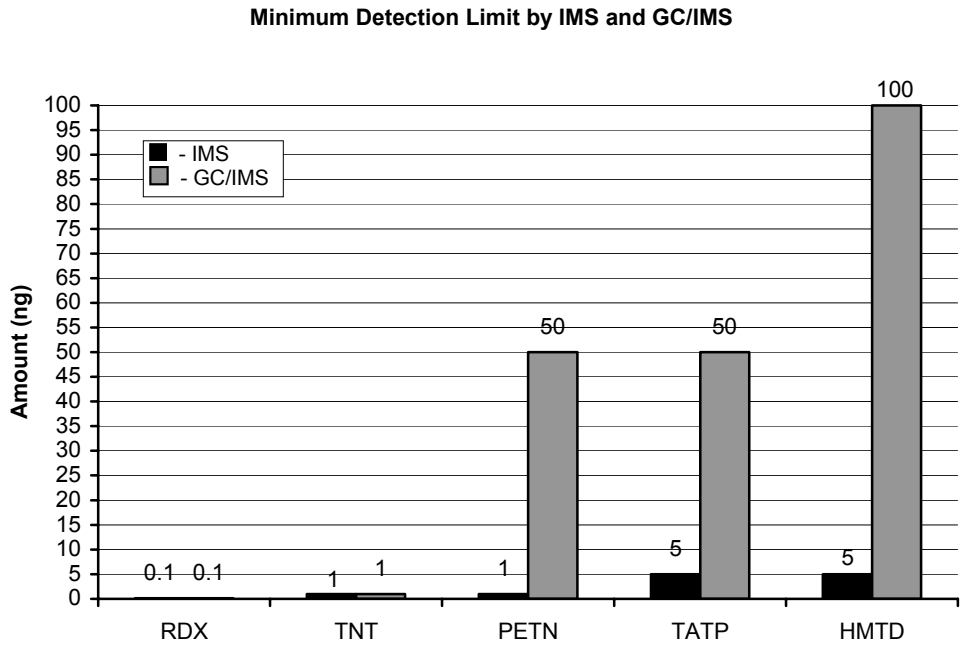


Figure 4-6: Limit of detection (ng) with GC-IONSCAN®. ■ IMS ■ GC/IMS

4.4.2 Upper Saturation Limit

A well-documented characteristic of IMS technology is the narrow linear range of instrument response versus mass of sample analyzed. Linear response of IMS is often limited to two orders of magnitude of sample mass because IMS instruments are relatively easy to overload due to the limited number of reactant ions available for analyte ion reactions. When all reactant ions are depleted, no further increase in analyte ion concentration is possible. Thus, sample size must be carefully controlled. The addition of GC to IMS is designed to help minimize the number of constituents present at any one time in the detector to prevent overload. The IMS and GC/IMS operational modes of the instrument were evaluated to determine if the addition of GC reduced the upper saturation limit of IMS.

Response curves are shown for the five explosive compounds in Figure 4-7. GC/IMS was expected to have increased the upper limit of the saturation concentration by limiting the amount of sample entering the IMS at any one time, preventing overload, and potentially increasing the dynamic range. However, the data is inconclusive. Note that with RDX (Figure 4-7a), IMS and GC/IMS appear to have reached saturation at the same concentration level. The instrument response between 50ng and 100ng is nearly the same, which suggests the instruments are saturated. With TNT (Figure 4-7b), IMS response does not appear to reach saturation, while GC/IMS appears to have reached saturation. GC/IMS saturation at the same or lower concentration as IMS may be attributed to inefficient collection of sample vapors in the sample trap. One approach to improve GC/IMS response may be to replace the sample trap with a new sample collection medium for a more efficient collection of sample vapors for transfer into the

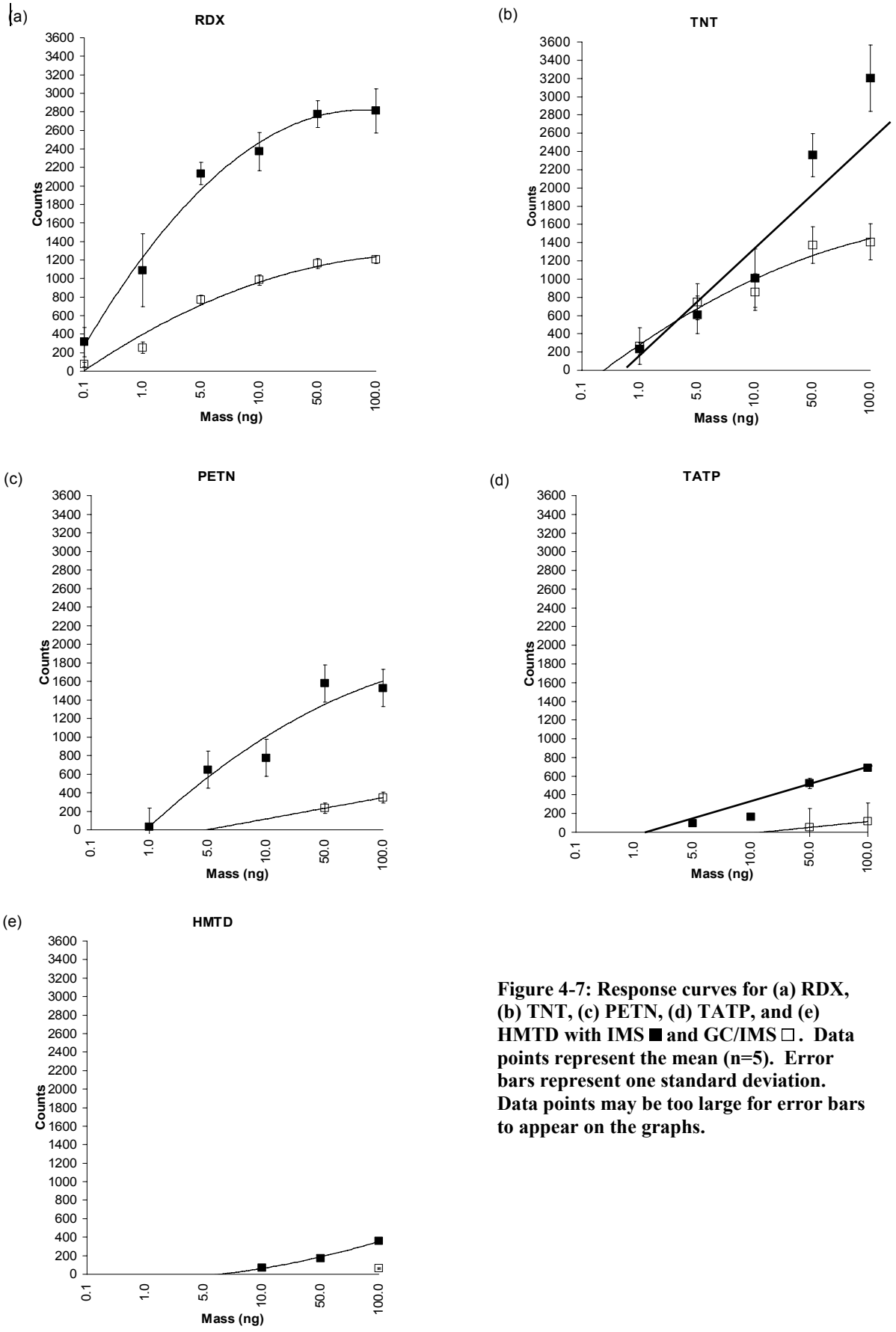


Figure 4-7: Response curves for (a) RDX, (b) TNT, (c) PETN, (d) TATP, and (e) HMTD with IMS ■ and GC/IMS □. Data points represent the mean (n=5). Error bars represent one standard deviation. Data points may be too large for error bars to appear on the graphs.

column. IMS and GC/IMS analysis of PETN (Figure 4-7c), TATP (Figure 4-7d), and HMTD (Figure 4-7e), are inconclusive with respect to upper limit of the saturation.

The response curves in Figure 4-7 also show that IMS produced higher signal response (peak amplitude) than GC/IMS at nearly all concentrations for all five explosive compounds. The increased signal response by IMS over GC/IMS at the same concentrations may be attributed to inefficient transfer of sample vapors into the column and/or detector. One approach to improve GC/IMS response may be to replace the PDMS coated sample loop (i.e. trap) with an alternate coating or a different sample collection medium for a more efficient transfer of sample vapors into the column. A second approach to improve GC/IMS response may be to replace the air circulation heated column with a resistively heated column with improved temperature programming rates that may allow for improved chromatography and more efficient transfer of sample vapors into the IMS detector.

4.4.3 Precision

Relative standard deviations (RSD) were used to assess the precision (reproducibility) of explosive compound analysis by examining the results of five replicate samples. The RSDs (average peak amplitude divided by the standard deviation) for IMS and GC/IMS analysis of the five explosive compounds are shown in Table 4-2 and Figure 4-8. The majority (33 of 40) of the RSDs were below 30%. The RSDs for TNT by GC/IMS were significantly lower than IMS ($p=0.043$, Wilcoxon signed ranks test). The RSDs for RDX by GC/IMS were lower than IMS for four concentrations and the same for two, but not statistically significant ($p=0.068$, Wilcoxon signed ranks test). No comparisons were made for PETN, TATP, or HMTD due to the different LODs and the range tested.

Few studies are available in the published literature on the reproducibility of IMS and GC/IMS measurements of explosive compounds. Studies that discuss reproducibility of IMS under similar conditions report RSDs for PETN, RDX, and TNT between 4 and 77% in the range of 50 pg to 125 ng.[97, 100] Dindal, *et al.*[101] reported RSDs for trace levels of RDX and TNT in soil samples at 54% and 51% and water samples at 20% and 26% using GC/IMS.

	TNT		RDX		PETN		TATP		HMTD	
	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS
100ng	11	4	8	4	4	23	6	27	9	13
50ng	10	2	5	5	6	25	10	26	17	*
10ng	32	14	9	6	25	*	8	*	31	*
5ng	34	11	6	6	18	*	21	*	63	*
1ng	29	27	36	24	48	*	*	*	*	*
0.1ng	*	*	50	22	*	*	*	*	*	*

Table 4-2: Precision of five replicate samples (mean % RSD for the sum of the product ion(s) maximum peak amplitude) *Less than the LOD.

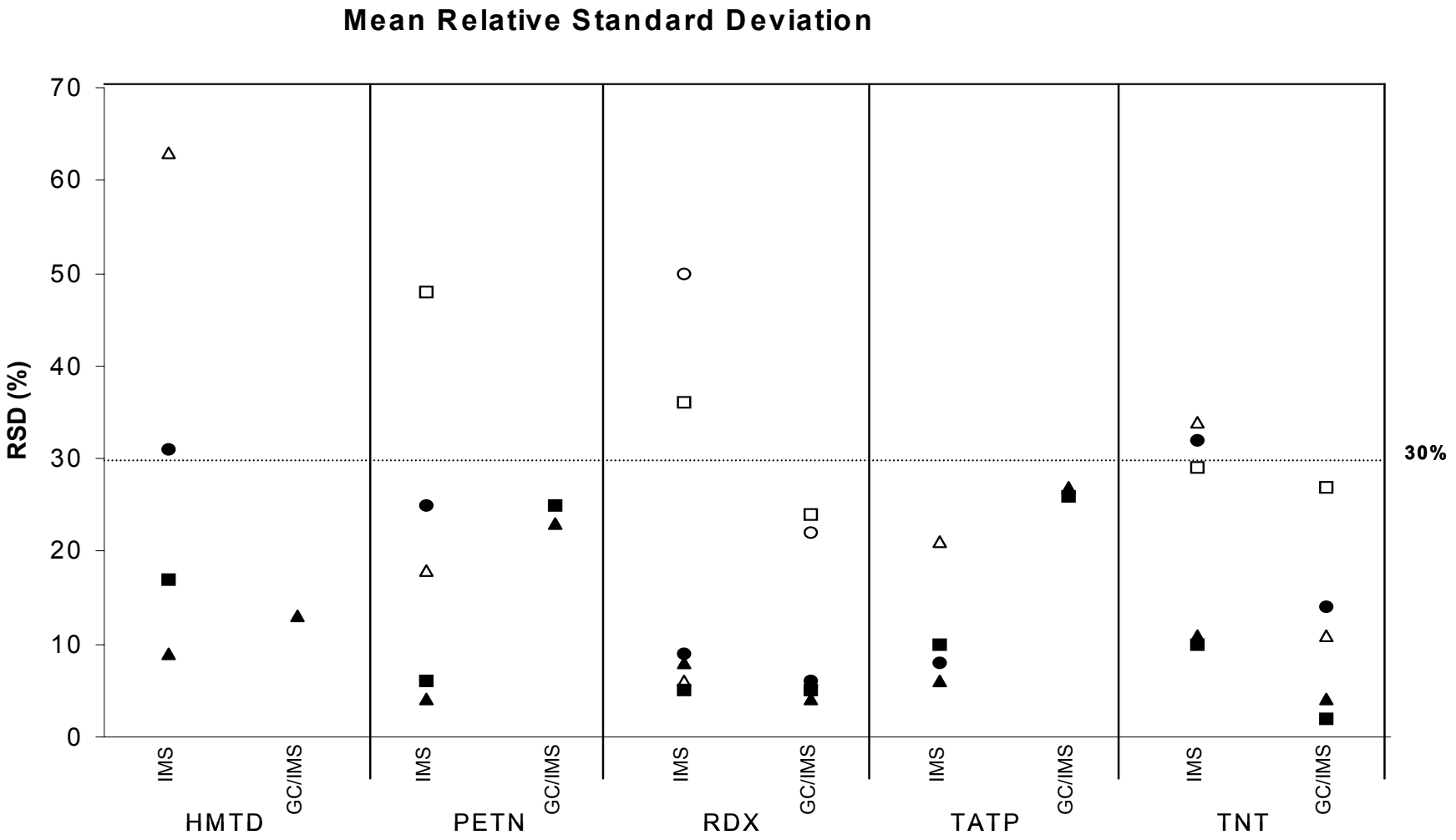


Figure 4-8: Precision of five replicate samples (mean % RSD for the sum of the analyte(s) maximum peak amplitude). ○ 0.1ng □ 1ng △ 5ng ● 10ng ■ 50ng ▲ 100ng

4.5 Interferent Analysis

4.5.1 Accuracy

The effect of chemical matrix interferents on IMS and GC/IMS detection was explored using four commercial products. One interferent per Teflon® swab was prepared and analyzed, as previously described (n=10). The quantity of interferent deposited on sample swabs was approximately 700µg for Interferent #1, 420µg for Interferent #2, 500µg for Interferent #3, and 450µg for Interferent #4. Table 4-3 summarizes the results of 'interferent only' sample analysis. A false positive is defined as an alarm for an explosive compound, at the given detection threshold (Table 4-1), when there actually was no explosive compound in the sample. 'Interferent only' samples analyzed by IMS resulted in seven false positives (two with Interferent #2 and five with Interferent #3). GC/IMS analysis of 'interferent only' samples resulted in zero false positives. The proportion of false positives was significantly higher for IMS (7/40) than for GC/IMS (0/40) (p=0.012, Fisher's exact test).

Interferent only	Interferent #1		Interferent #2		Interferent #3		Interferent #4	
	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS
Number of samples	10	10	10	10	10	10	10	10
Number of false positives in 10 samples	0	0	2	0	5	0	0	0

Table 4-3: Summary of chemical matrix interferents analyzed by IMS and GC/IMS.

Plasmagrams of the 'interferent only' samples collected by IMS analysis were complex due to the multi-component chemical makeup of the interferents. Figure 4-9 shows IMS analysis of Interferent #3. $(H_2O)_nO_2^-$ and $(H_2O)_3Cl^-$ reactant ions rapidly decreased in intensity as the product ions created from Interferent #3 components increased in intensity. $(H_2O)Cl^-$ reactant ions were completely depleted for a brief period

during the analysis. Depletion of reactant ions by an interferent, such as this, could potentially suppress or prevent detection of analyte(s) of interest because no reactant ions would be available to transfer charge to the analyte(s).

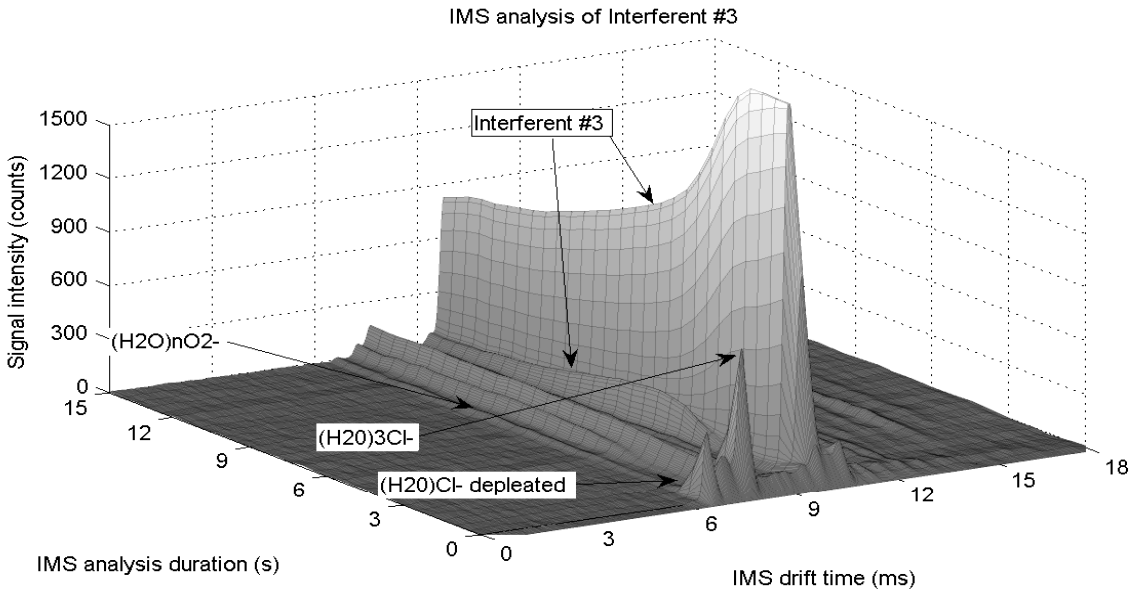


Figure 4-9: IMS analysis of Interferent #3.

Figure 4-10 shows GC/IMS analysis of Interferent #3. The pre-separation provided by the GC segregated the charge tansfer within the IMS ionization region, unlike IMS only analysis. The pre-separation of Interferent #3 components minimized the number of components present at any one time and prevented depletion of the reservoir of reactant ions. The pre-separation of Interferent #3 components can be observed in Figure 4-10 by the distinct analyte peaks in the individual IMS scans, collected from front to back.

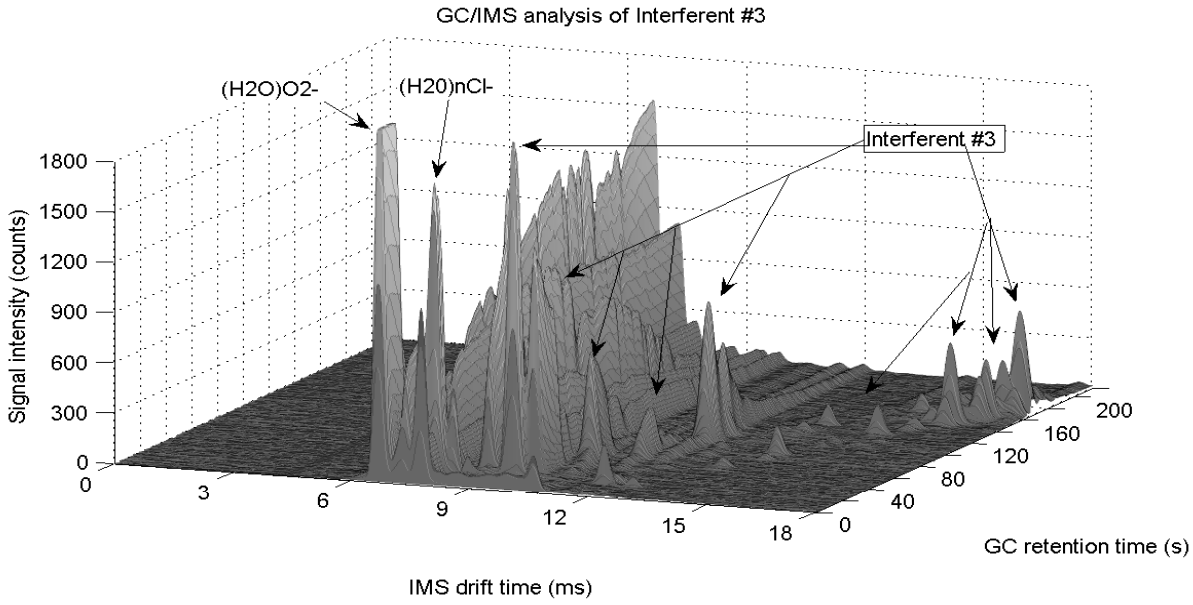


Figure 4-10: GC/IMS analysis of Interferent #3.

Figure 4-11 shows IMS analysis of Interferent #4. $(H_2O)_nO_2^-$ and $(H_2O)_3Cl^-$ reactant ions decreased in intensity as the product ions created from Interferent #4 components increased in intensity. Interferent #4 components remained in the IMS for the duration of analysis. Frequently, the interferents remained in the IMS for the duration of analysis (Figures 4-9 and 4-11). This resulted in carry-over of the interferents into the first instrument blank collected after IMS analysis of an 'interferent only' sample. After intervals, ranging from 30 seconds to 5 minutes, the drift gas was able to purge the interferent from the instrument and the original reactant ion intensity was restored. Subsequent analyses could then be continued. The same phenomenon was observed for Interferents #1 and #2. IMS plasmagrams of Interferents #1 and #2, respectively, are provided in Appendix A.

