THE FORENSIC ANALYSIS OF TRIACETONE TRIPEROXIDE (TATP) PRECURSORS AND SYNTHETIC BY-PRODUCTS

by

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ABSTRACT

Triacetone Triperoxide (TATP) is a primary high explosive that can be synthesized using commercially available starting materials and has grown in use among terrorists over the past several years. Additives present in the precursors were investigated to see if they carry through the TATP synthesis and can be detected in the final product potentially aiding in the identification of the source.

Additives identified in the acetones were also identified in pre-blast and in some post-blast samples. However, these additives are present in trace quantities relative to the TATP, which coupled with the volatility and short lifetimes of some of the additives in TATP samples limit their detection in pre-blast and post-blast material. TATP prepared with different acids in the laboratory could generally be discriminated by observing the change in composition of the headspace of the samples upon heating and by IMS analysis of the crystals.

The analysis of TATP synthesized on a larger scale was compared to the laboratory results of pre-blast material and post-blast debris. As in the laboratory samples, organic additives were also detected in the large-scale pre-blast samples and the identification of the additives in post-blast debris was consistent with the results obtained in the laboratory detonations.

To my mother and sister

"The fact is, there is no foundation, no secure ground, upon which people may stand today if it isn't the family."

- Mitch Albom

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LIST OF ACRONYMS/ABBREVIATIONS

AN	Ammonium nitrate
ANFO	Ammonium nitrate fuel oil
APCI	Atmospheric pressure chemical ionization
ASA	Combination of lead styphnate, lead azide, and aluminum
CAS	Chemical Abstracts Service
CID	Collision Induced Dissociation
CI	Chemical ionization
Da	Dalton
DADP	Diacetone diperoxide
DDNP	Diazodinitrophenol
DESI	Desorption electrospray ionization
DI	Deionized
ECD	Electron capture detector
EI	Electron ionization
ESI	Electrospray ionization
FID	Flame ionization detector
GC	Gas chromatography
HME	Homemade explosive
HMTD	Hexamethylene triperoxide diamine
HMX	Cyclotetramethylene tetranitramine

HPLC	High performance liquid chromatography
IC	Ion chromatography
IED	Improvised explosive device
IMS	Ion mobility spectrometry
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
LC	Liquid chromatography
LMCO	Low-mass cutoff
MS	Mass spectrometry
M/Z	Mass to charge ratio
NG	Nitroglycerin
NIST	National Institute of Standards and Technology
NMR	Nuclear magnetic resonance
PBX	Plastic-bonded explosives
PDMS/DVB	Polydimethylsiloxane/divinylbenzene
PETN	Pentaerythritol tetranitrate
Ppm	Parts per million
RDX	Cyclotrimethylene trinitramine
SPME	Solid-phase microextraction
TATP	Triacetone triperoxide
TCD	Thermal conductivity detector
TEA	Thermal energy analysis

TLC	Thin layer chromatography
TNT	Trinitrotoluene
UV	Ultraviolet
TrATrP	Tetraacetone Tetraperoxide
VBIED	Vehicle born improvised explosive device

CHAPTER 1: BACKGROUND

Introduction to Explosives

An explosion is simply the release of a large amount of energy due to the rapid physical change of the explosive material from a solid or a liquid to a gas [1]. Explosives are divided into two categories – low explosives and high explosives - based on the type of chemical reaction that takes place and the speed at which it proceeds. High explosives are then further characterized by their use as either a primary or secondary explosive, with secondary explosives being divided based on military or commercial use. Improvised explosive devices (IEDs) which have become popular among terrorists and amateur chemists can employ numerous combinations of high and low explosives.

Depending on the way the material behaves when ignited or detonated, it can be classified into either a low explosive or a high explosive. Low explosives will deflagrate, or burn rapidly at intense temperatures and are usually accompanied by popping or hissing sounds; high explosives, however, will detonate. Detonation is the process by which the energetic material decomposes due to a shockwave rather than via a thermal reaction. The speed of the reaction is also a contributing factor as to which category energetic materials fall into. The reactions of low explosives proceed at a slower rate than high explosives, even though both reactions proceed at very fast rates; the velocity of a low explosive is in the cm/s range, while the velocity of a detonation for a high explosive is km/s [2].