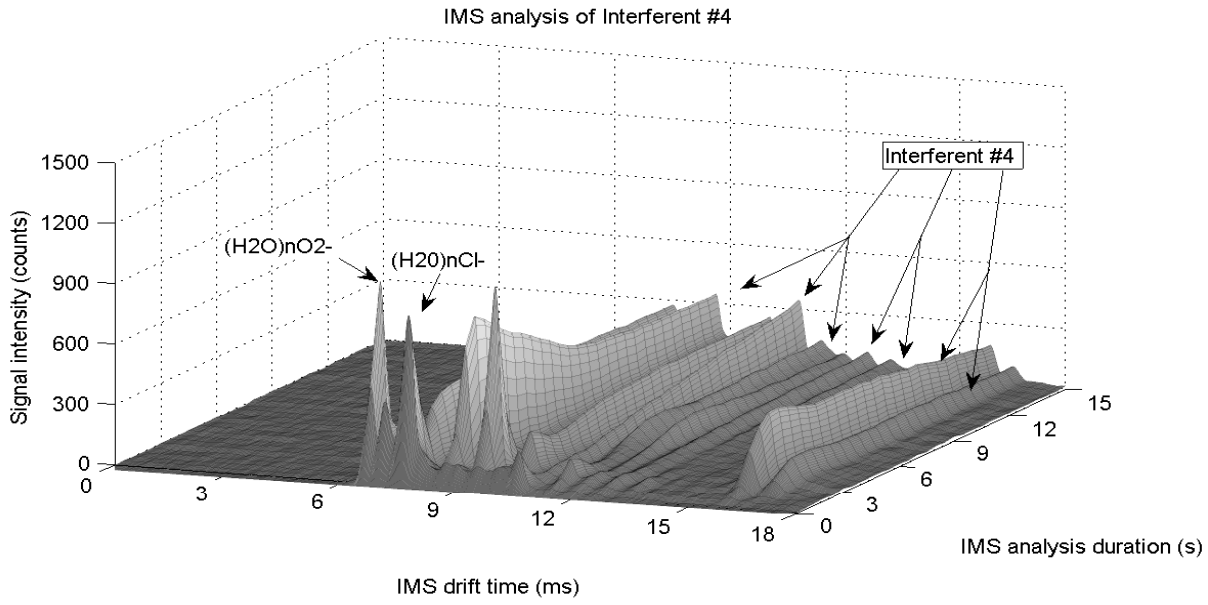


Figure 4-11: IMS analysis of Interferent #4.

Figure 4-12 shows GC/IMS analysis of Interferent #4. The separation of Interferent #4 components can be clearly observed by the separated peaks in the individual IMS scans. Unlike with IMS analysis of Interferent #4 (Figure 4-11), nearly all Interferent #4 components have been purged from the detector by the end of the GC/IMS analysis duration. The reactant ion(s) have also re-intensified as Interferent #4 components passed through the drift region and charge transfer reactions completed. The same phenomenon was observed for Interferents #1 and #2. GC/IMS chromatograms of Interferents #1 and #2, respectively, are provided in Appendix A.

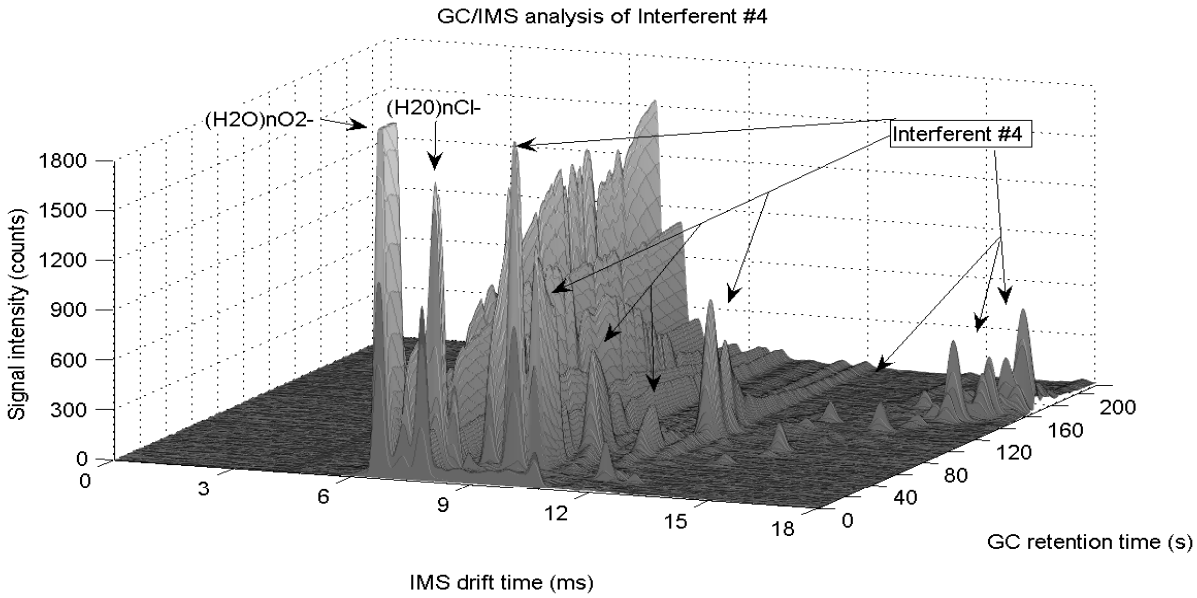


Figure 4-12: GC/IMS analysis of Interferent #4.

GC/IMS analysis of 'interferent only' samples (Figures 4-10 and 4-12) did not produce carry over of the interferents into the first instrument blank collected after GC/IMS analysis of an 'interferent only' sample. Near complete restoration of the baseline and original reactant ion(s) occurs toward the end of the analysis (approximately 3 minutes) and delays in subsequent GC/IMS analysis were not experienced. This is most likely attributed to the preferential sample loop collection properties and GC separation of interferent components, which prevented overload and suppression of the IMS and enabled the drift gas to purge the interferent more rapidly. In addition, the average sample throughput rate for GC/IMS was one sample every 6 minutes 13 seconds for GC/IMS compared to one sample every 21 seconds for IMS. The drift gas was able to purge the interferent during the longer analysis duration of GC/IMS.

An instrument blank was collected before and after each 'interferent only' sample analysis to ensure restoration of the baseline, restoration of the original reactant ion

intensity, and that carry over was not observed. IMS plasmagrams and GC/IMS chromatograms of Interferents #1 and #2, respectively, are provided in Appendix A.

4.6 Interferent and Explosive Compound Mixture Analysis

After evaluating the detection capabilities of IMS and GC/IMS with each of the five explosives and each of the four interferents separately, the effects of detecting the explosives amidst the interferents were evaluated. Teflon® swabs were prepared with the interferents and then spiked with a single explosive compound (at least one order of magnitude higher than the LOD) and subsequently analyzed, as previously described (n=5).

4.6.1 Accuracy (Interferent and Explosive Compound Mixtures)

A false positive is defined as an instrument response, in which the technology alarmed for an explosive compound in the mixture that was not present. A false negative was defined as an instrument response, in which the technology did not alarm for the explosive compound in the mixture. For IMS and GC/IMS to identify a chemical, an analyte peak(s) must conform to the detection algorithm parameters in the instrument. The results are summarized in Table 4-4.

	Interferent	IMS			GC/IMS		
		Correct	**False Positive**	**False Negative**	**Correct**	**False Positive**	**False Negative**
HMTD IMS (10ng) GC/IMS (500ng)	#1	4	-	1	5	-	-
	#2	5	1*	-	5	-	-
	#3	5	3*	-	5	-	-
	#4	0	3**	2	5	-	-
PETN IMS (10ng) GC/IMS (100ng)	#1	5	-	-	4	-	1
	#2	4	1**	-	4	-	1
	#3	2	1**	2	5	-	-
	#4	0	2**	3	5	-	-
RDX IMS (10ng) GC/IMS (10ng)	#1	5	-	-	5	-	-
	#2	5	-	-	4	1**	-
	#3	5	-	-	5	-	-
	#4	5	5*	-	5	-	-
TATP IMS (10ng) GC/IMS (500ng)	#1	5	-	-	5	-	-
	#2	5	-	-	5	-	-
	#3	5	-	-	5	-	-
	#4	5	-	-	1	-	4
TNT IMS (10ng) GC/IMS (10ng)	#1	5	-	-	5	-	-
	#2	5	-	-	0	-	5
	#3	0	2**	3	5	-	-
	#4	2	3*	-	5	-	-
	TOTAL	77 of 100	21	11	88 of 100	1	11

Table 4-4: Summary of IMS vs. GC/IMS analysis of explosive compounds in the presence of interferents. The dry mass of Interferents #1, #2, #3, and #4 deposited on a sample swab was approximately 700µg, 420µg, 500µg, and 450µg, respectively.
***Instrument did alarm for the correct explosive in the sample; however, the instrument also alarmed for an additional explosive compound(s) that was not in the sample.**
****Instrument alarmed for an explosive compound(s) that was not in the sample.**

4.6.1.1 False Positives

IMS analysis yielded 21 false positive alarms in 100 interferent/explosive combination samples. Of the 21 false positives, 12 occurred when the instrument alarmed for the correct explosive in the sample, but also alarmed for an additional explosive compound(s) that was not in the sample. IMS analysis of the multi-component interferent/explosive samples sometimes resulted in incomplete separation of the analytes interferent ion peaks with the same drift time as the explosive compounds programmed in the IMS, which produced false positive alarms. Of the 21 false positives, nine occurred when the instrument did not alarm for the explosive compound in the sample, but for an explosive compound(s) that was not in the sample. The failure to identify the correct explosive compound in four of the nine false positive responses occurred because the detection algorithm criterion for detecting multiple analyte peak(s) was not met. The use of multiple analyte peak(s) detection is a widely used method to improve selectivity and minimize false positives. The detection algorithm is set to search for more than one analyte peak, rather than a single analyte peak; alarming only when multiple analyte peaks are present to reduce false positives. While this can improve accuracy, if the additional analyte peak(s) is not detected (which occurred in these four instances) the instrument will not alarm for the analyte of interest. Collectively, these results highlight the fact that an IMS has limited capabilities when analyzing complex mixtures and tends toward false positive responses.

Using GC/IMS, the number of false positive responses was substantially reduced to one false positive in 100 interferent/explosive combination samples. For this single false positive response, GC/IMS did not alarm for RDX, but for an explosive compound(s) that

was not in the sample. The false positive occurred because the RDX peak amplitude was below the minimum threshold set in the detection algorithm. The response curves previously presented (Figure 4-7) show that GC/IMS produced lower signal response than IMS at nearly all concentrations for all five explosives. Specifically, the mean GC/IMS signal response to 10ng RDX by GC/IMS was 57% lower than the mean IMS signal response. Loss of sample may have occurred at the SPD, in the six-port valve switching, or through the sample loop (i.e. trap). A more efficient transfer of sample vapors into the column and the detector with GC/IMS may improve signal response and further reduce the occurrence of false positives with GC/IMS.

4.6.1.2 False Negatives

IMS analysis resulted in 11 false negative responses in 100 interferent/explosive combination samples. The false negative responses by IMS were triggered by one of four conditions:

1) The instrument was programmed to alarm when the detection algorithm criterion was met for two analyte peaks; however one of the analyte peaks was below the minimum threshold set in the detection algorithm criteria.
2) The analyte peak was not resolved from an interferent component. The analyte peak did not meet the detection algorithm criteria for the peak width at half the maximum amplitude because the analyte peak was too broad.
3) The analyte peak amplitude did not meet the minimum threshold in the detection algorithm criteria.
4) The instrument was programmed to alarm when the analyte peak was present on successive IMS scans; however, the analyte peak was present in only a single IMS scan.

GC/IMS analysis also resulted in 11 false negative responses in 100 interferent/explosive combination samples. The false negative responses by GC/IMS were only triggered by conditions (1) and (2) above.

The effect of peak broadening with GC/IMS may be corrected by improving the oven temperature control using a column design with improved temperature control that may enhance the chromatography (i.e performance). The effect of analyte peaks not meeting the minimum detection threshold with GC/IMS may be corrected by obtaining a more efficient transfer of targeted analytes to the detector by replacing the sample loop with a new sample collection medium (trap) for a more efficient transfer of sample vapors into the column, and/or by replacing the column design for more efficient transfer of sample vapors into the detector.

4.6.2 Instrument Response (Interferents and Explosive Compound Mixtures)

In addition to examining the accuracy (false positive/false negative) of explosive compound detection amidst the interferents, IMS and GC/IMS signal response for the pure explosive compounds was compared to signal response for the explosive compounds with each interferent. The maximum peak amplitude was used for comparison. Figure 4-13 summarizes the results. The solid line at 100% represents the normalized signal response of IMS or GC/IMS with the pure explosive compounds. The shaded areas represent ± one standard deviation from the normalized signal response of IMS and GC/IMS with the pure explosive compounds. A suppressed response of an explosive compound amidst an interferent was defined as mean signal response that was more than one standard deviation from the normalized signal response of the pure explosive compound. False positive (fp) and false negative (fn) responses are annotated on Figure 4-13.

The interferents used in this study had suppressing effects on IMS signal response to the explosive compounds in the presence of the interferents in 8 of the 20 tests. The suppression of the IMS signal response was due to the inability of IMS to separate the complex multi-component interferent/explosive combination samples. This effect was practically eliminated with GC/IMS, in which signal response to the explosive compounds in the presence of the interferents was suppressed in 1 of the 20 tests. A rigorous analysis of chemical matrix interferents and the ions they produce in IMS was not within the scope of this research.

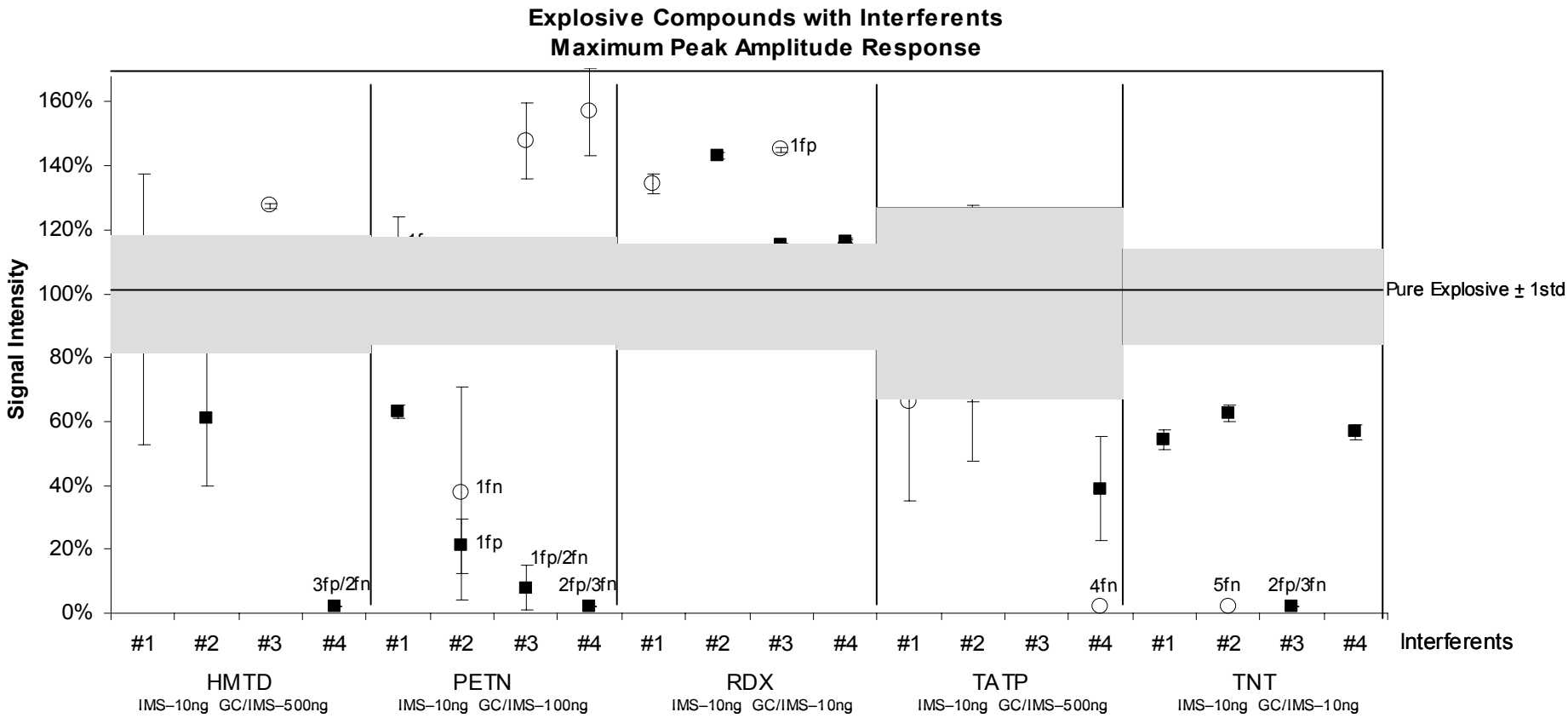


Figure 4-13: Effect of chemical matrix interferents on HMTD, PETN, RDX, TATP, and TNT analysis. ■ IMS ○ GC/IMS. The solid line represents the normalized signal response of a pure explosive compound with IMS and GC/IMS. The shaded area represents ± one standard deviation from the normalized signal response of pure explosive compound with IMS and GC/IMS. fn = false negative fp = false positive

4.6.2.1 Hexamethylene triperoxide diamine (HMTD)

IMS signal response to HMTD with Interferents #1 and #3 was within one standard deviation of the signal response to pure HMTD. IMS signal response to HMTD with Interferent #2 was suppressed by 39%. IMS did not correctly identify HMTD in the presence of Interferent #4 (2 false positives and 3 false negatives).

GC/IMS signal response to HMTD with Interferents #1, #2, and #4 was within one standard deviation of the signal response to HMTD. Interestingly, GC/IMS signal response to HMTD with Interferent #3 was enhanced beyond one standard deviation of the pure HMTD response. It is possible that the interferent ion chemistry proved favorable for HMTD-chloride cluster $(HMTD+Cl)^-$ ion formation, resulting in increased amplitude of $(HMTD+Cl)^-$ peaks. When more nitrates are in a sample, lower intensity $(HMTD+Cl)^-$ peaks can be observed. Delineation of this effect is beyond the scope of this research; however, it is important to notice that the GC/IMS data yielded better signal response in all cases for HMTD in the presence of the interferents than IMS alone.

4.6.2.2 Pentaerythritol tetranitrate (PETN)

All four interferents suppressed IMS signal response to PETN. IMS did not correctly identify PETN in the presence of Interferent #4 (2 false positives and 3 false negatives). GC/IMS signal response to PETN was not suppressed by Interferents #1, #3 and #4 and GC/IMS signal response to PETN with Interferent #1 was within one standard deviation of pure PETN. GC/IMS signal response to PETN with Interferents #3 and #4 was enhanced. As with the HMTD samples, it is possible that the interferent ion chemistry also proved favorable for $(PETN+Cl)^-$ formation, resulting in increased

amplitude of $(PETN + Cl)^-$ peaks. When more nitrates are in a sample, lower intensity $(PETN + Cl)^-$ peaks can be observed. Delineation of this effect is beyond the scope of this research. While GC/IMS signal response to PETN with Interferent #2 was suppressed, it is important to notice that the GC/IMS data yielded a better signal response in all cases for PETN than IMS alone.

4.6.2.3 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX)

Neither IMS nor GC/IMS signal response to RDX was suppressed by the four interferents. IMS signal response to RDX with Interferents #1, #3, and #4 was within one standard deviation of pure RDX. GC/IMS signal response to RDX with Interferents #1, #2, and #4 was within one standard deviation of pure RDX. IMS signal response to RDX with Interferent #2 and GC/IMS signal response to RDX with Interferent #3 were enhanced beyond one standard deviation of pure RDX. The enhanced signal response may be due to the phenomena observed with HMTD and PETN in which ion chemistry proved favorable for RDX chloride adduct formation, resulting in increased amplitude of $(RDX+Cl)^-$ peaks.

4.6.2.4 Triacetone triperoxide (TATP)

IMS signal response to TATP with Interferents #1, #2, and #3 was within one standard deviation of the signal response to pure TATP. IMS signal response to TATP with Interferent #4 was suppressed by 61%. GC/IMS signal response to TATP with Interferents #1, #2, and #3 was within one standard deviation of the signal response to pure TATP. GC/IMS signal response to TATP with Interferent #4 resulted in four false negatives because the peak amplitude was below the minimum detection threshold.

4.6.2.5 2,4,6 Trinitrotoluene (2,4,6 TNT)

IMS signal response to TNT was suppressed by all four interferents. IMS signal response to TNT with Interferent #3 resulted in two false positive and three false negative responses. GC/IMS signal response to TNT with Interferents #1, #3, and #4 was within one standard deviation of pure TNT. GC/IMS did not detect TNT in the presence of Interferent #2 because the drift time shifted outside of the 45 μs window in the detection algorithm.

The following IMS plasmagrams and GC/IMS chromatograms from analysis of pure TNT and TNT with Interferent #1 are included, in Figure 4-14, to illustrate the reduced signal intensity of an explosive compound caused by an interferent:

(a) IMS analysis of 10ng TNT
(b) IMS analysis of 10ng TNT with ~ 700μg Interferent #1
(c) GC/IMS analysis of 10ng TNT
(d) GC/IMS analysis of 10ng TNT with ~ 700μg Interferent #1

IMS analysis of 10ng TNT (Figure 4-14a) shows that TNT ($(TNT-H)^-$) was detected at 12.637ms throughout the analysis duration. The maximum peak amplitude recorded in this sample was 878 counts at one second after sample introduction. IMS analysis of 10ng TNT sample with Interferent #1 (Figure 4-14b) shows that TNT was also detected at a similar drift time (12.711ms). Three distinct analyte peaks from Interferent #1 components can be observed in Figure 4-14b. The competitive distribution of charge, due to the presence of Interferent #1 components resulted in a suppression of signal response to TNT. The maximum peak amplitude recorded in this sample, at one second into the analysis duration, was 606 counts versus 878 counts with no interferent. This corresponds to a 31% drop in signal intensity for the TNT in this sample. The mean

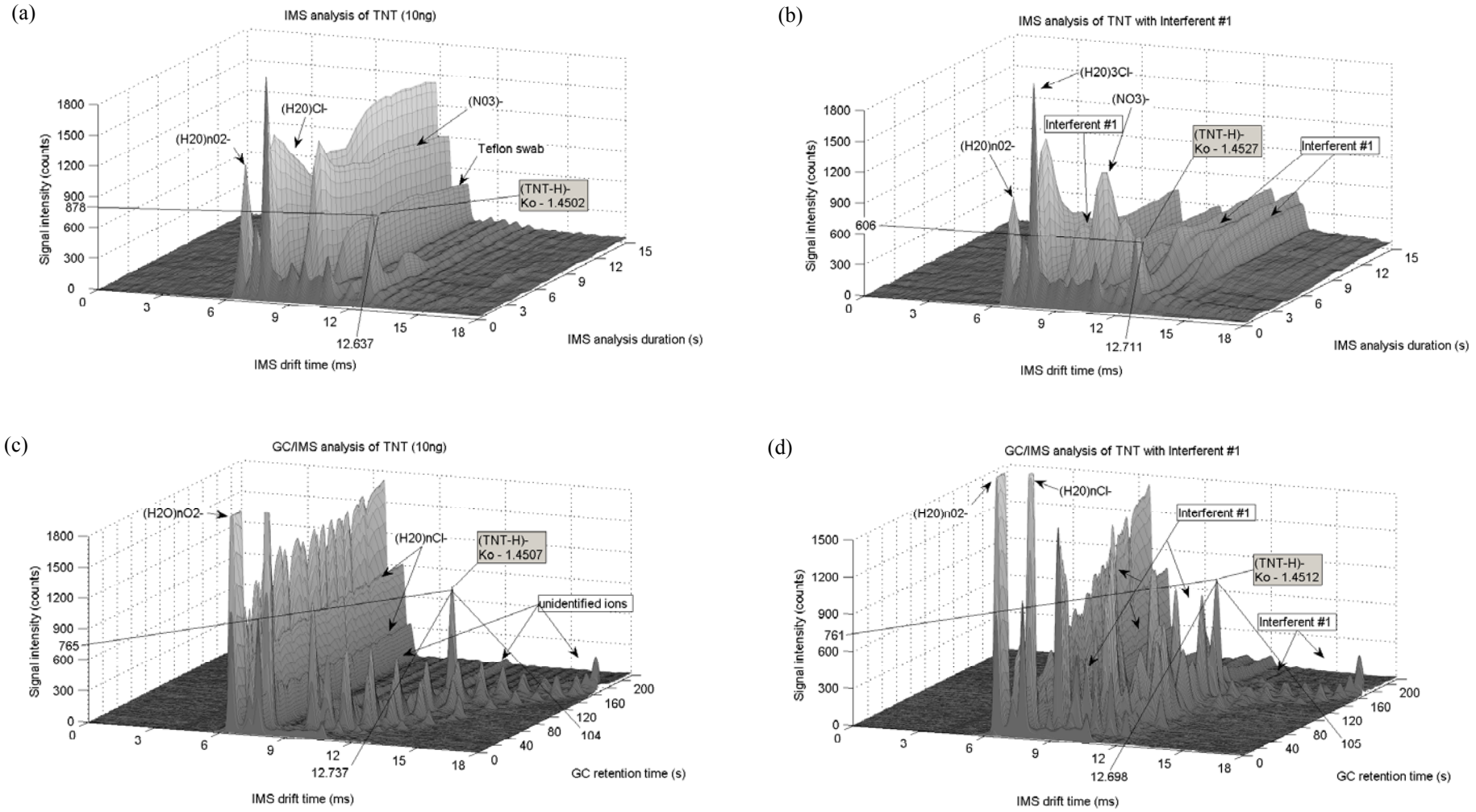


Figure 4-14: IMS plasmagrams and GC/IMS chromatograms of pure TNT and TNT with Interferent #1

drop in signal intensity (n=5) for TNT with Interferent #1 versus pure TNT was 46%, which was beyond one standard deviation of signal response to pure TNT.

The GC/IMS chromatogram of analysis of 10ng TNT (Figure 4-14c) shows the 3-dimensional analysis of GC retention time and IMS drift time plotted against signal intensity. The TNT peak is more clearly observed at 104 sec GC retention time and 12.737ms IMS drift time. The maximum peak amplitude recorded for TNT in this sample was 765 counts. GC/IMS signal response was consistently less than the IMS signal response for all five explosives, which is likely due to loss of analyte at connection points with the six-port valve, sample loop, column, and transfer lines. Additional peaks, of little analytical interest can also be observed in the GC/IMS chromatogram.

GC/IMS analysis of 10ng TNT with Interferent #1 (Figure 4-14d) shows that TNT was detected at a similar retention time (105s) and drift time (12.698ms) as 10ng TNT without Interferent #1(Figure 4-14c) by GC/IMS analysis. The introduction of column effluent into the IMS spread the competitive distribution of charge into the individual IMS scans. Many separate analyte peaks, resulting from Interferent #1 components, were measured between 7 and 15 ms during the first 110 seconds of analysis. This is unlike IMS analysis of TNT with Interferent #1 (Figure 4-14b) in which three distinct analyte peaks were observed for the duration of analysis. The maximum peak amplitude recorded for TNT with Interferent #1 by GC/IMS (Figure 4-14d) in this sample was 761 counts while the maximum peak amplitude recorded in the sample for TNT with no interferent (Figure 4-14c) was 765 counts. This corresponds to less than 1% drop in signal intensity by GC/IMS for the TNT in the sample, unlike IMS only analysis which resulted in a 46% drop in signal intensity (Figure 4-14b). The mean drop in signal

intensity (n=5) with GC/IMS for TNT with Interferent #1 versus pure TNT was 13%, which was with in one standard deviation of signal response to TNT with no interferent.

IMS plasmagrams and GC/IMS chromatograms of HMTD, PETN, RDX, TATP and TNT with Interferents #1, #2, #3, and #4 are provided in Appendix B.

4.6.3 Precision (Interferents and Explosive Compound Mixtures)

After collecting and comparing the precision of IMS and GC/IMS with pure explosive compounds, analysis was conducted to compare the precision (reproducibility) of IMS and GC/IMS analysis of the explosive compounds amidst the interferents by examining the results of five replicate samples. RSDs (mean peak amplitudes divided by the standard deviation) were used to assess the precision of the analysis by IMS and GC/IMS. The RSDs are shown in Table 4-5 and Figure 4-15. The majority (28 of 39) of the RSDs were below 30% and very similar to the RSDs observed for the explosive compounds without interferents (see Table 4-2). No distinguishing differences between IMS and GC/IMS RSDs were observed. No studies are available in the published literature on the reproducibility of IMS and GC/IMS measurements of explosive compounds amidst interferents.

Interferent	HMTD		PETN		RDX		TATP		TNT	
	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS
None	32	16	19	37	16	12	31	21	13	14
#1	*(1fn)	21	16	*(1fn)	18	17	15	35	30	12
#2	31	4	*(1fp)	*(1fn)	13	*(1fp)	43	35	26	*(5fn)
#3	15	5	*(1fp/2fn)	34	7	4	25	15	*(2fp/3fn)	13
#4	*(3fp/2fn)	15	*(2fp/3fn)	39	6	13	33	*(4fn)	24	12

Table 4-5: Precision of five replicate chemical matrix interferent/explosive samples as percent (%) RSD. *RSDs were not calculated due to false positive and/or false negative instrument response. fp = false positive fn = false negative

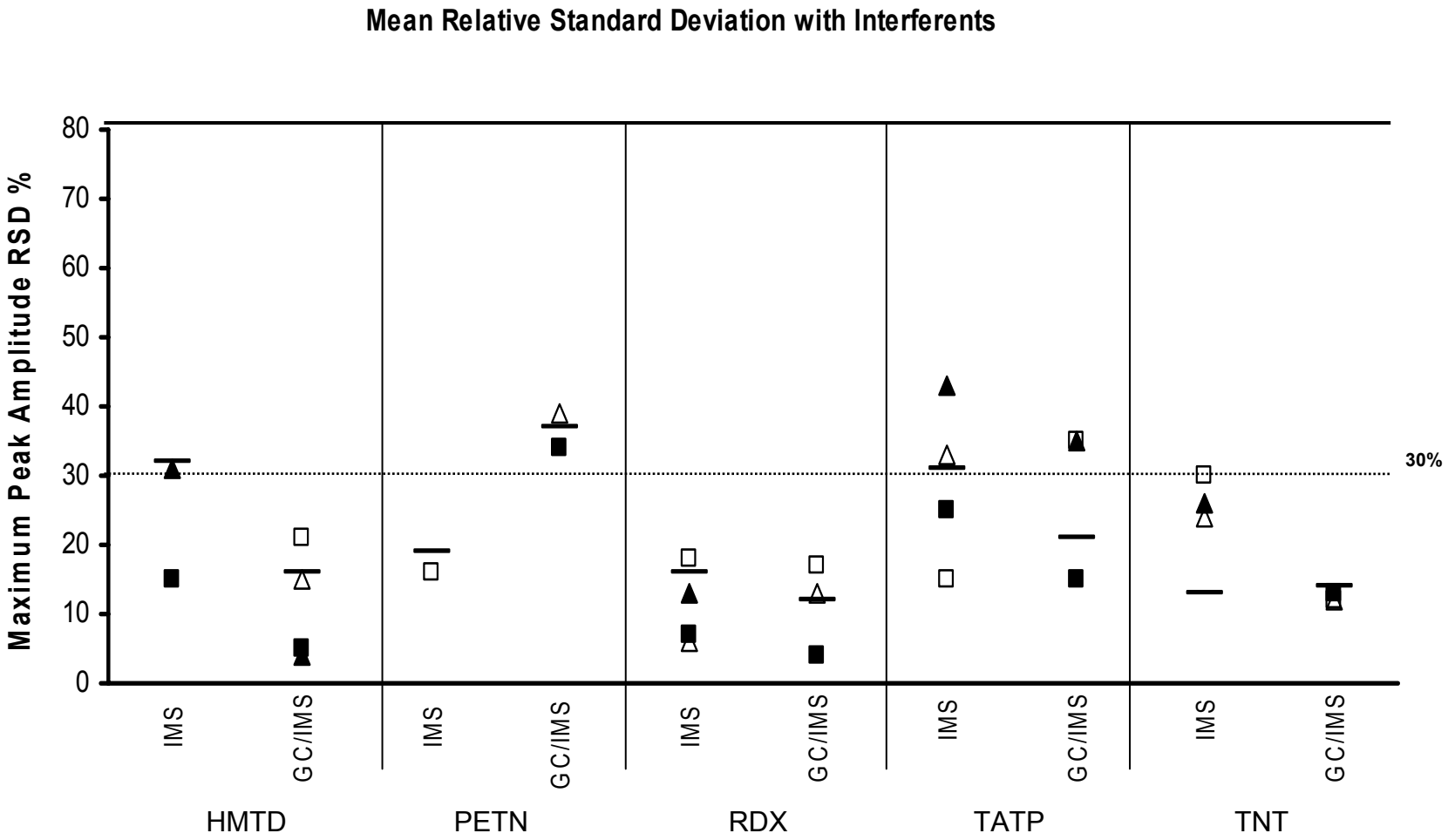


Figure 4-15: Precision of five replicate interferent/explosive combination samples as percent RSD. RSDs were not calculated in cases where false positive/false negative instrument response was observed. ─ pure explosive □ Interferent #1 ▲ Interferent #2 ■ Interferent #3 △ Interferent #4.

5 Discussion and Conclusions

The primary objective of this research was to determine if GC/IMS would improve upon a current chemical detection method, IMS, being used in the field for explosive compound analysis. The performance characteristics of the IMS and GC/IMS operational modes of the GC-IONSCAN® were evaluated to determine the sample throughput rate, limit of detection (LOD), upper saturation limit, precision, and accuracy. Five explosive compounds (HMTD, PETN, RDX, TATP, and TNT) were used. In addition, the capability to discern (accuracy and precision) the explosive compounds amidst four chemical matrix interferents was evaluated.

IMS is a proven technology for field portable detection of vapor phase explosive compounds due to its high sensitivity and rapid analysis. The average throughput for IMS analysis of pure explosive compounds was one sample every 21 seconds; while as expected, the GC/IMS average throughput of pure explosive compounds was much longer with one sample analysis every 6 minutes 13 seconds. However, IMS analysis of 'interferent only' and interferent/explosive combination samples resulted in slower throughput, with times ranging from 30 seconds to 5 minutes due to overload and suppression of the reactant ion population. Analysis times of 'interferent only' and interferent/explosive combination samples by GC/IMS did not result in a lengthier throughput. LODs for the five explosive compounds showed IMS was more sensitive than GC/IMS for HMTD, PETN and TATP most likely due to sample losses throughout connection points in the GC/IMS system. While GC/IMS was expected to have increased the upper limit of the saturation concentration, the data was inconclusive. IMS and GC/IMS appeared to have reached saturation at the same concentration (100ng) with

RDX; GC/IMS appeared to have reached saturation at 100ng with TNT, while IMS response appeared to have not reached saturation; the limits of saturation for HMTD, PETN, and TATP were inconclusive.

The inferior resolution capability of IMS resulted in a statistically significant ($p=0.012$) number of false positive responses (7 out of 40) when tested against 'interferent only' samples while GC/IMS analysis resulted in zero false positive responses in 40 interferent samples. When attempting to discern explosive compounds in the presence of the interferents, IMS analysis yielded 21 false positive responses in 100 interferent/explosive combination samples. GC/IMS analysis yielded 1 false positive response in 100 interferent/explosive combination samples. Furthermore, IMS experienced greater suppression of signal response to the explosive compounds amidst the interferents than GC/IMS. The interferents suppressed the IMS signal response to the explosive compounds in 8 of 20 tests. This effect was practically eliminated with GC/IMS, in which signal response to the explosive compounds amidst the interferents was suppressed in 1 of 20 tests. Incomplete separation and obscure analyte peaks lead to inaccurate detection and identification by IMS resulting in more false positive responses.

The combination of GC to IMS shows the potential to overcome the difficulties IMS encounters when attempting to identify individual components in a mixture by separating the components before detection. While the limit of detection for HMTD, PETN and TATP was higher with GC/IMS than IMS, the differences were modest. Assessment of precision (reproducibility) to explosive compound response, using relative standard deviation (RSD), revealed RSDs for TNT by GC/IMS were significantly lower than IMS ($p=0.043$). Differences in RSDs for RDX, HMTD, PETN, and TATP were

negligible. GC/IMS consistently had less signal intensity to the explosive compounds than IMS; however, the coupling of GC to IMS showed reduced false positive results for 'interferent only' samples and was more accurate at identifying explosive compounds in the presence of interferents through improved resolution of chemical species. GC/IMS produced no false positives with 'interferent only' samples. Analysis of explosive compounds in the presence of the interferents showed GC/IMS produced fewer false positive (1 versus 21) than IMS. The most significant limitation observed with the GC/IMS throughput rate was the lengthy cooling rate of the air circulation oven. Three approaches to improve GC/IMS response may be considered: (1) replace the sample loop with an improved sample collection medium (trap) for a more efficient collection of sample vapors or (2) characterize and improve the transfer efficiency of sample vapors to the column or (3) replace the air circulation heated column with a resistively heated column with improved temperature programming rates that may allow for improved chromatography and more efficient transfer of sample vapors into the IMS source.

5.1 Applications

The combined technologies of GC and IMS should be seen as a step in improving the complex problem of reducing false positives where many non-targeted substances, create complex matrixes and interfere with IMS analysis. GC/IMS technology could potentially be used in explosive compound search operations of airport passengers and baggage, forms of transportation, structures, or improvised explosive devices (IED) for confirmation of 'IMS only' positive responses, if the speed of response can be improved. The average cooling time of the air circulation oven from 200°C to 100°C was 1 minute

51 seconds (n=10). Alternatively, 5m resistively heated column designs have been shown to cool from 350°C to 40°C in less than 60 seconds.[66] This translates to an approximate 50 fold decrease in cooling time via a resistively heated column design.[99]

5.2 Study Limitations

1. IMS instruments are not capable of identifying unknown chemical compounds with confirmatory confidence: Even with the additional step of differentiating chemical compounds using a GC column prior to obtaining ion drift time information, a GC/IMS does not provide unequivocal analyte identification.

2. False alarm rate: The detection probability and false alarm rate of a detector can only realistically be determined in an operational setting. Only four interferents were tested in this study. Additional complex matrices and actual field data should be studied.

3. Sample interferent collection technique: The collection of wipe samples can be prone to human error and is user dependent. For example, in the collection of Interferent #3 and #4 samples, the area wiped, pressure used, and amount of sampling media actually contacting the sampling surface factored into the final response.

4. Actual concentrations: The evaluation of false positive and false negative results can be influenced by the actual concentration of the interferents.

5. Environmental conditions: The precision may not be reflective of field situations because temperature influences IMS and all samples were collected within carefully controlled laboratory conditions.

5.3 Additional Research

Follow-on research in this area should include:

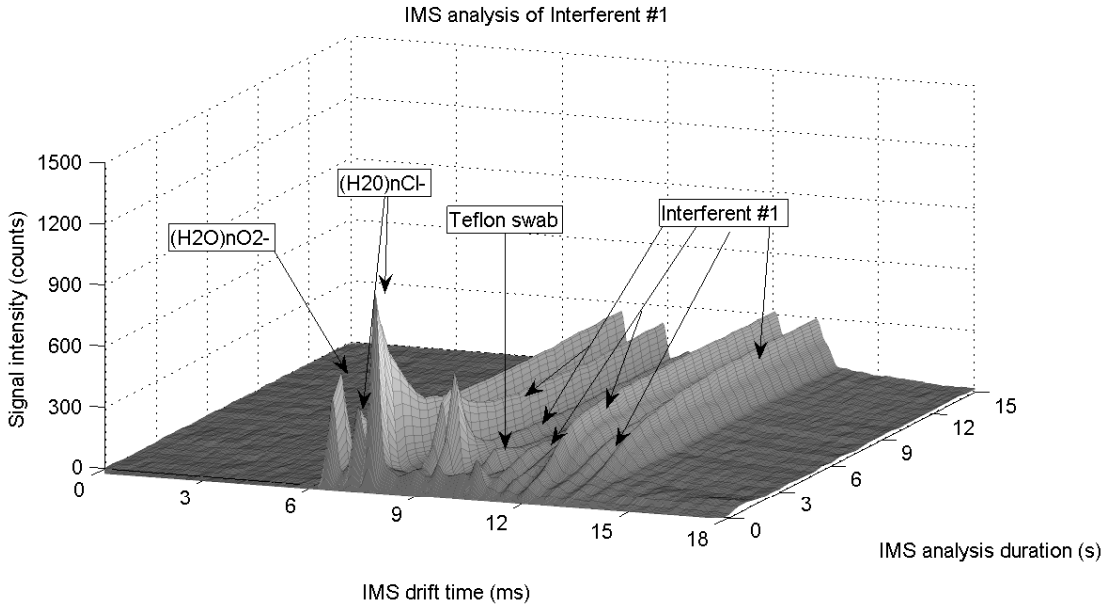
1. Sensitivity of GC/IMS: While the GC/IMS tested in this study had good selectivity and good dynamic range, the sensitivity was less than 'IMS only'. Test an improved sample collection medium (trap) for a more efficient collection and transfer of sample vapors into the column.

2. Fast GC/IMS: Develop and test a GC/IMS instrument that will employ a low thermal mass GC column to permit rapid pre-separation of complex sample mixtures to improve upon the capabilities to distinctly identify analytes of interest and further reduce the number of false positive results currently experienced in the field with IMS.

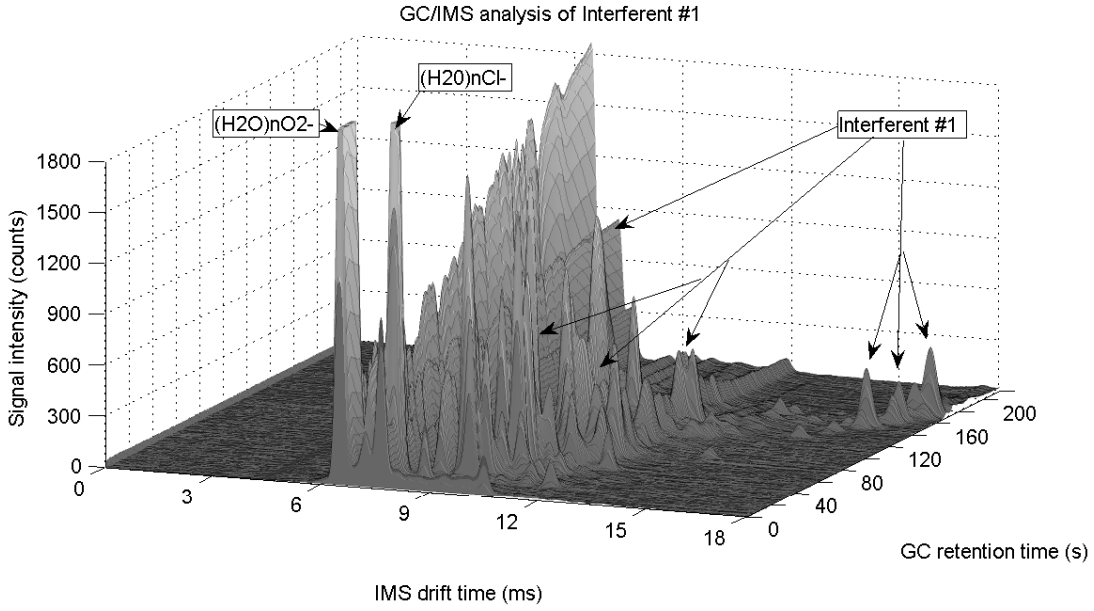
3. GC/MS Analysis of Interferents: This study used common consumer products for interferents. GC/MS analysis may help determine the individual components that quenched the various explosives tested during IMS analysis.