High explosives can be sub-classified into primary or secondary explosives. Primary explosives are typically used as initiators to detonate the main charge, typically a secondary

explosive. Primary explosives are much more sensitive than secondary explosives to heat, friction, and shock, and will detonate either confined or unconfined, therefore making them more unstable than secondary explosives. Secondary explosives are less sensitive to heat, friction, and shock and will only detonate when initiated by a sufficient amount of energy such as through the use of a primary explosive; however, the explosions are more powerful than those of a primary explosive. Based on their use, secondary explosives get classified as either military or commercial explosives.

Low Explosives

Low explosives, also known as propellants because they are used to launch projectiles, are mixtures that contain a fuel and an oxidizer which deflagrate rather than detonate; however, low explosives can detonate if confined in an enclosed container. This is possible because when an energetic material undergoes deflagration, it releases gases. If the material is confined, these gases become trapped, causing the pressure to build up and subsequently causing an increase in the temperature of the material, which accelerates the rate of deflagration. Propellants are typically comprised of energetic materials such as black powder or smokeless powder, plasticizers, and stabilizers, among other various inorganic compounds to improve ignitability [2]. The first known propellant was black powder and is typically a combination of potassium or sodium nitrate, charcoal, and sulfur. Once commonly used in firearms as gunpowder, black powder was eventually replaced by smokeless powders which produce far less smoke upon discharge of the weapon; the use of black powder today is more limited, but it is still used in the production of emergency flares and firecrackers. Although contrary to their name, smokeless

powders still produce smoke after a firearm has been discharged, but considerably less as compared to that of black powder. In 1886, Vieille created the first smokeless powder by combining nitrocellulose with ether-alcohol; this later became known as a single-based smokeless powder (only containing nitrocellulose) [3]. Two years later, Alfred Nobel discovered that nitrocellulose could be combined with nitroglycerin to create a smokeless powder he named Ballistite, which was the first double-based powder [1]. Triple based smokeless powders contain nitrocellulose, nitroglycerin, and nitroguanidine as the main compounds.

Secondary Explosives

Secondary explosives are typically used as the main charge in a detonation and are the most powerful of all energetic materials. They are classified according to the applications they are used for. Examples of military explosives include picric acid, TNT, tetryl, PETN, RDX, and HMX; examples of commercial explosives include nitroglycerin (NG), dynamite, and a collection of blasting agents.

Military Explosives

Black powder was the first explosive employed for military use; however, most of the current military explosives are nitrated organic compounds. The list of military explosives employed today is rather extensive.

Picric acid was first discovered by Glauber in 1742, but it was not until 1885 that Turpin stated picric acid was a good replacement for black powder and in 1894, Panpushko discovered

its true explosive potential [4]. Until then, black powder was used in ammunition, but at the start of the twentieth century, picric acid replaced it; picric acid has since been phased out by other more well known explosives, namely TNT. Tetryl was developed in 1877 by Mertens and was briefly used in blasting caps during the early 1900s [4]. There are many isomers of TNT, but the most explosive is 2,4,6-trinitrotoluene and was discovered in 1880 by Hepp [4]. TNT is the most commonly employed military explosive either on its own or in a mixture with other energetic materials; it is very stable and resistant to heat, friction, and shock and is fairly simple to produce [5]. PETN was initially discovered in 1894 by nitrating pentaerythritol and was frequently a charge used in blasting caps; because of its instability, it is typically mixed with a variety of other explosives, such as with TNT to create "Pentolite." Henning first discovered RDX in 1899 but it was not employed as a military explosive until World War II and was typically combined with TNT to increase its explosive power. There are two types of RDX – Type A RDX and Type B RDX. The production of RDX was rather difficult and resulted in an abundance of additives and low yields. Bachmann was the first to produce RDX with a low impurity level, which is known as Type B RDX. Those additives, however, carried an explosive property of their own and were eventually developed into the explosive HMX. Pure RDX, Type A RDX, was finally discovered by Brockman. Compared to RDX, HMX has a higher ignition temperature and is more stable, but the explosive power is not as great [4]. Plastic-bonded explosives (PBX) are one of the newest military advances. They are well known for their power, detonation velocity, stability, and insensitivity to shock and high temperatures [3]. Typically PBX explosives are created from RDX, PETN, HMX or a combination thereof and aluminum, binders, and a plasticizer; two of the most well known PBX explosives are Composition C-4

(91% RDX/9% plasticizer) and SEMTEX (a combination of RDX/PETN) [3]. Figure 1 provides chemical structures for common military explosives.