Appendix A

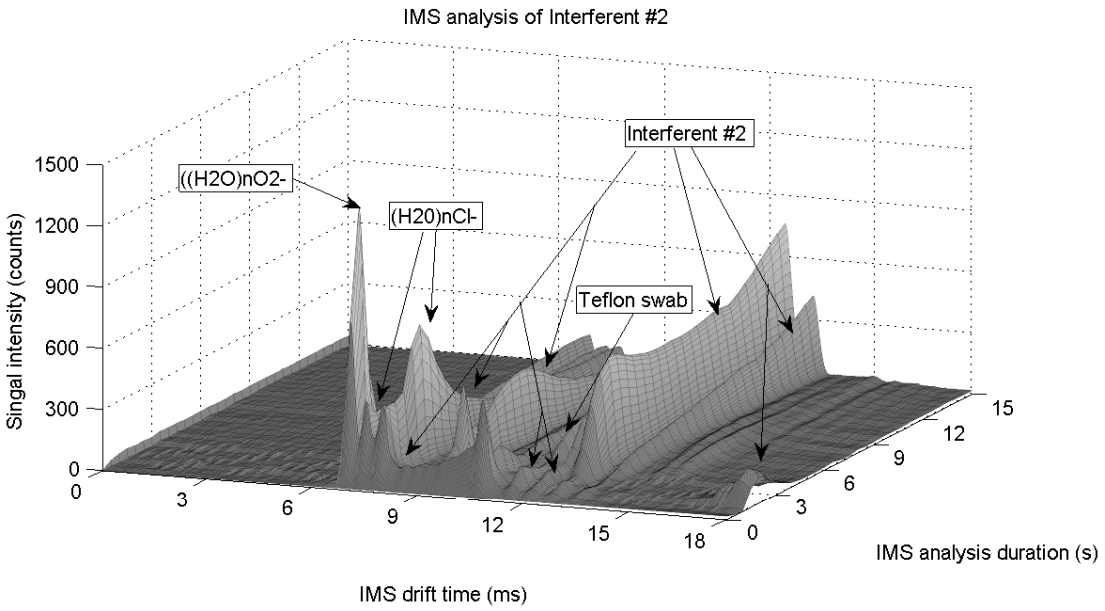
IMS analysis of Interferent #1



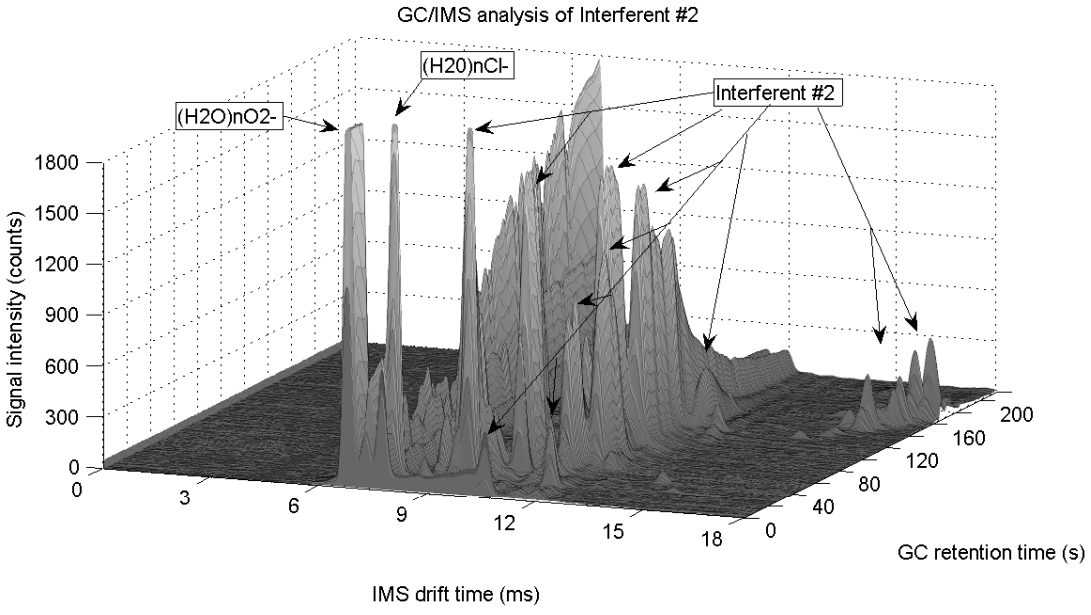
GC/IMS analysis of Interferent #1



IMS analysis of Interferent #2



GC/IMS analysis of Interferent #2



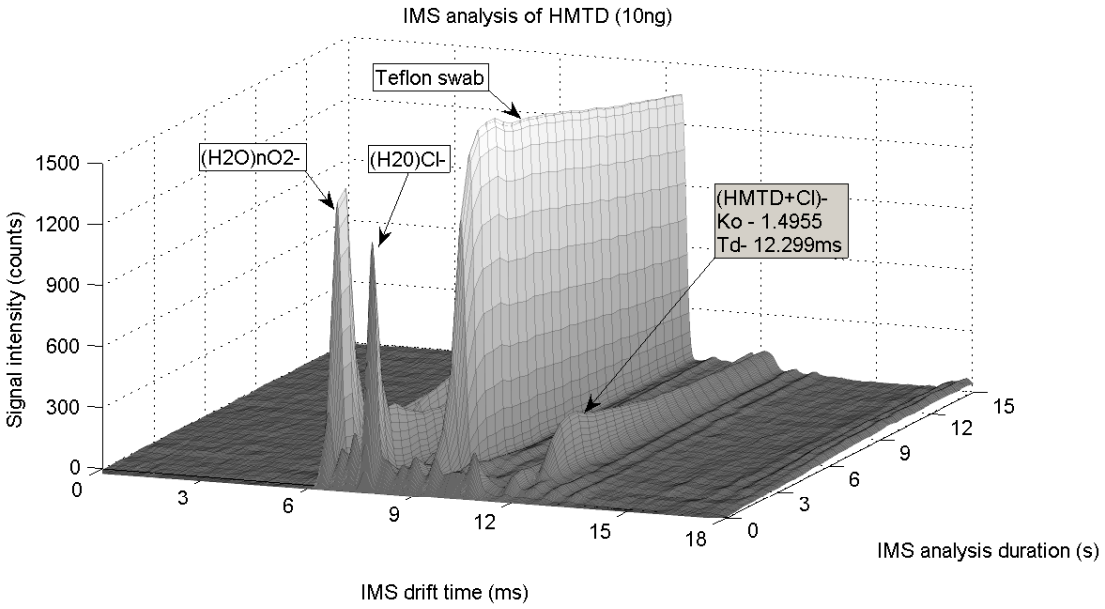
Appendix B

The following IMS plasmagrams and GC/IMS chromatograms of the five explosive compounds with the four interferents are included to further demonstrate the suppression effects.

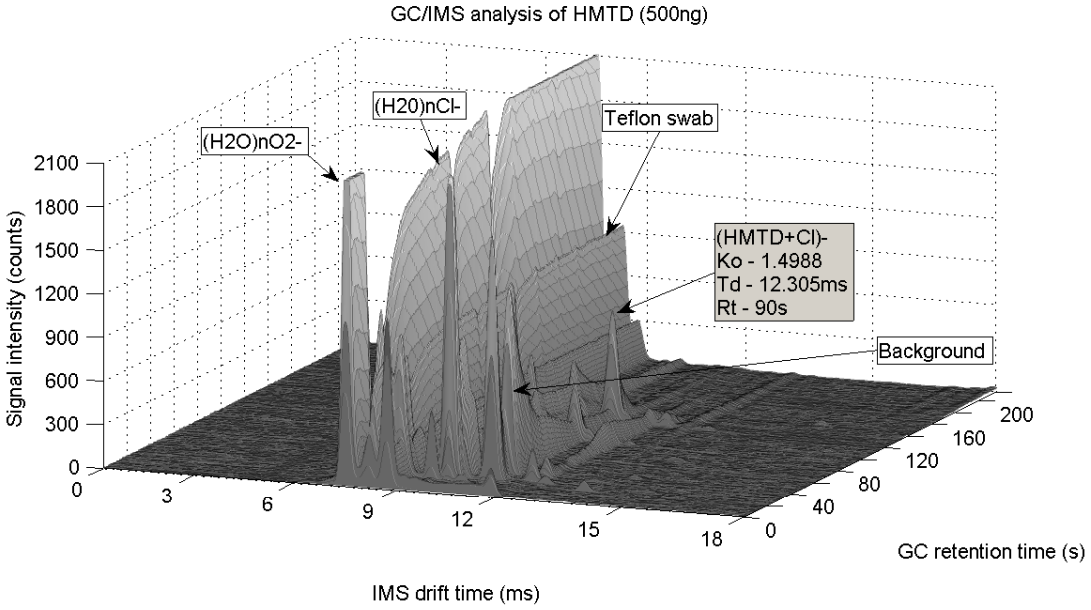
Interferent	HMTD		PETN		RDX		TATP		TNT	
	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS	IMS	GC/IMS
No Interferent	A	B	K	L	U	V	EE	FF	OO	PP
#1	C	D	M	N	W	X	GG	HH	QQ	RR
#2	E	F	O	P	Y	Z	II	JJ	SS	TT
#3	G	H	Q	R	AA	BB	KK	LL	UU	VV
#4	I	J	S	T	CC	DD	MM	NN	WW	XX

Table B-1: Reference for IMS plasmagrams and GC/IMS chromatograms.

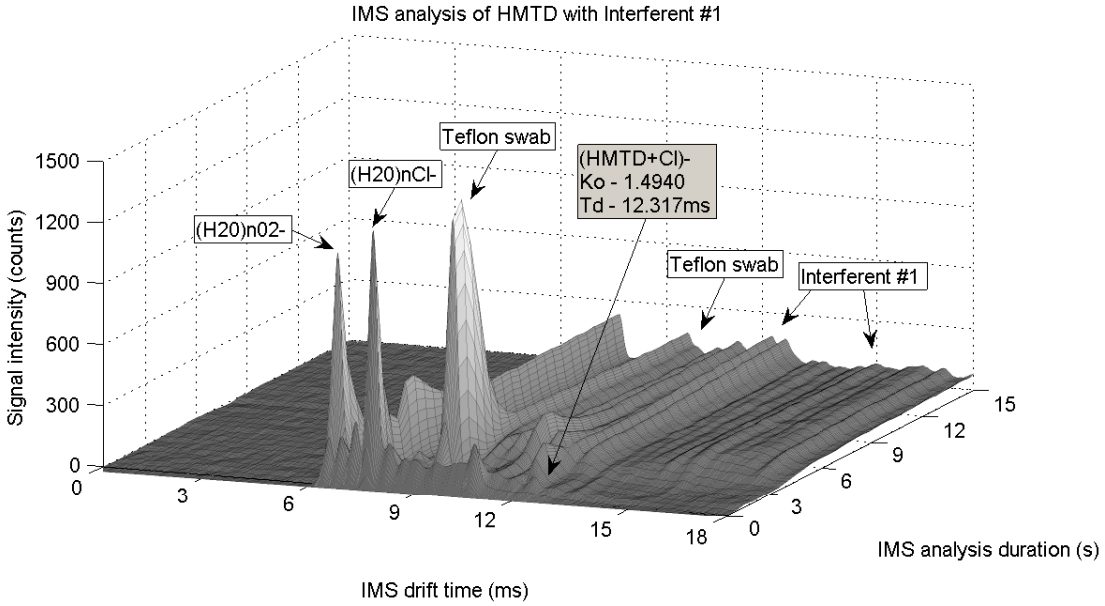
(A) IMS analysis of HMTD



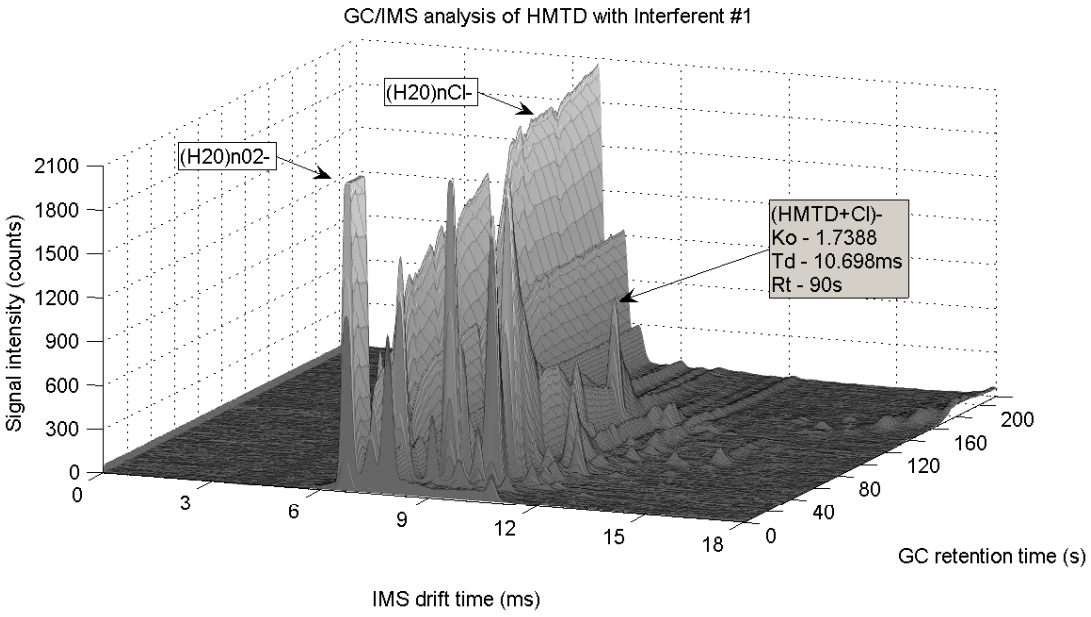
(B) GC/IMS analysis of HMTD



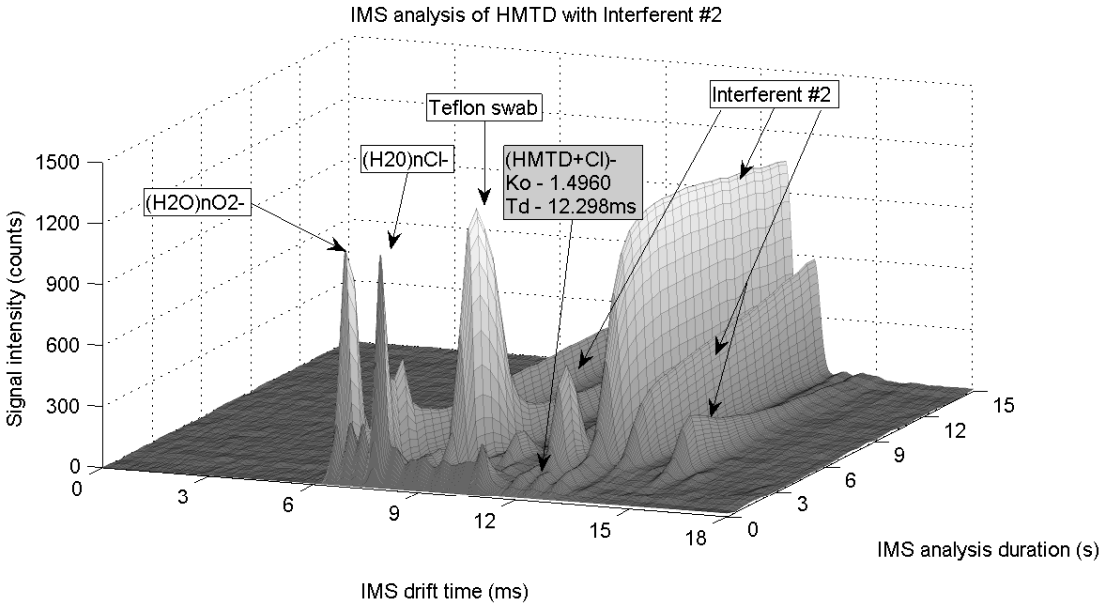
(C) IMS analysis of HMTD with Interferent #1



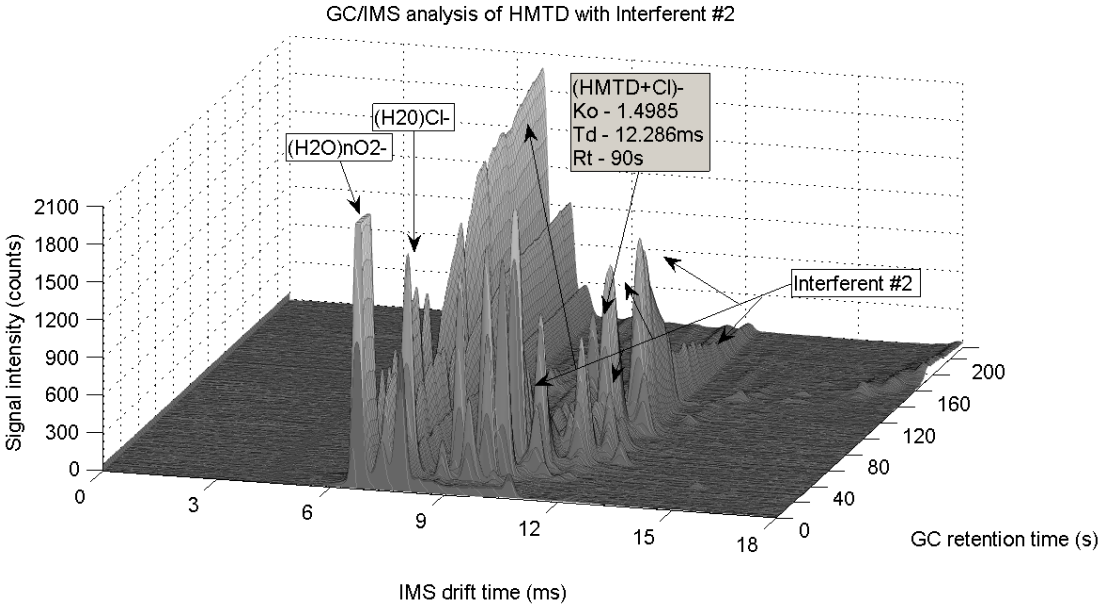
(D) GC/IMS analysis of HMTD with Interferent #1



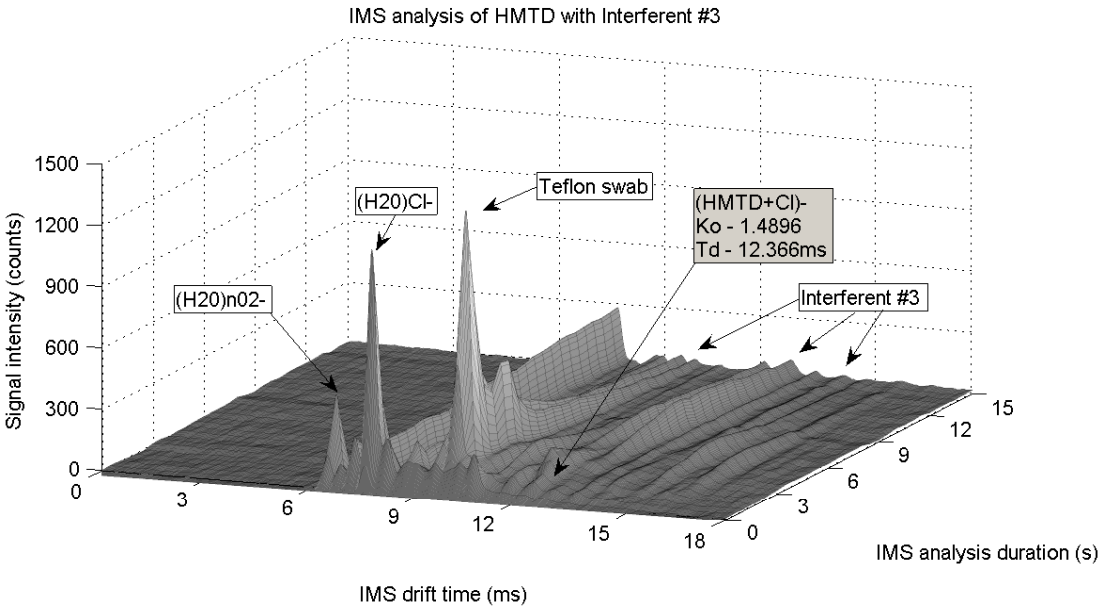
(E) IMS analysis of HMTD with Interferent #2



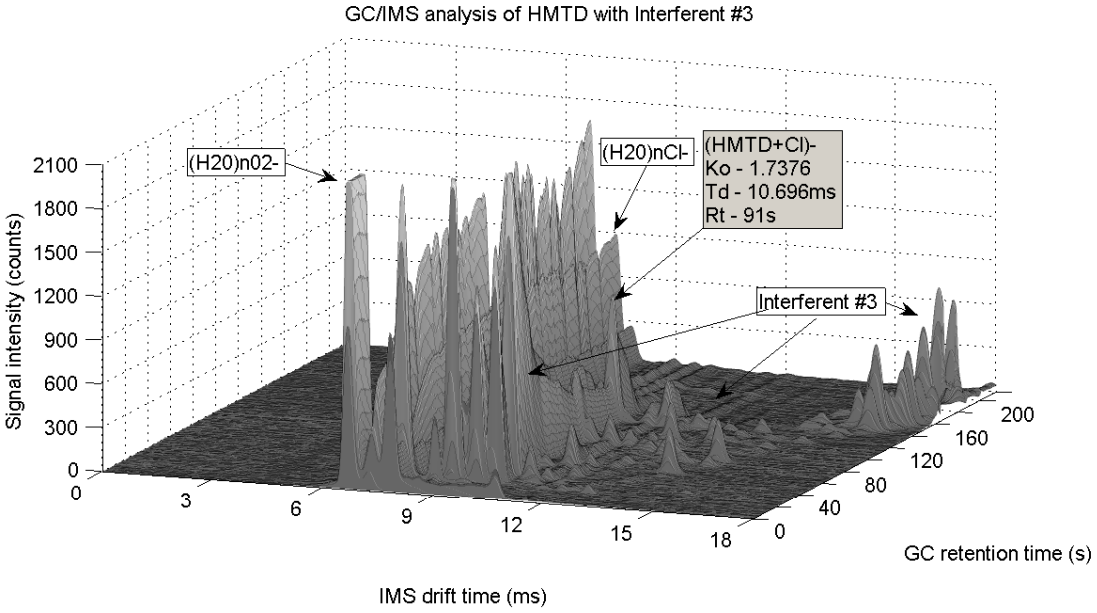
(F) GC/IMS analysis of HMTD with Interferent #2



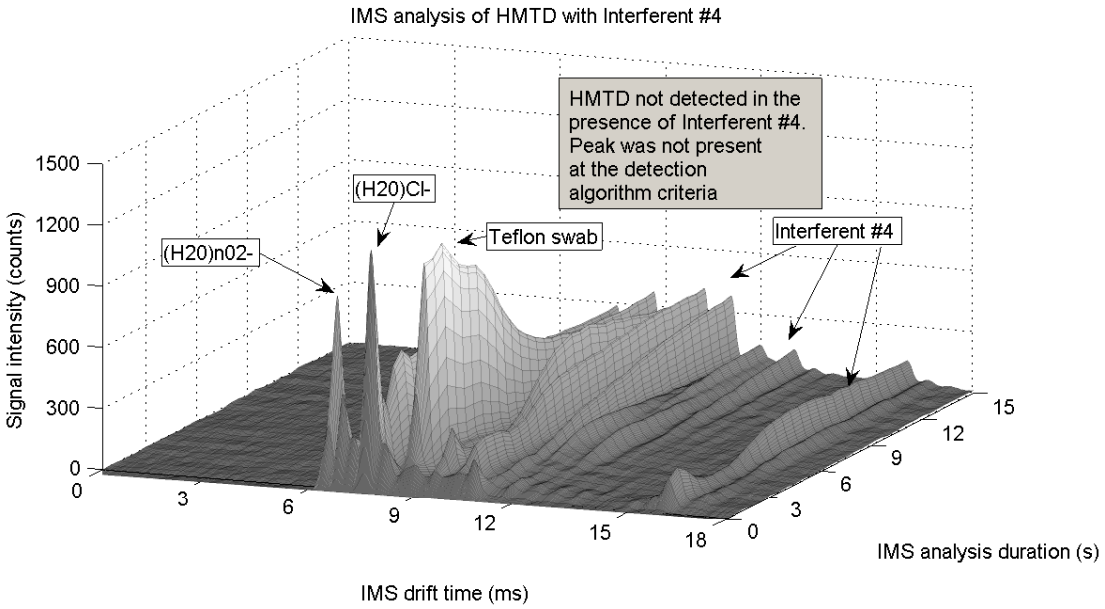
(G) IMS analysis of HMTD with Interferent #3



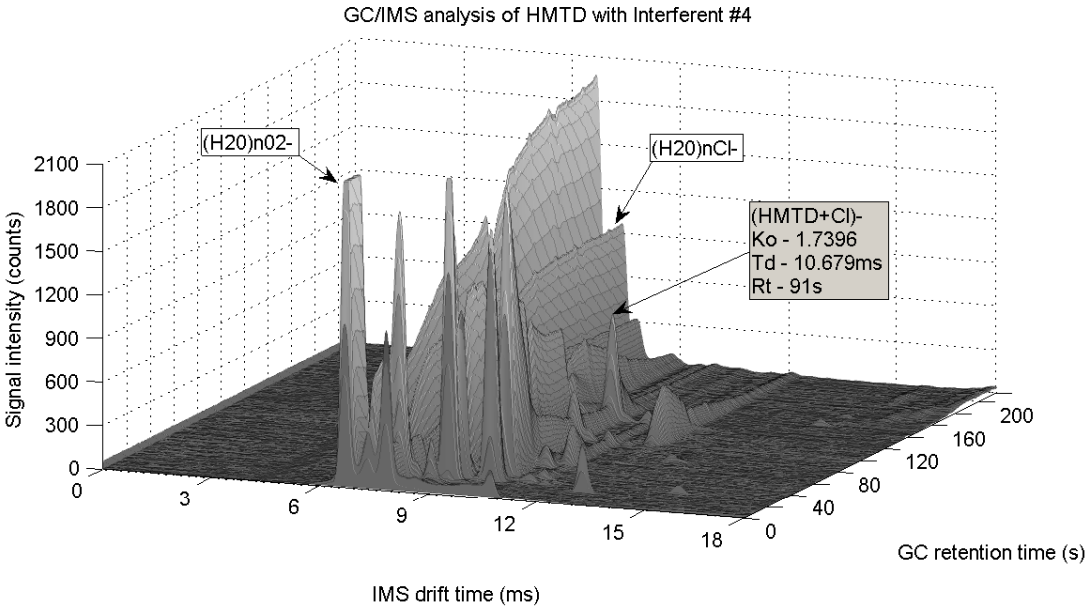
(H) GC/IMS analysis of HMTD with Interferent #3



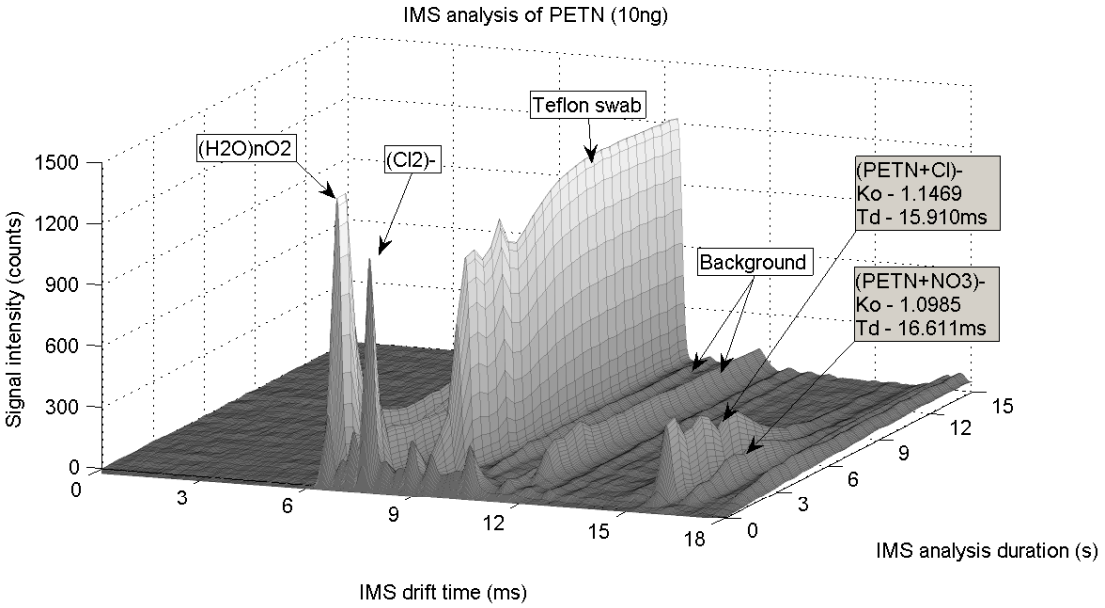
(I) IMS analysis of HMTD with Interferent #4



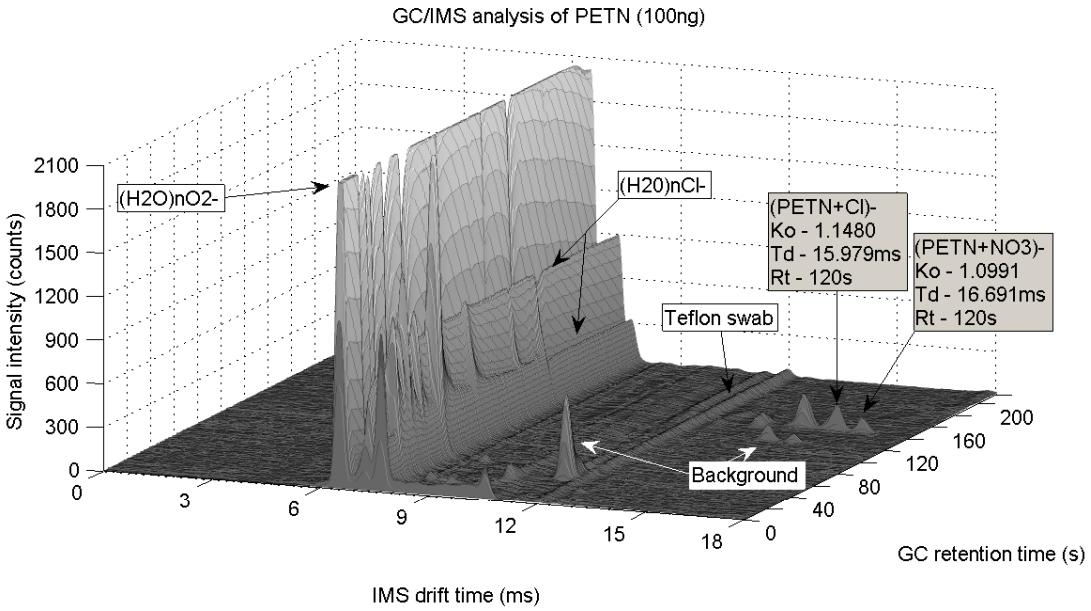
(J) GC/IMS analysis of HMTD with Interferent #4



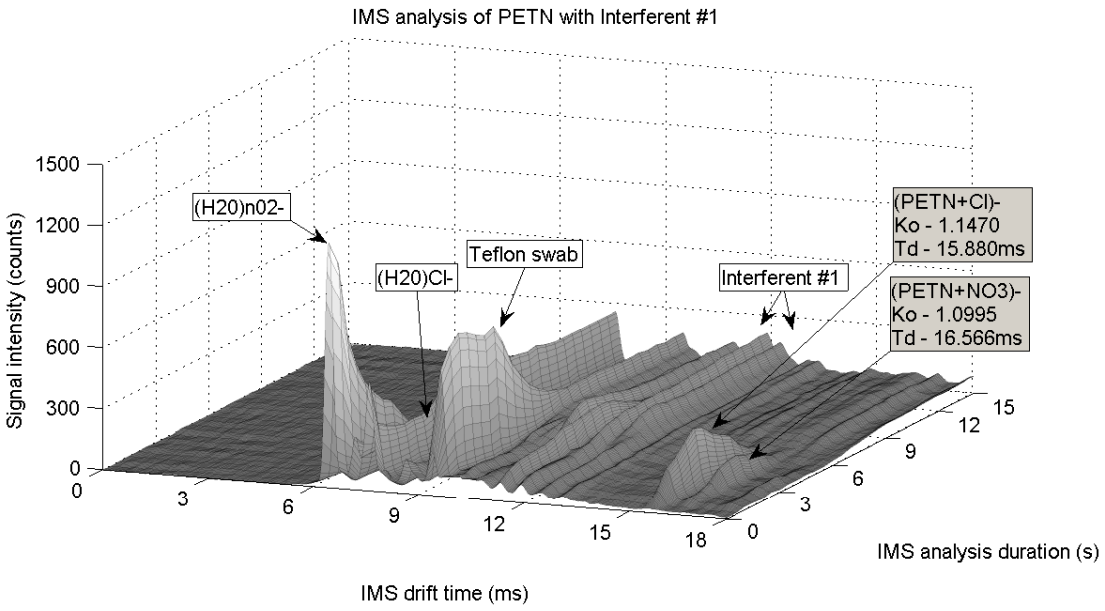
(K) IMS analysis of PETN



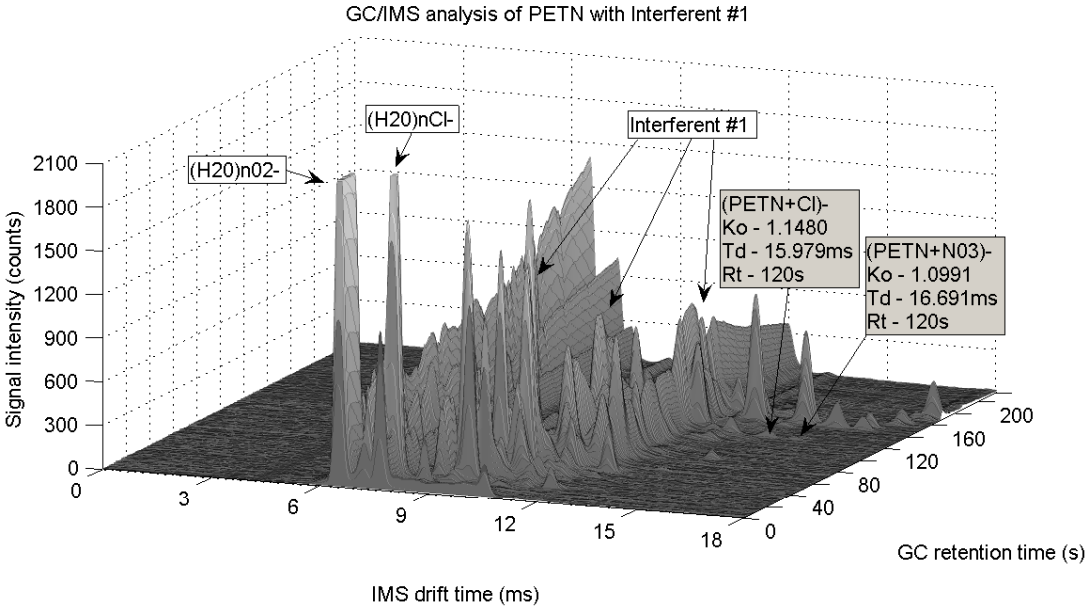
(L) GC/IMS analysis of PETN



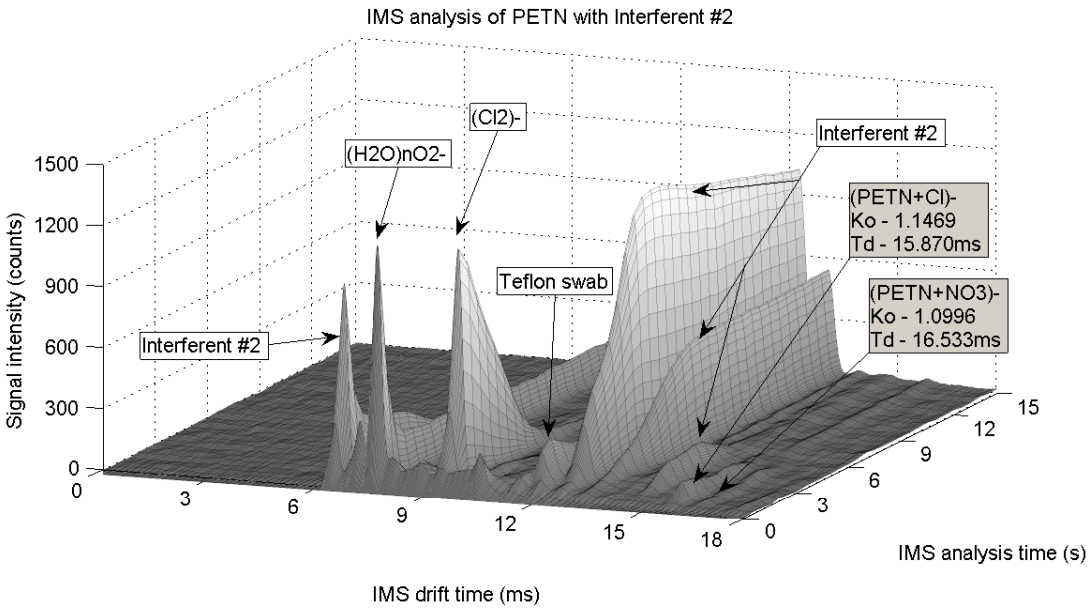
(M) IMS analysis of PETN with Interferent #1



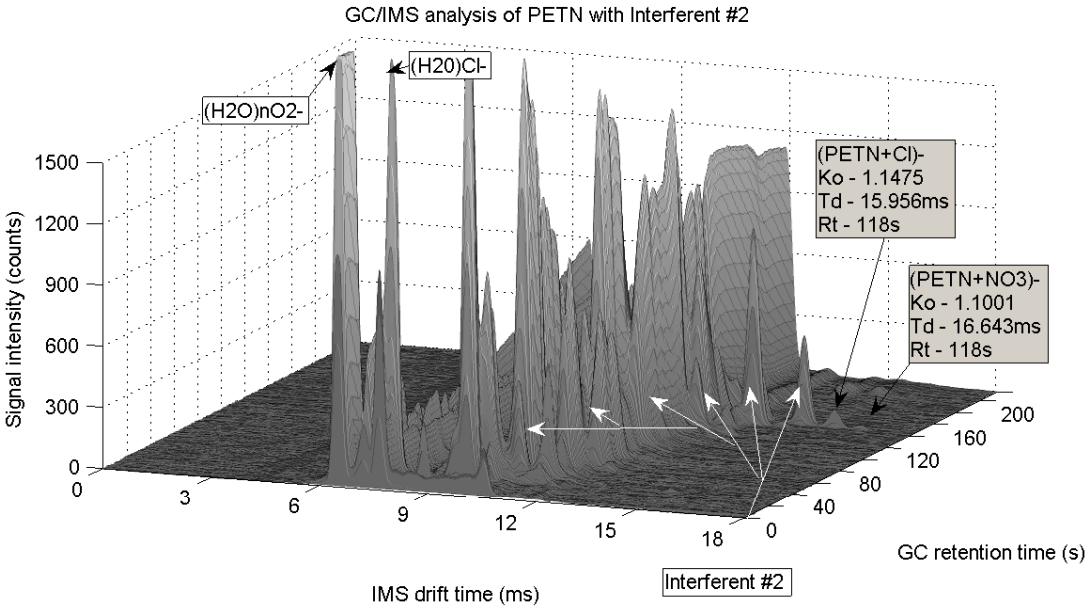
(N) GC/IMS analysis of PETN with Interferent #1



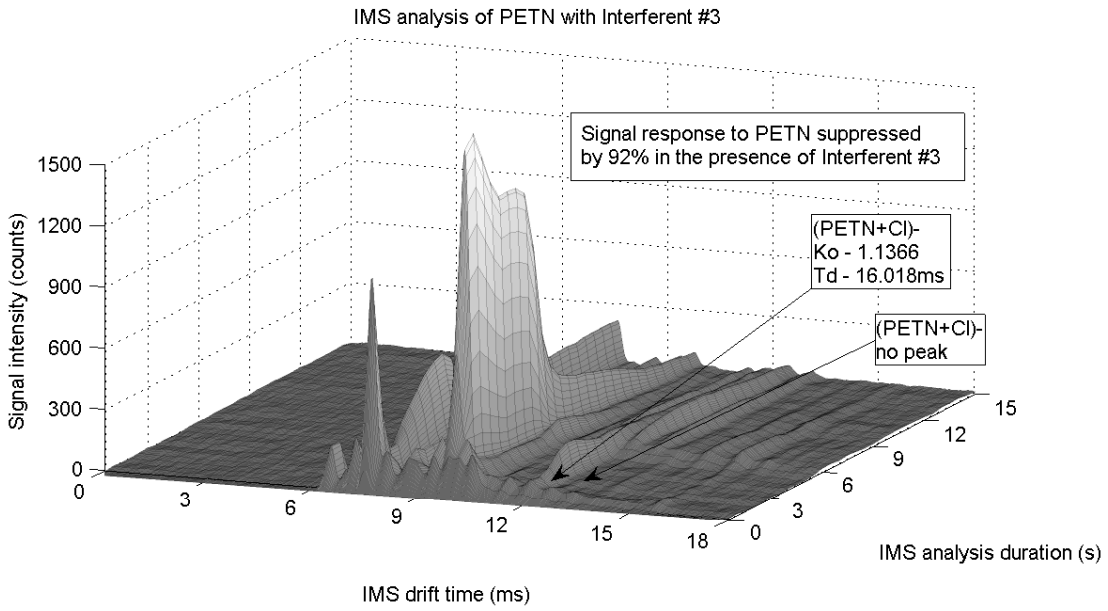
(O) IMS analysis of PETN with Interferent #2



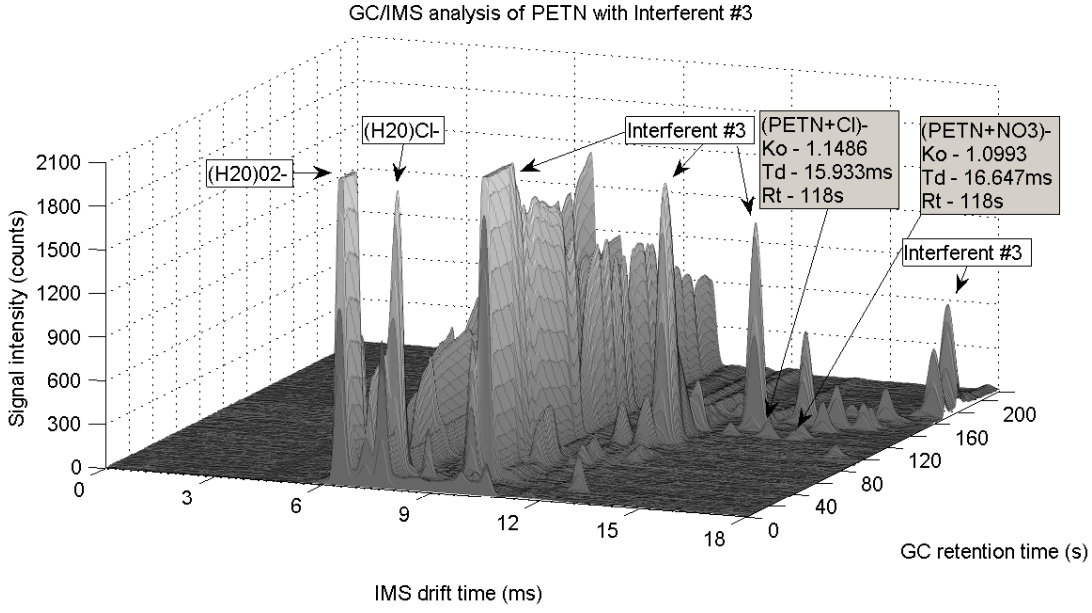
(P) GC/IMS analysis of PETN with Interferent #2



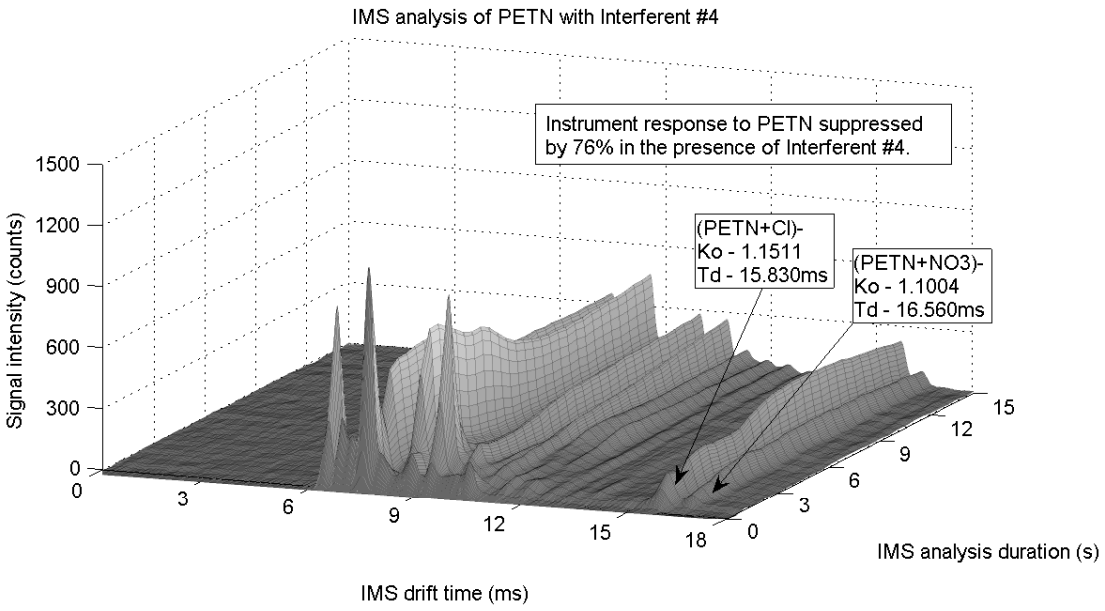
(Q) IMS analysis of PETN with Interferent #3