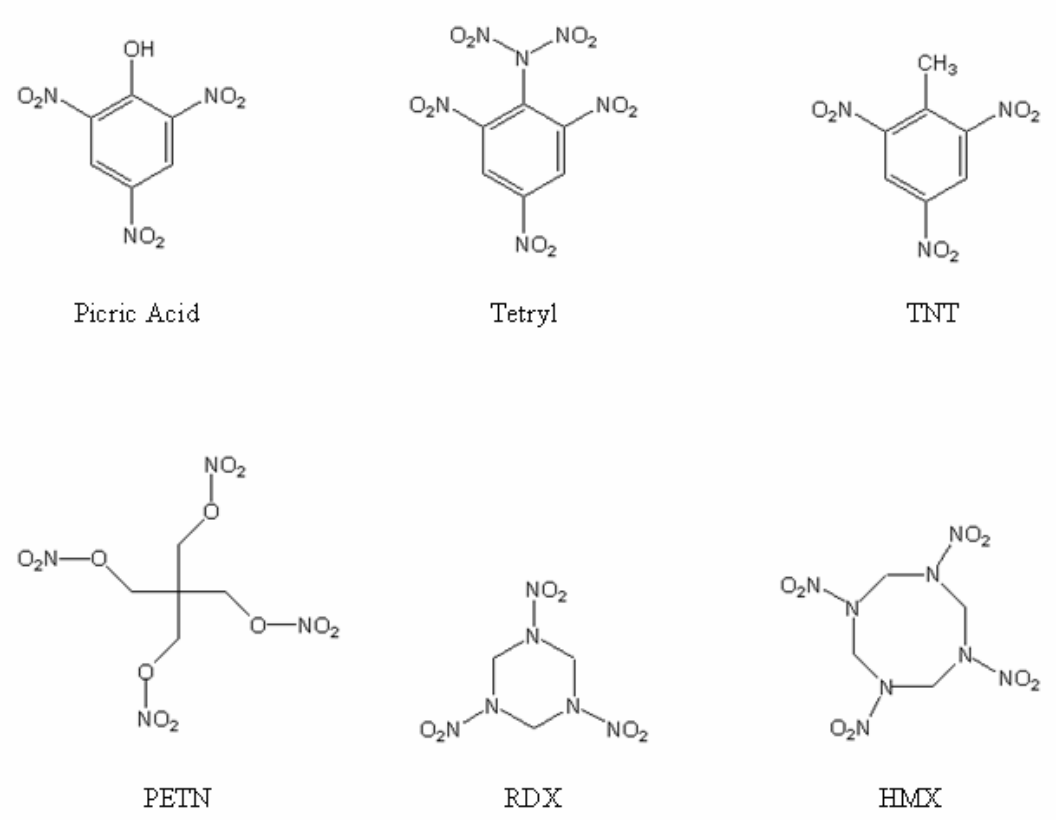


Figure 1: Structures of common military explosives

Commercial Explosives

Like military explosives, black powder was the first commercial explosive, but its use in mining for large-scale explosions was rather problematic due to the manner black powder had to be initiated.

Sobrero was the first to develop nitroglycerin (NG) from adding glycerol to a mixture containing both nitric and sulfuric acid in 1846; however, it was Alfred Nobel that first put it to use as a commercial explosive in blasting caps [3, 4]. As a liquid explosive, NG is a hazard due to its toxicity and it is very unsafe to handle due to its instability, so Nobel decided to combine it with diatomaceous earth (kieselguhr) and named his creation 'dynamite.' Nobel was also the one to realize a gelatin could be created by adding nitrocellulose to NG which led to the development of gelatin dynamite. It was not until 1867, however, when Ohlsson and Norrbin discovered that the addition of ammonium nitrate (AN) to dynamite increased its explosive potential. Ammonium nitrate was discovered centuries ago by Glauber but was not reported to have explosive properties until 1849 by Reise and Millon. AN is produced in a granular form if it is to be used in explosives or ammunition. A method known as "prilling" that was used to produce lead shot via a shot-tower concept was employed to create AN for use in fertilizers because it creates a small porous sphere that is safer to handle [3].