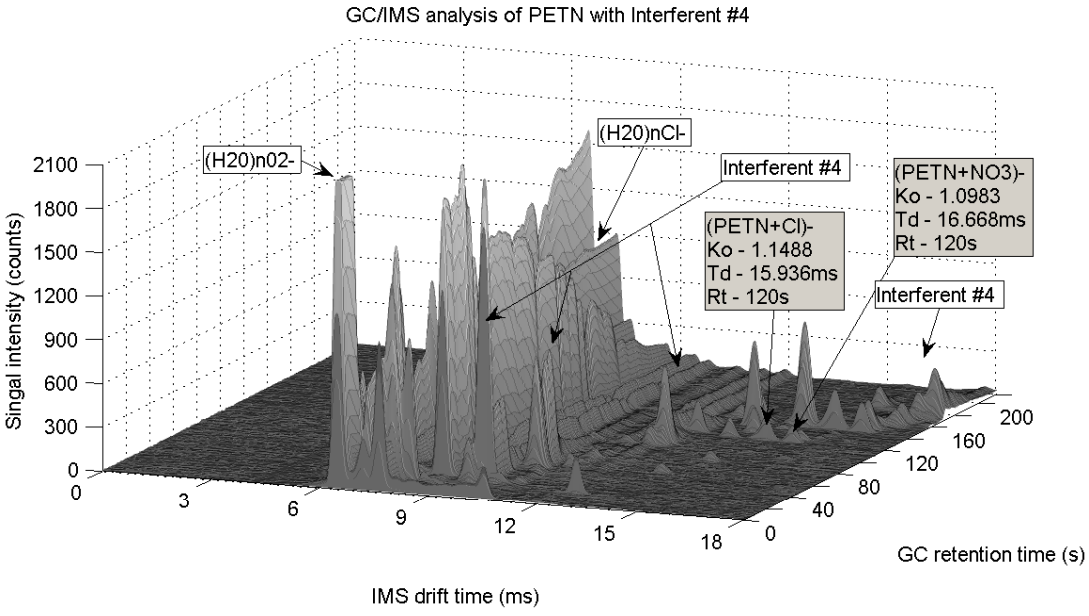
(R) GC/IMS analysis of PETN with Interferent #3



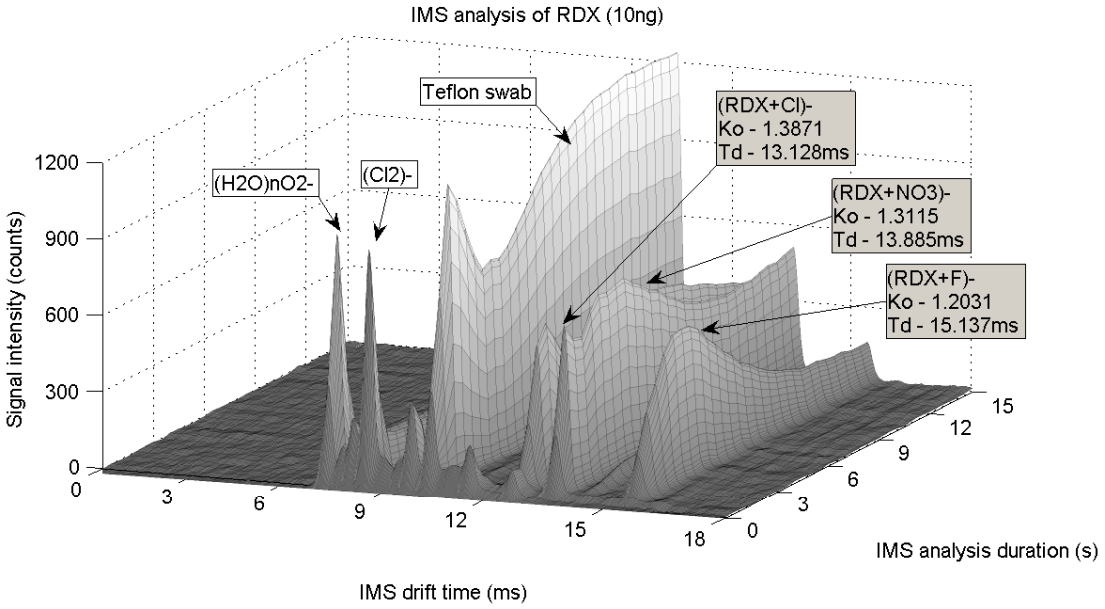
(S) IMS analysis of PETN with Interferent #4



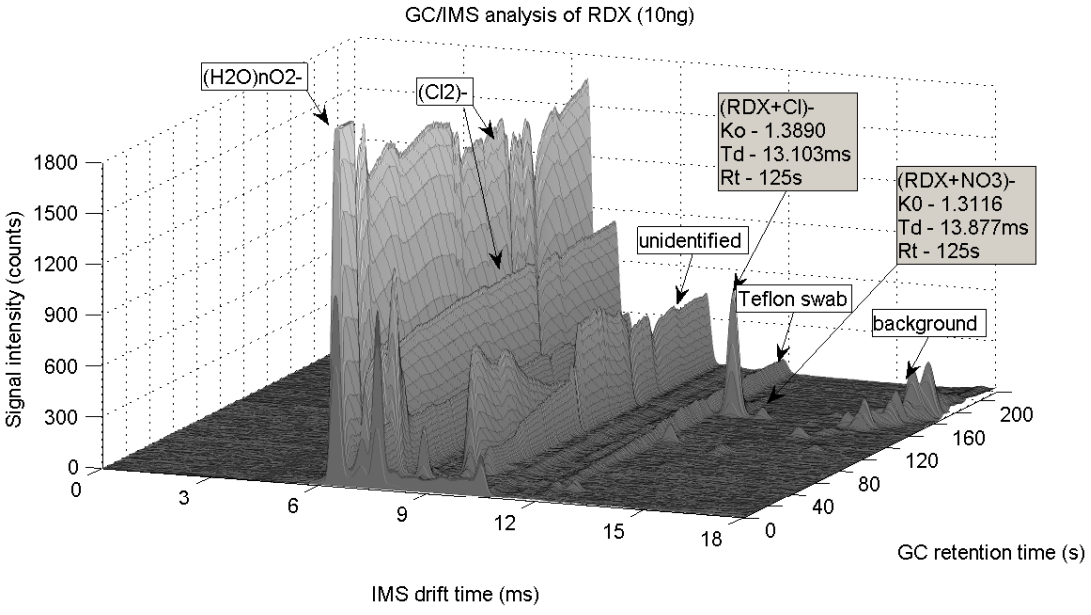
(T) GC/IMS analysis of PETN with Interferent #4



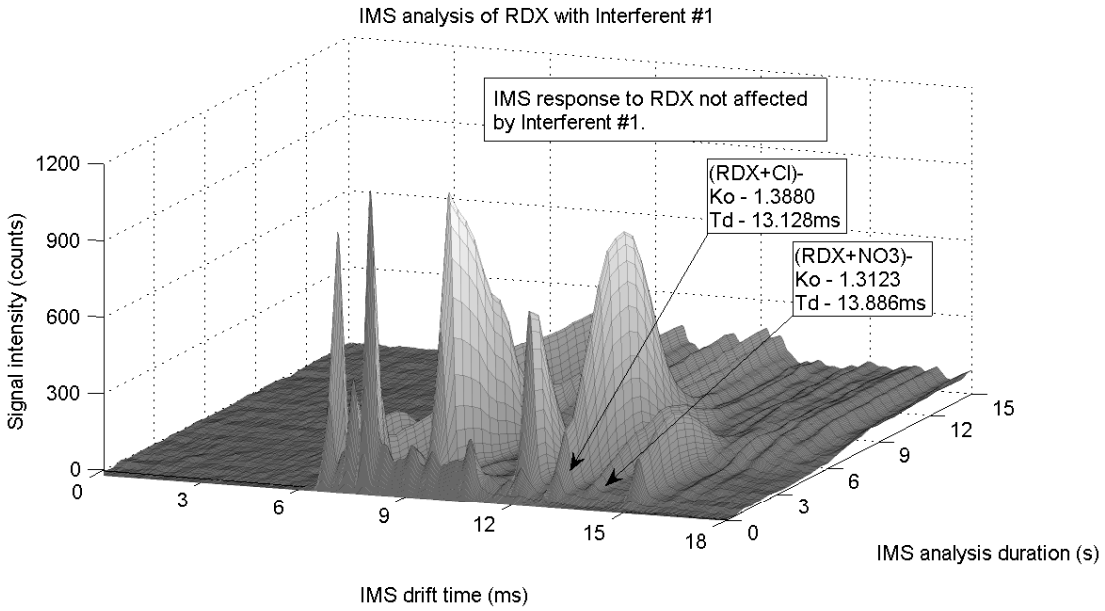
(U) IMS analysis of RDX



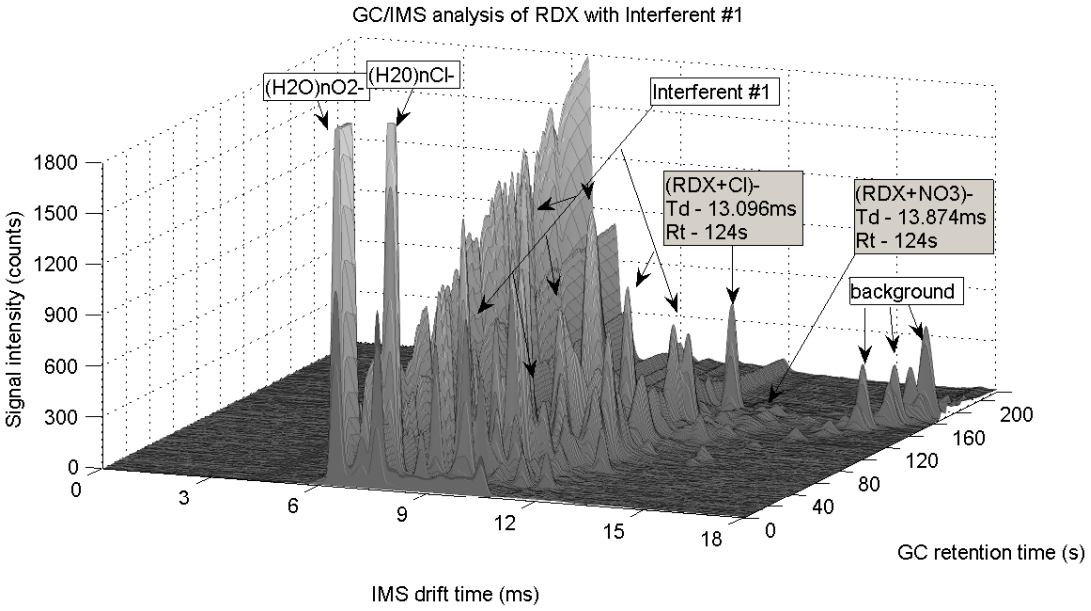
(V) GC/IMS analysis of RDX



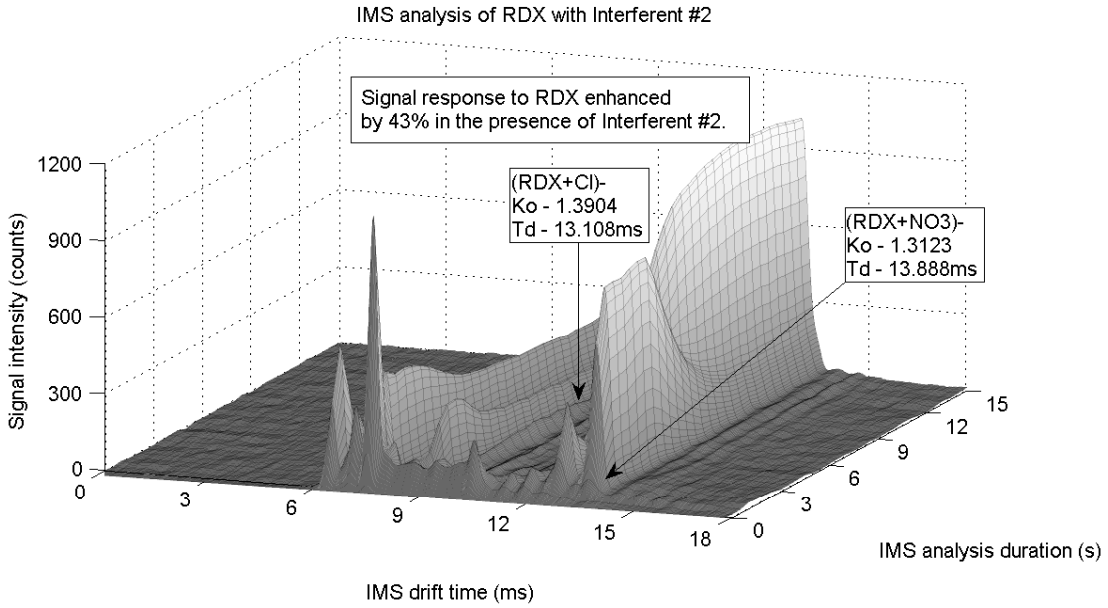
(W) IMS analysis of RDX with Interferent #1



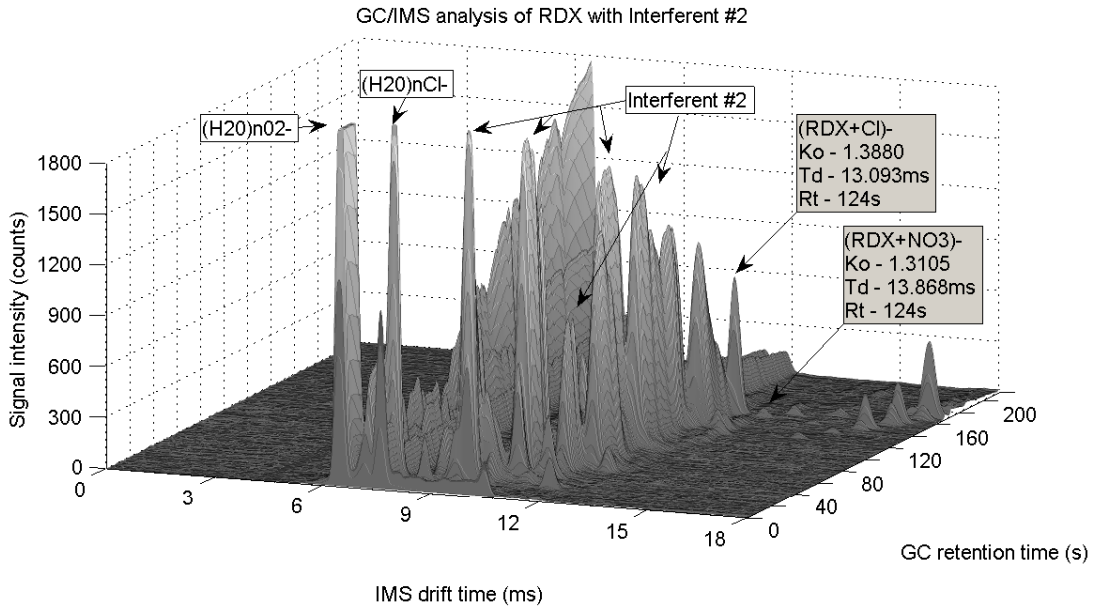
(X) IMS analysis of RDX with Interferent #1



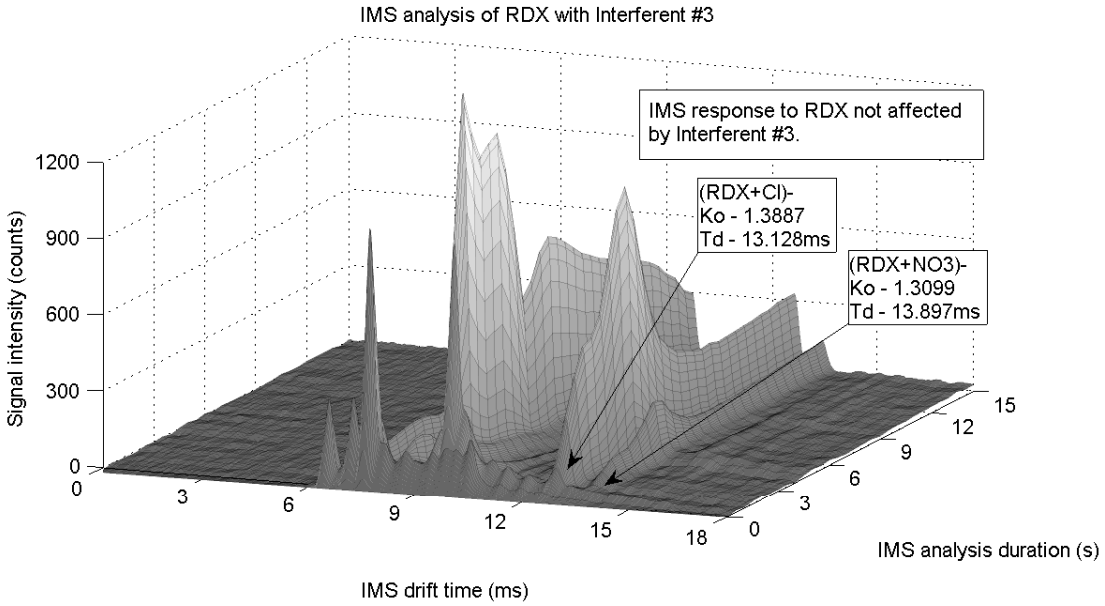
(Y) IMS analysis of RDX with Interferent #2



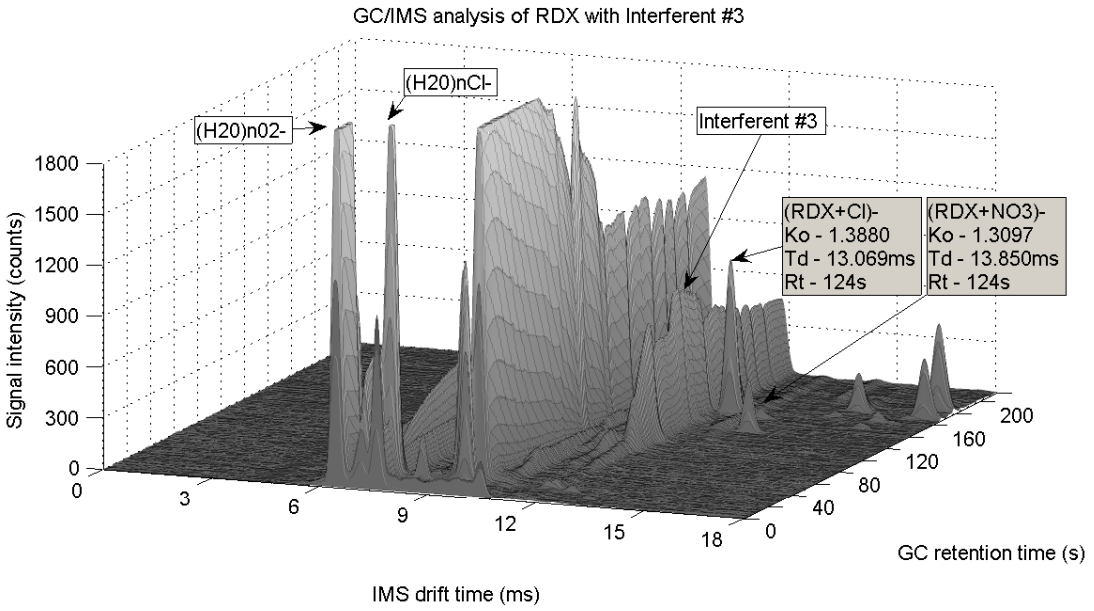
(Z) GC/IMS analysis of RDX with Interferent #2



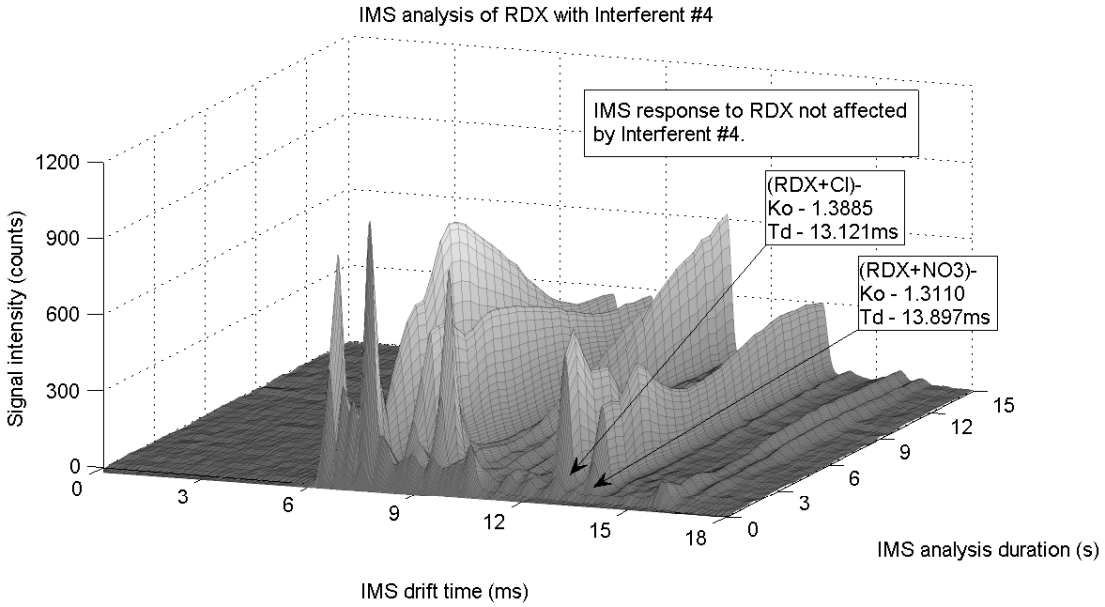
(AA) IMS analysis of RDX with Interferent #3



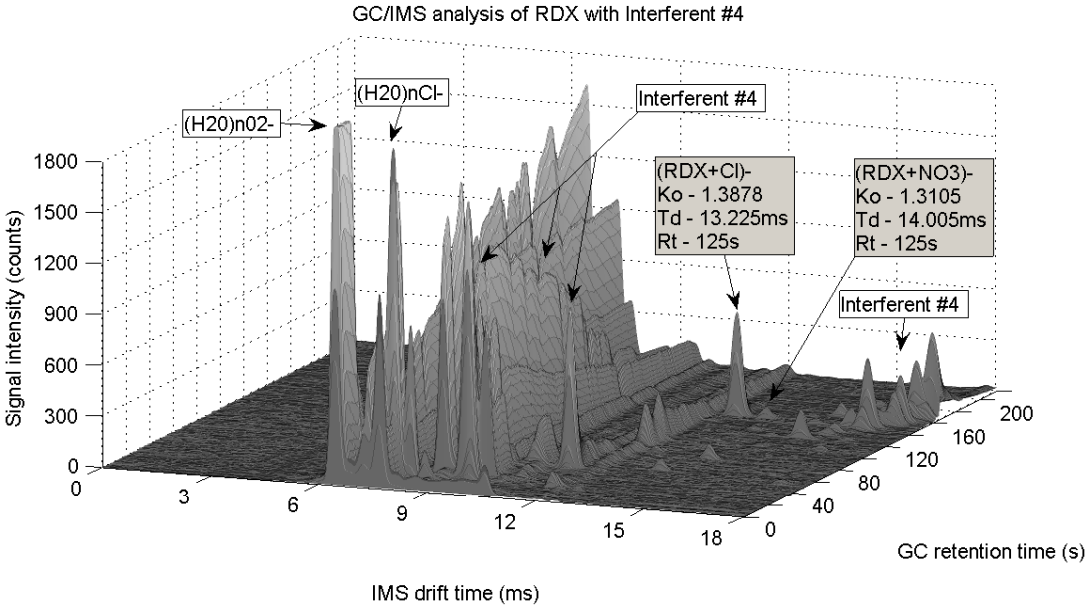
(BB) GC/IMS analysis of RDX with Interferent #3



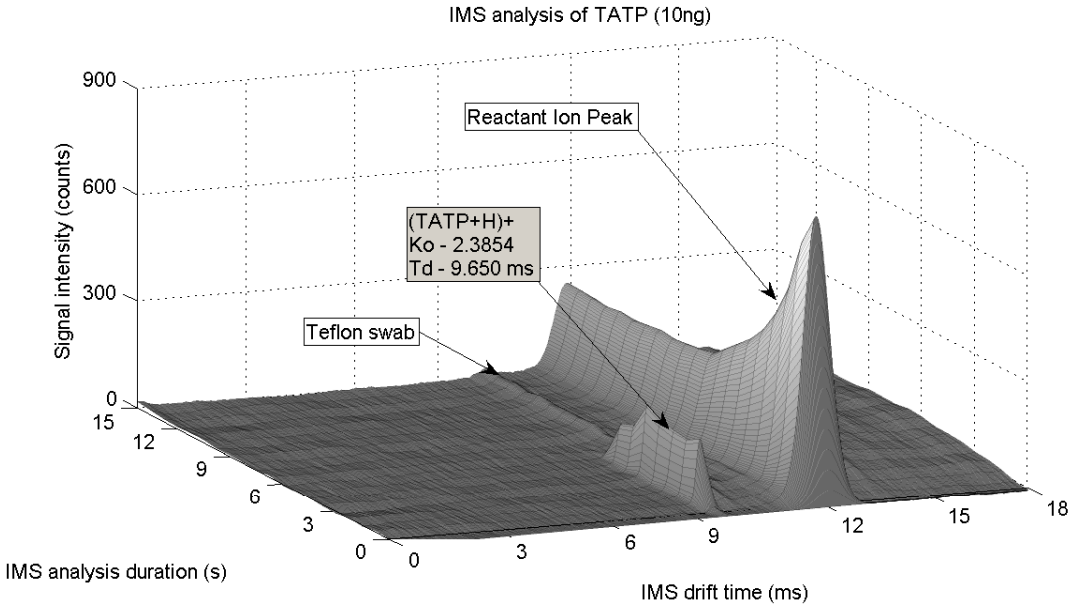
(CC) IMS analysis of RDX with Interferent #4



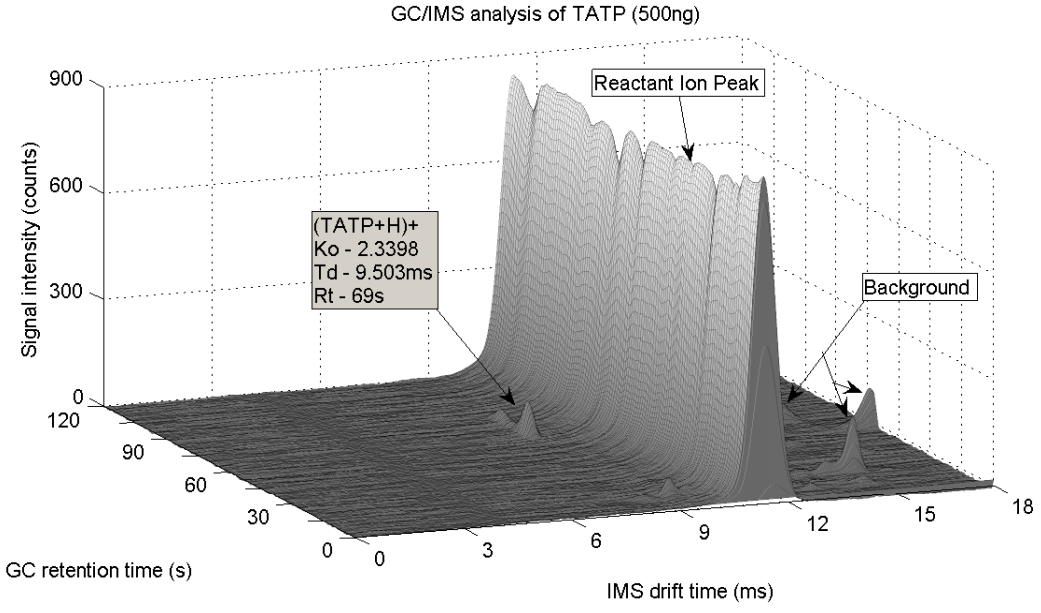
(DD) GC/IMS analysis of RDX with Interferent #4



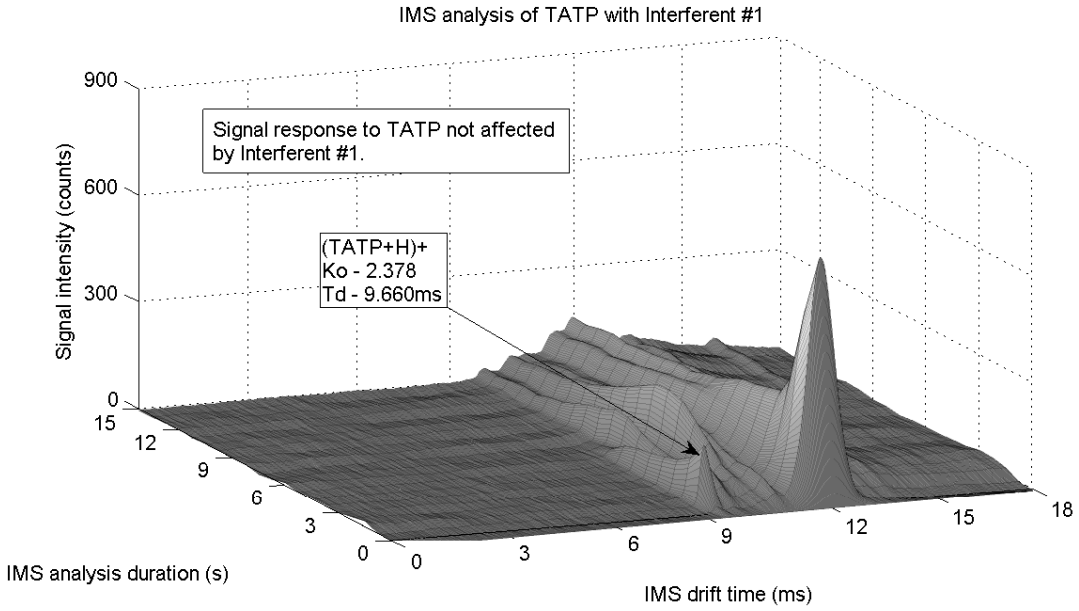
(EE) IMS analysis of TATP



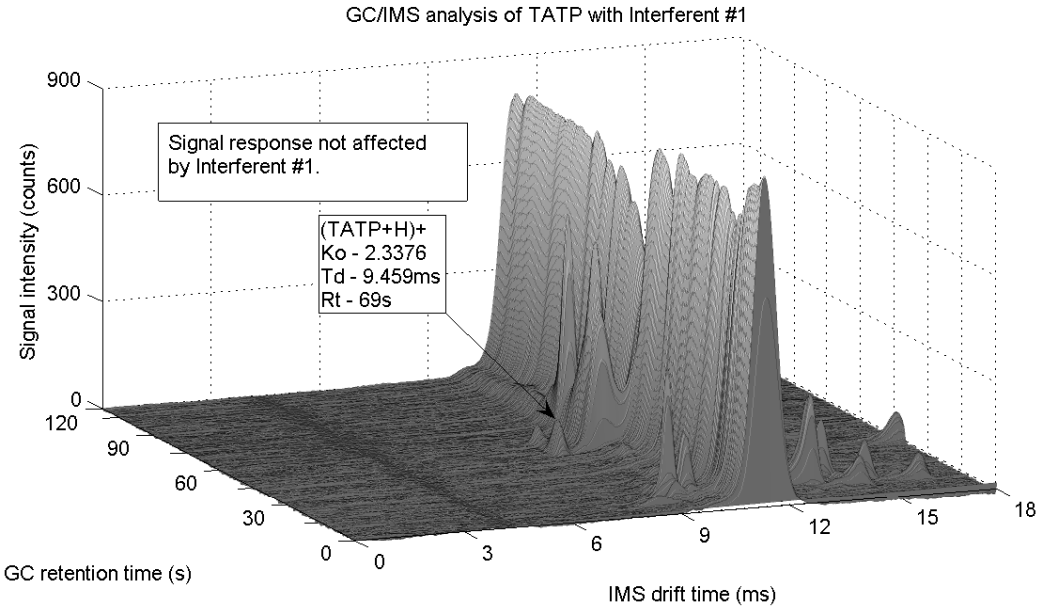
(FF) GC/IMS analysis of TATP



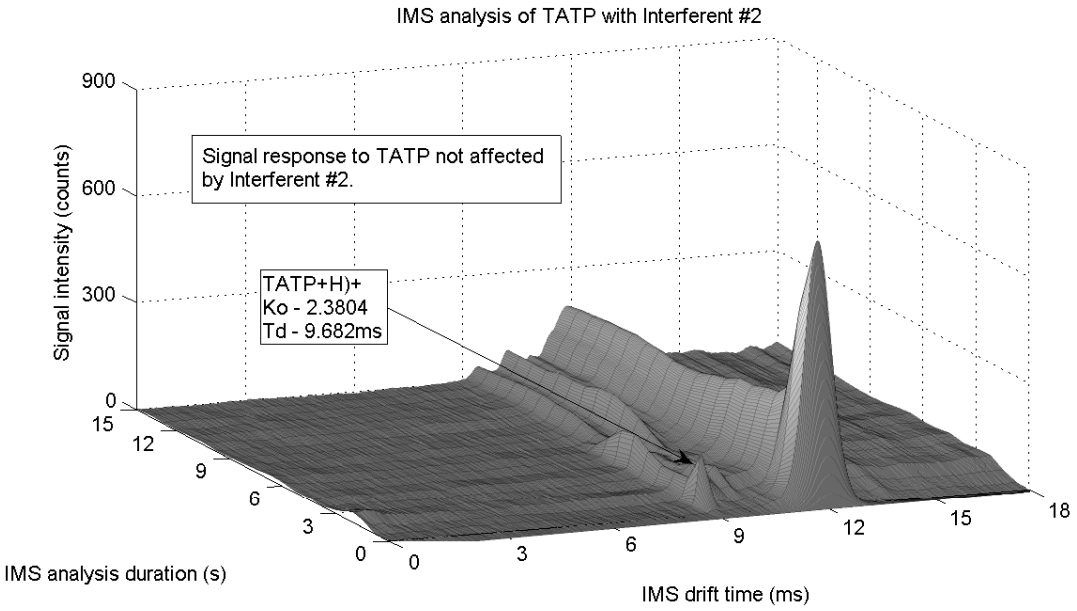
(GG) IMS analysis of TATP with Interferent #1



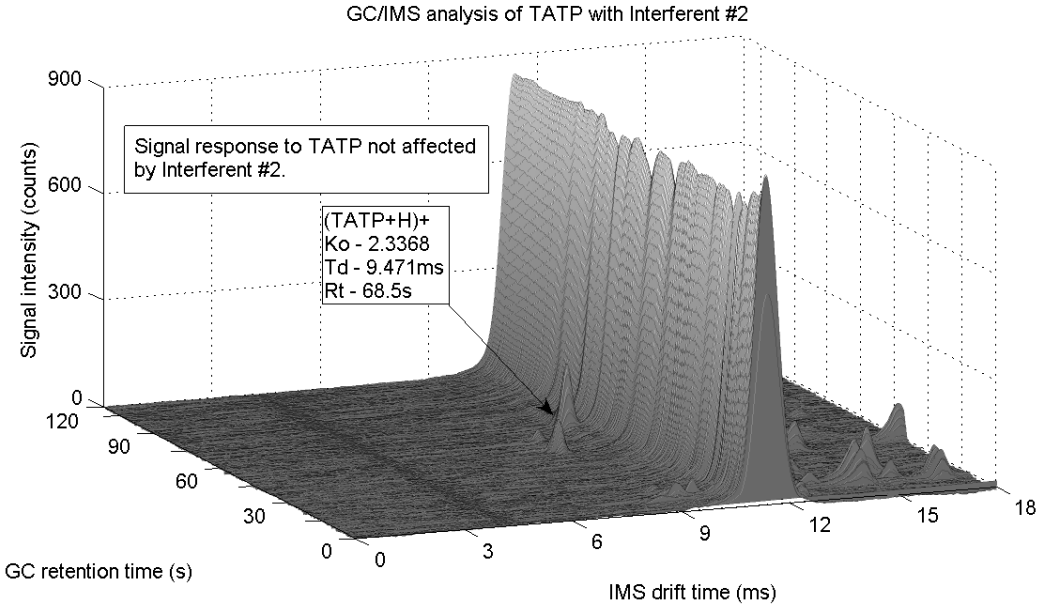
(HH) GC/IMS analysis of TATP with Interferent #1



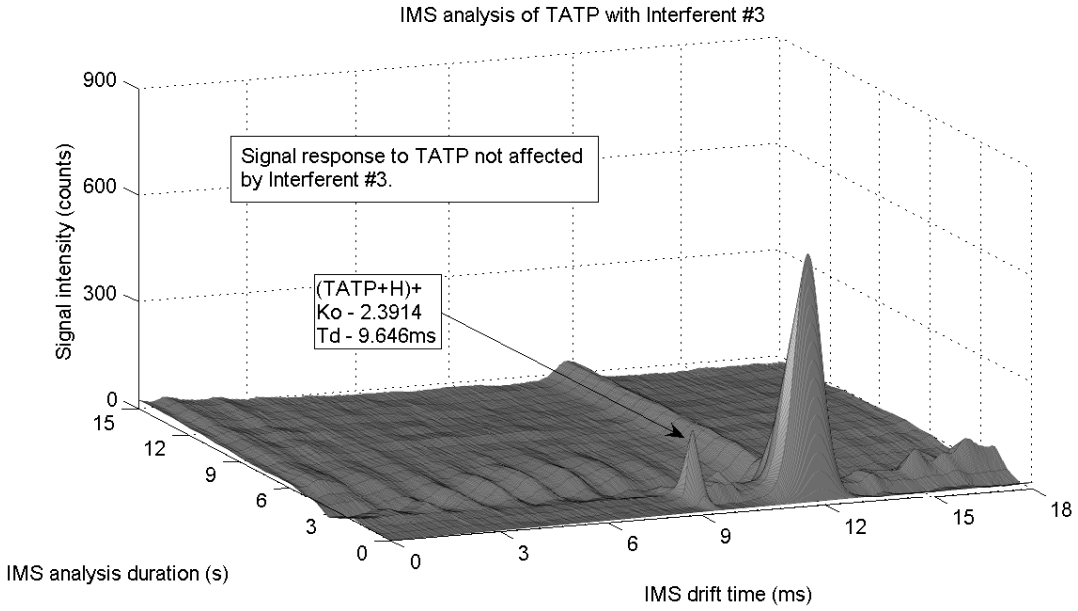
(II) IMS analysis of TATP with Interferent #2



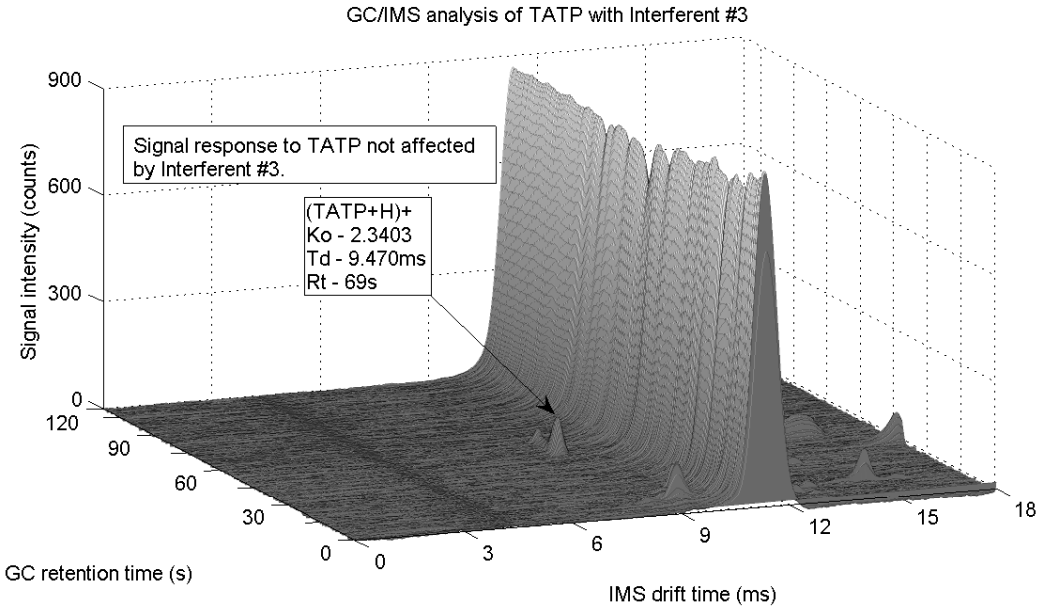
(JJ) GC/IMS analysis of TATP with Interferent #2



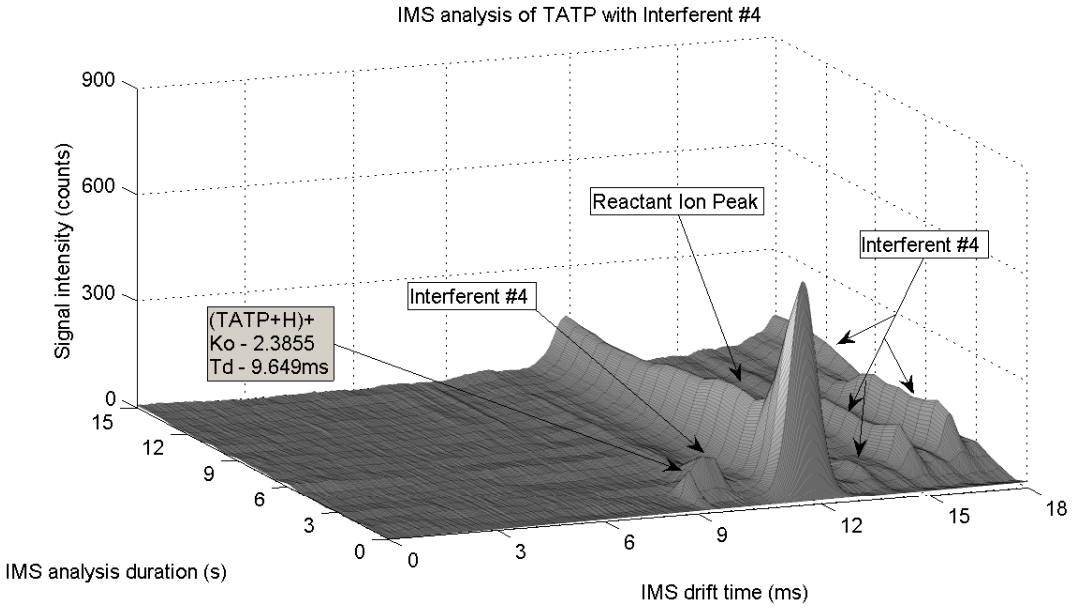
(KK) IMS analysis of TATP with Interferent #3



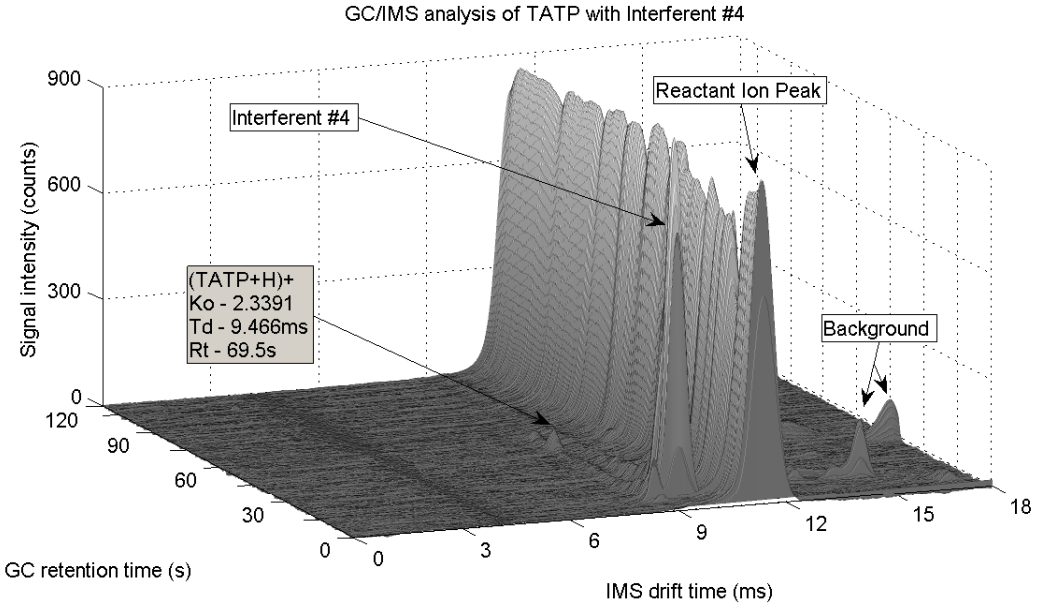
(LL) GC/IMS analysis of TATP with Interferent #3