Commercial explosives also contain blasting agents such as Ammonium Nitrate/Fuel Oil (ANFO), slurry, water gel, and emulsion explosives, which are sometimes referred to as tertiary explosives. Blasting agents are mixtures of a fuel and an oxidizing agent that are used for blasting and are normally detonated via a primary explosive. ANFO is the most common blasting agent; however its explosive properties are rather poor due to its lack of water

resistance, low density, and slow detonation rate [3]. Slurry explosives were produced to eliminate the problems encountered with ANFO. They are typically borax cross-linked and consist of AN, water, a gel, a sensitizer such as microballoons, and often aluminum flakes for added energy [3]. A distinction was made between slurry and water gel explosives in the 1960s. A slurry is thickened by using a polysaccharide that is not cross-linked; a water gel contains a cross-linking agent that links the thickener to form a chemical bond [3]. Emulsion explosives consist of two immiscible liquids with one liquid suspended within the other - the fuel surrounding the oxidizer. The particle size of the oxidizer is small which improves the detonation power and by surrounding it with a fuel, oil, or wax, it also becomes water resistant. Microballoons are often added to emulsion explosives as a source of oxygen to increase sensitivity and prevent settling in bore holes. Figure 2 gives the structures for NG and AN.

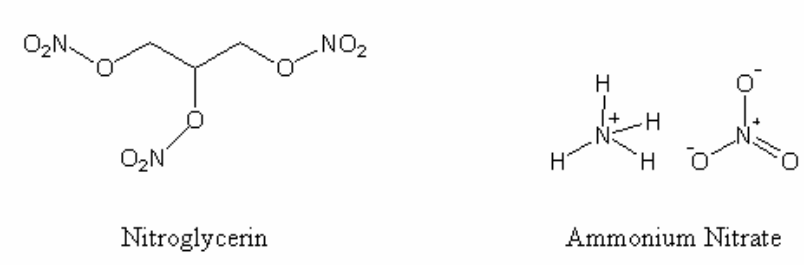


Figure 2: Structures of common commercial explosives

Primary Explosives

Primary explosives are often used to detonate a secondary explosive because their detonation is rapid and powerful enough to produce a shock wave that can detonate another explosive; their explosive power is generally less than that of secondary explosives, however, due to their sensitivity to heat, shock, and friction and their ability to be ignited by a simple flame or spark, they are used in small quantities. Primary explosives are often found in detonators and blasting caps and can be initiated with a firing pin or from the shock produced by an exploding bridge wire [2].

Discovered by von Lowenstern during the 17th century, mercury fulminate was the first primary explosive; however, it did not gain use as an explosive until the start of the 19th century after Edward Howard determined that it could be used to initiate black powder. Typically a gray powder, mercury fulminate is impact and friction sensitive as well as thermally unstable, and because it is a mercury containing compound, it is toxic [2]. In 1891, Curtius created lead azide through the addition of lead acetate to either sodium or ammonium azide. Two years later, an explosion led to an investigation into the explosive properties of lead azide, but it was not until 1907 that Wohler proposed lead azide as a substitute for mercury fulminate; it finally gained use as an explosive in 1920. Lead azide is more stable than mercury fulminate in dry conditions, but becomes unstable when exposed to moisture, an oxidizer, or ammonia. In comparison to mercury fulminate, it is less sensitive to impact but more sensitive to friction [4]. Due to its decreased sensitivity to impact, it is often combined with lead styphnate in detonators which increases its ignitability. Similarly synthesized as lead azide, silver azide will initiate at a lower temperature than lead azide and is even less sensitive to impact and friction [4]. A common

primary explosive that is often found in commercial blasting caps is diazodinitrophenol (DDNP). It is far less sensitive to impact and friction than the other primary explosives, is non-hygroscopic and only slightly soluble in water [2]. In 1910, Tetrazene was discovered by Hoffmann and Roth, and its explosive properties were first presented by Rathsburg in 1921. Stable at room temperature, it is a pale yellow crystalline material that is slightly hygroscopic, ignites easily, and is more sensitive to impact and friction than mercury fulminate [2, 4]. Tetrazene's detonation power is greater if it is unconfined and therefore it is unsuitable to use in a detonator; it is typically employed as a sensitizing agent in blasting caps. Lead styphnate can be produced by adding lead nitrate to magnesium styphnate. It is non-hygroscopic and cannot be dissolved in most organic solvents; it is also thermally stable, but is very sensitive to flame and spark and is a hazard to handle [4]. Lead styphnate is commonly combined with lead azide and aluminum to create the ASA mixture used in detonators and is frequently used in blasting caps.

Peroxide explosives have become increasingly popular among terrorists and amateur chemists due to the readily available starting materials and seemingly simple, although highly dangerous, synthesis. Triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) do not contain any nitro functional groups but do contain multiple peroxide linkages which have the ability to explode. Compared to the strength of TNT, TATP is about 88% as powerful and HMTD is 60% [7]. Although both explosives have been around since the end of the 19th century, they have never gained military use due to their extreme sensitivity to heat, shock, and friction. Wolffenstein first synthesized TATP in 1895 [8], but it did not start gaining popularity as an explosive until the late 1900s and has become even more popular due to the increase of information available on the internet and the ease of purchasing the starting materials.

HMTD was discovered by Legler during the same time period, and although it is not as powerful as TATP, it is more sensitive and can also react with metals which increase its ability to detonate [6]. Figure 3 provides the structures for the common primary explosives.

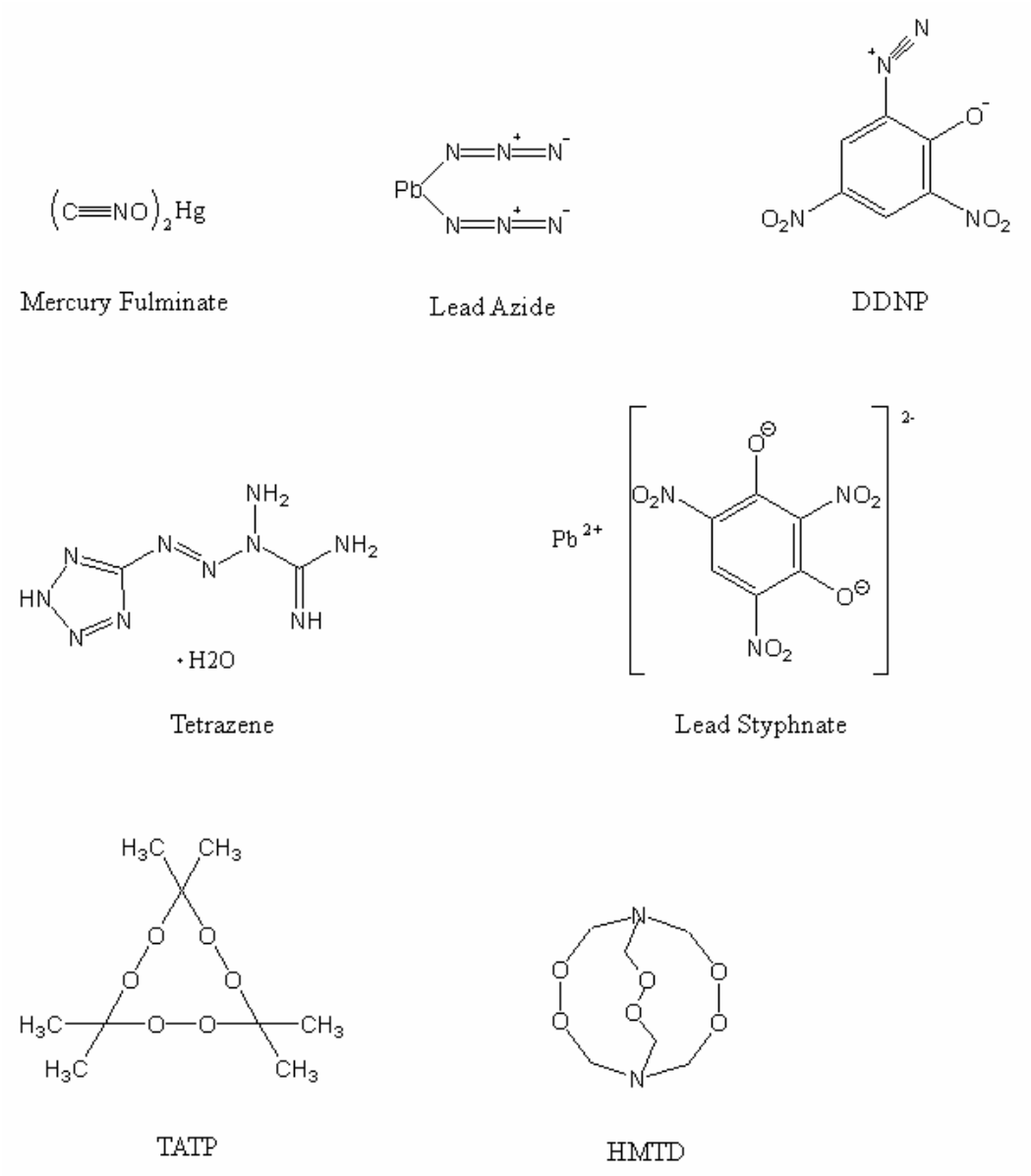


Figure 3: Structures for common primary explosives

TATP

Triacetone triperoxide (TATP), also known as the "Mother of Satan" because it presents as much danger to the maker as it does to the target, is one of the most sensitive explosives with an explosive power almost as strong as TNT [7, 9]. It can be synthesized by combining acetone, hydrogen peroxide, and acid, all three of which can be purchased commercially and the recipe can easily be obtained on the internet, making this one of the easiest HMEs to make but also one of the most dangerous.

TATP has no military use and can only be purchased as a dilute standard due to its sensitivity, and its high vapor pressure of approximately 0.03 torr allows it to readily sublime at room temperature making storage difficult and dangerous [2, 10-12]. There are no chromophoric groups within the molecule so TATP does not have a bound excited state in the UV or visible spectral energy range nor does it fluoresce [13]. Unlike most explosives that contain nitro groups, TATP undergoes an entropic explosion and generally does not generate any heat or flame upon detonation but rather produces ozone and acetone molecules [11]. Due to its chemical structure, when one peroxide bond breaks, a chain reaction follows which cleaves the other C-O and O-O bonds, forming new molecules and not generating any heat [11]. TATP readily forms adducts with ions when analyzed by chemical ionization (CI); TATP can then dissociate to produce fragment ions in which the adduct ion is still attached [14-16]. The melting point for pure TATP is in the range of 95-98.5°C [8, 10, 17, 18] but impurities present in a sample will lead to a depressed melting point that has often been reported to be as low as 73-79°C [6].