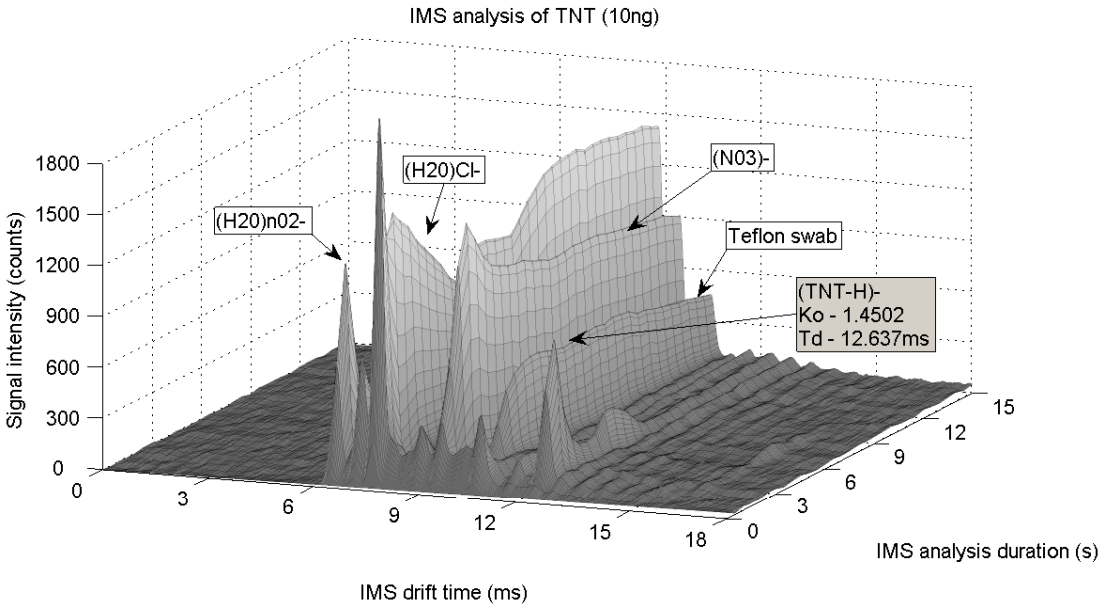
(MM) IMS analysis of TATP with Interferent #4



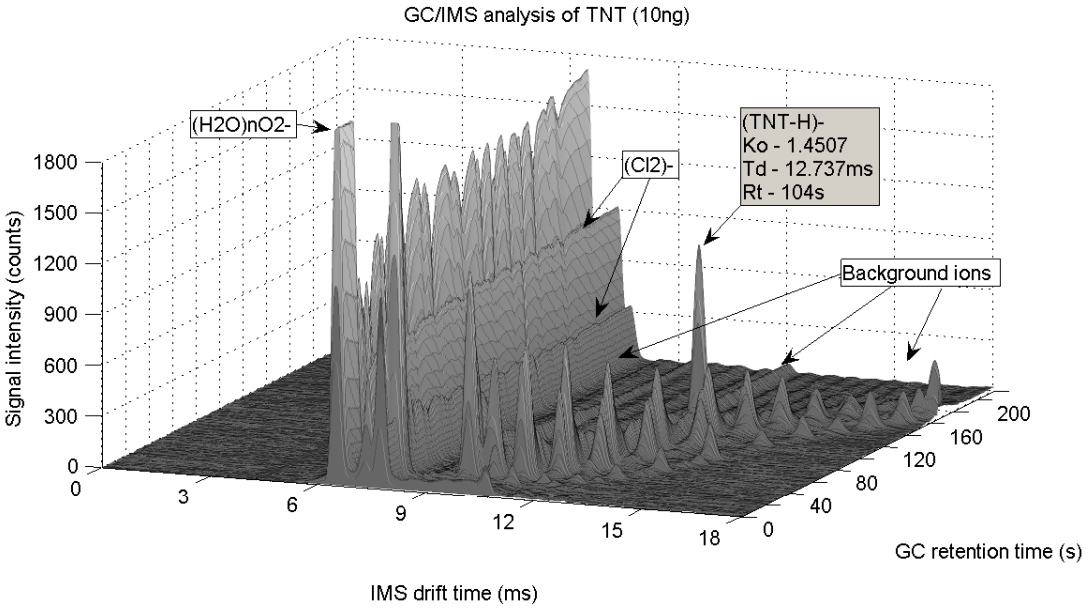
(NN) GC/IMS analysis of TATP with Interferent #4



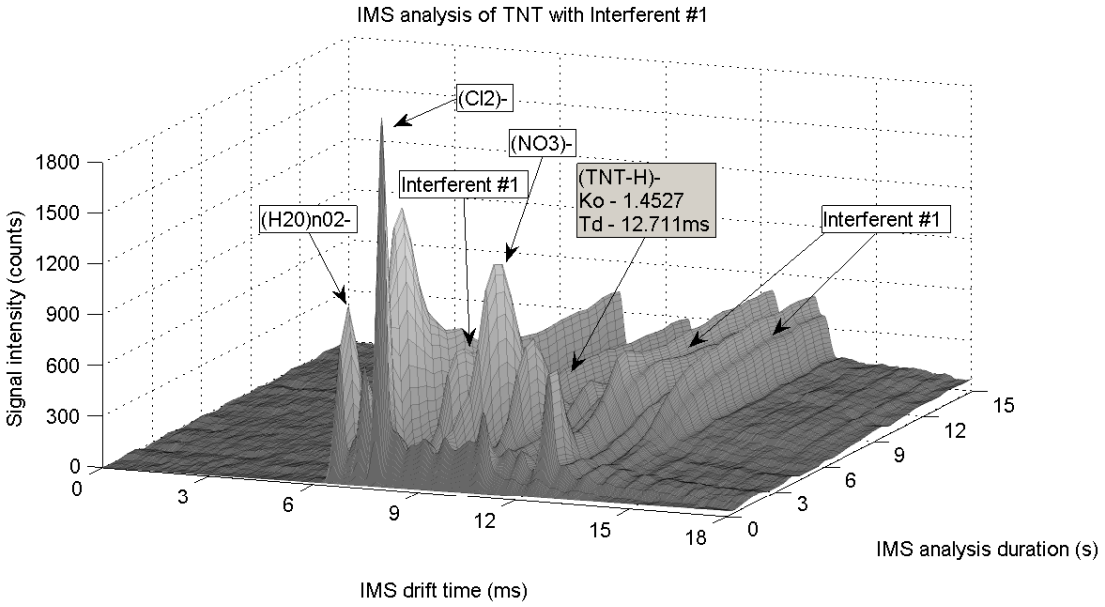
(OO) IMS analysis of TNT



(PP) GC/IMS analysis of TNT



(QQ) IMS analysis of TNT with Interferent #1



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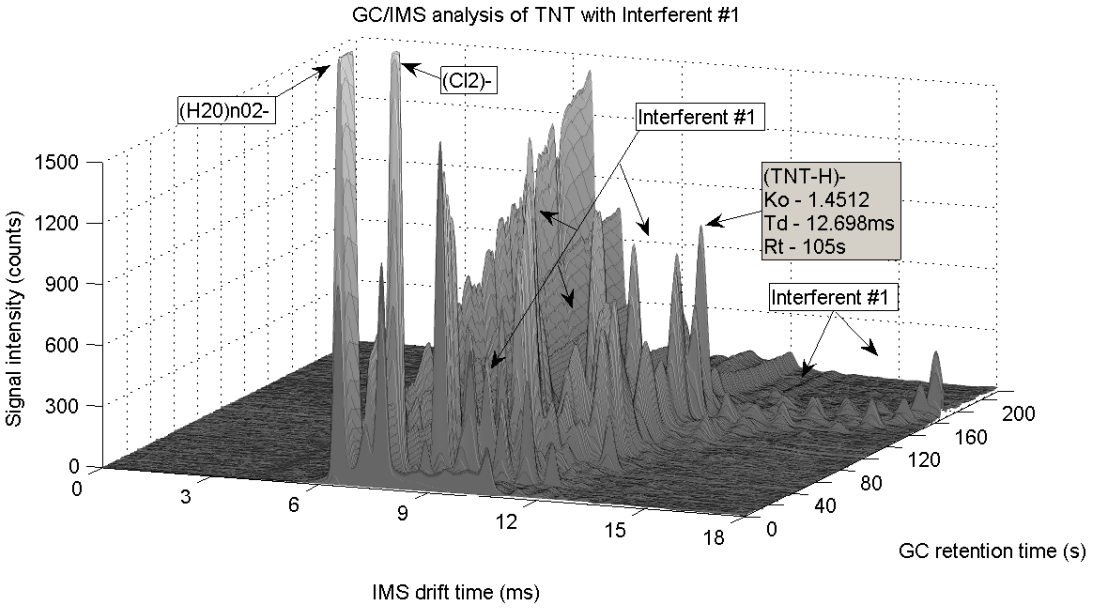
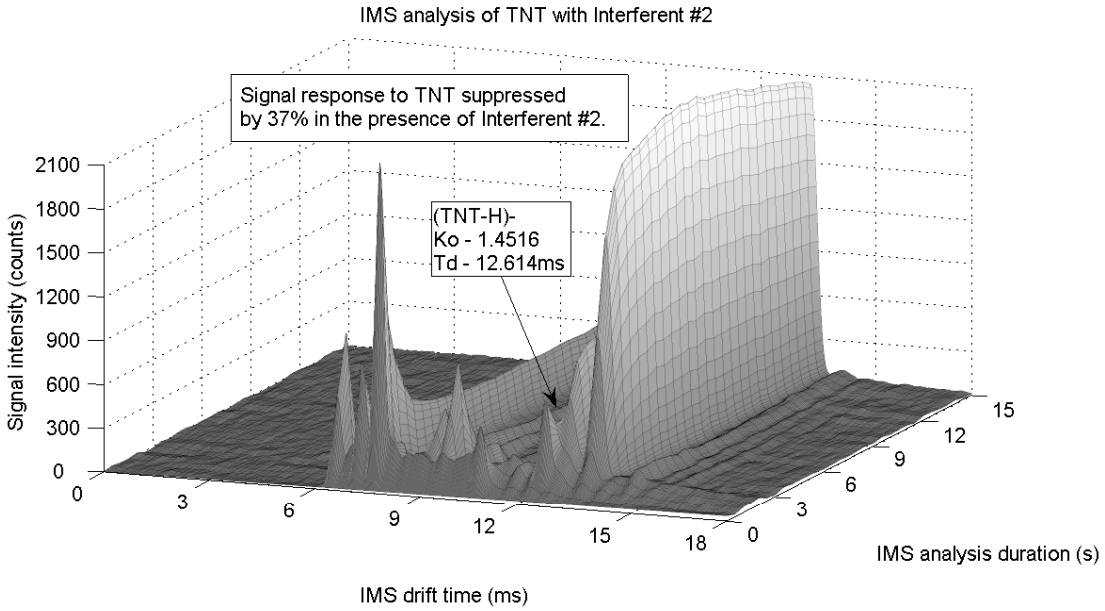
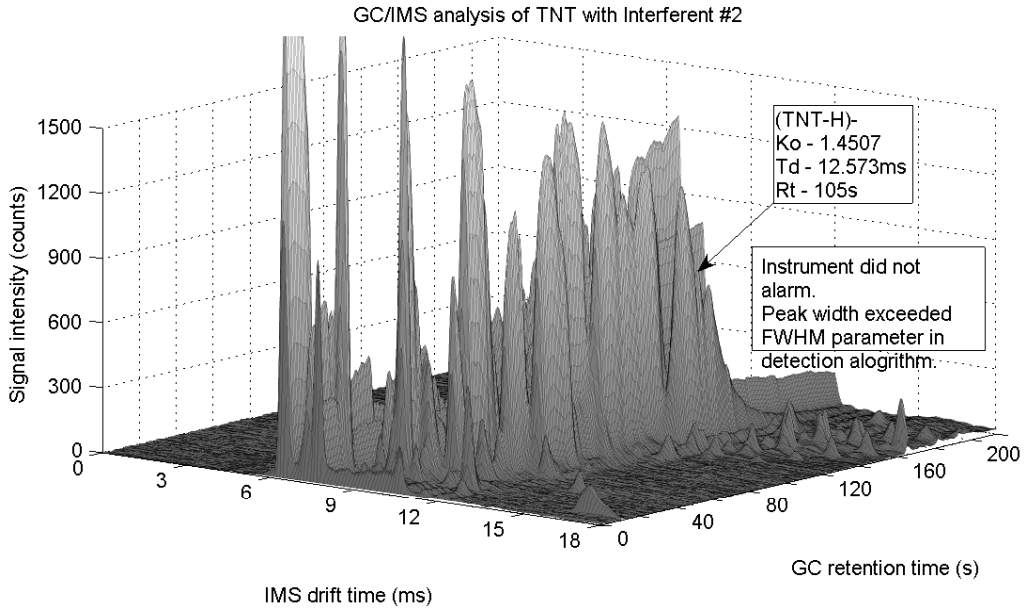


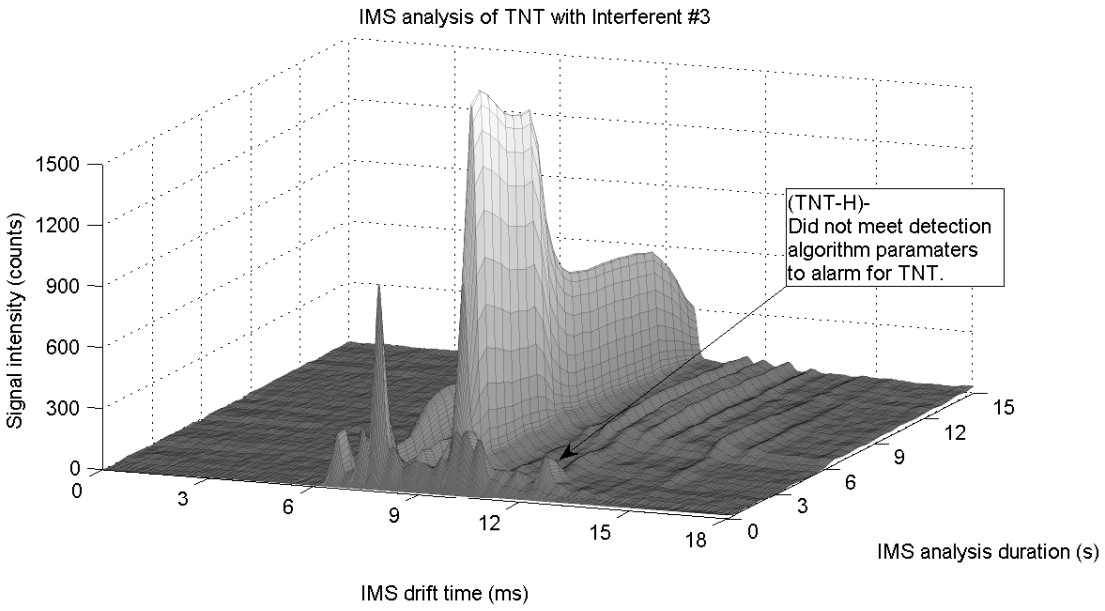
(SS) IMS analysis of TNT with Interferent #2



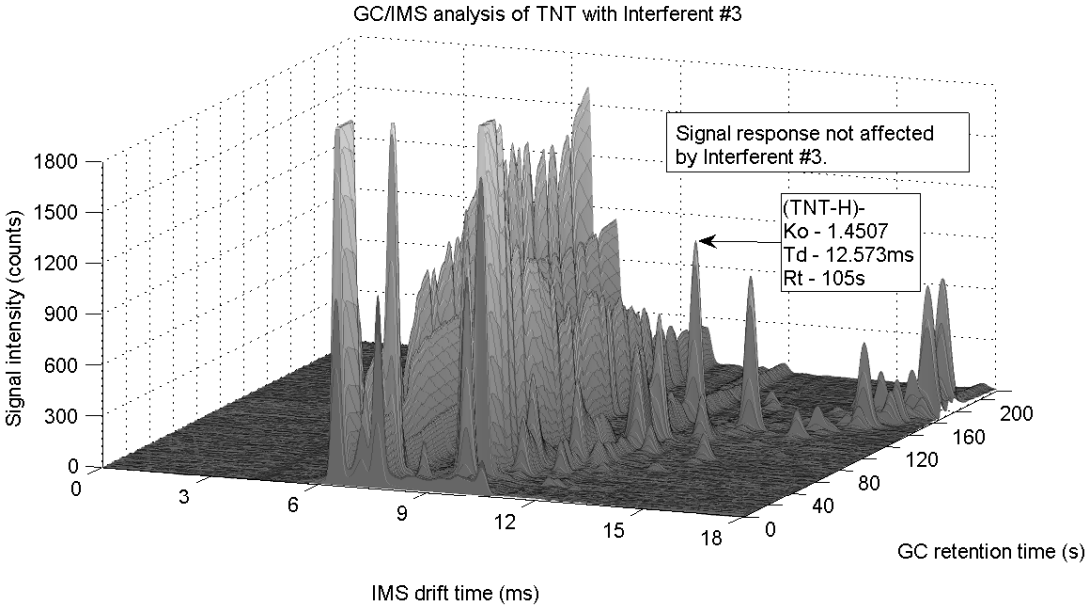
(TT) GC/IMS analysis of TNT with Interferent #2



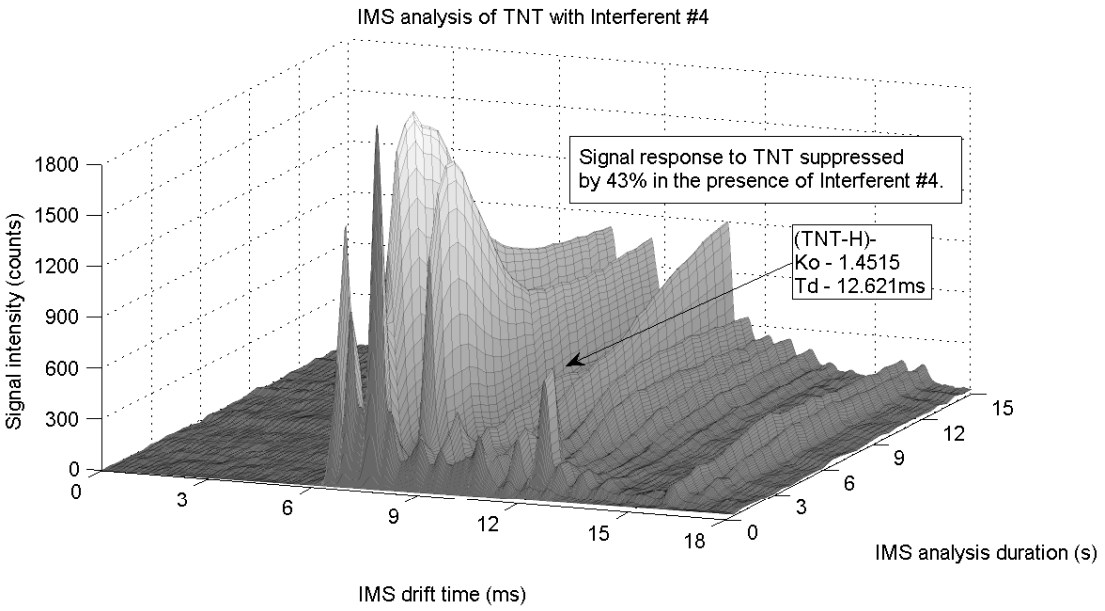
(UU) IMS analysis of TNT with Interferent #3



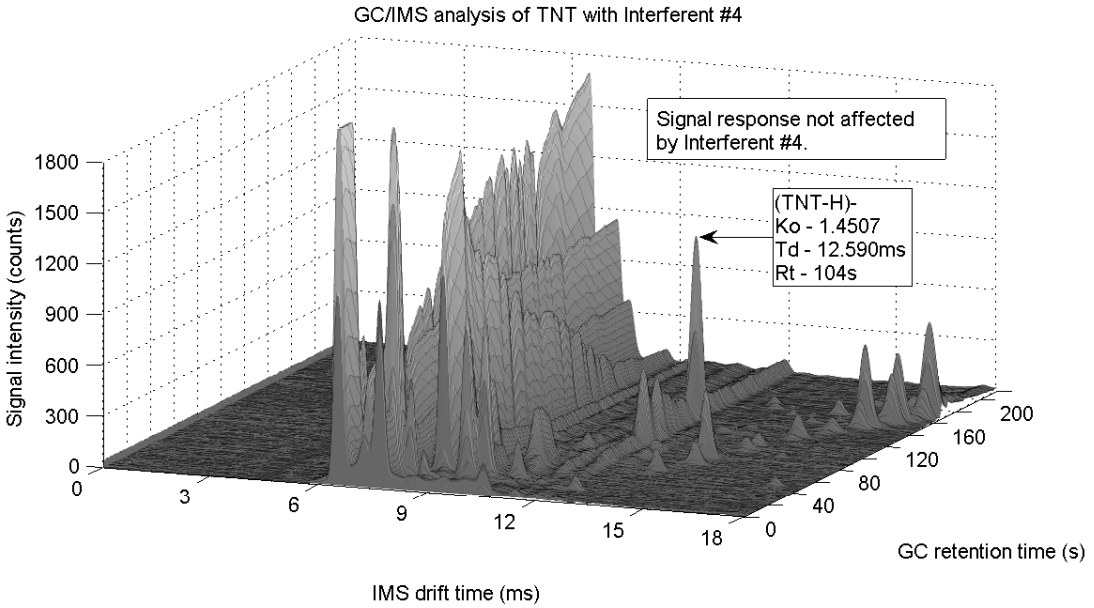
(VV) GC/IMS analysis of TNT with Interferent #3



(WW) IMS analysis of TNT with Interferent #4



(XX) GC/IMS analysis of TNT with Interferent #4



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Curriculum Vitae

Lieutenant Commander Greg Cook was commissioned into the Navy's Medical Service Corps as an Industrial Hygiene Officer in December 1993. He is a graduate of Old Dominion University, M.S. in Environmental Health and Murray State University, B.S. in Occupational Safety & Health.

After completing Officer Indoctrination School, Lieutenant Commander Cook was assigned to Naval Medical Center Portsmouth, Virginia where he served as a staff Industrial Hygiene Officer. His subsequent tours include duty as Assistant Safety Officer onboard the USS ENTERPRISE aircraft carrier; Department Head of Industrial Hygiene at Naval Hospital Okinawa, Japan; and Safety Officer at Shore Intermediate Maintenance Activity (SIMA) Mayport, Florida. In July 2003, he reported to the Uniformed Services University of the Health Sciences and began full-time duty in pursuit of a PhD in Environmental Health Science.

His decorations include the Navy and Marine Corps Commendation Medal (two awards), Navy and Marine Corps Achievement Medal (three awards), Meritorious Unit Commendation (three awards), National Defense Service Medal (two awards), Armed Forces Expeditionary Medal, Armed Forces Service Medal, Sea Service Deployment Ribbon, Navy and Marine Corps Overseas Service Ribbon (2 stars), and the NATO Medal.