Studies on the kinetics of the reaction of acetone and hydrogen peroxide and on the decomposition of TATP have been reported. A couple of studies have reported that reacting acetone and hydrogen peroxide lead to the formation of 2-hydroxy-2-hydroperoxypropane as well as TATP [19, 20]. When the ratio of acetone to hydrogen peroxide was increased, the main product formed after reacting for a few days was TATP [21]. Sauer reported that the peroxides identified in the experiment are intermediate products that further undergo reactions to form the cyclic trimer, TATP. Another study found that the decomposition of TATP begins with the breaking of one of the peroxide bonds and that the decomposition is first order with an activation energy of 151 kJ/mol yielding acetone as a major product [22]. The degradation of TATP in the presence of acid has also been reported. Armitt exposed solid TATP to acid vapor for a period of time, and found that the type of acid used has an effect on the decomposition products and how fast decomposition proceeds [23].

In recent years, TATP has gained popularity among terrorists and has been used in a variety of terrorist attacks all around the world. On August 9, 2001, a suicide bomber blew himself up outside a Sbarro restaurant in Israel, killing himself, 14 others, and injuring around 130 people [24]. Only a few months later, on December 22, 2001, Richard Reid, more commonly known as the "shoe bomber," attempted to ignite explosives in his shoe on American Airlines Flight 63. His shoe contained both PETN and TATP [25]. On July 7, 2005, three suicide bombers entered the London underground subway system and killed themselves and 52 others after detonating homemade explosives (HMEs) that they were carrying on board three different trains; a second attack was made on a double decker bus outside [26]. The HMEs contained TATP and HMTD and were detonated by using an alarm on a cell phone [27]. Joel

Henry Hinrichs III, a student at the University of Oklahoma, killed himself outside a packed football stadium around halftime of the University of Oklahoma-Kansas game. On October 1, 2005, Hinrichs was seated on a bench outside the stadium when his backpack that contained two to three pounds of TATP detonated [28]. Investigators recovered numerous containers of TATP stored in Hinrichs's apartment along with various chemicals to create the explosive; isopropanol was used to neutralize the TATP so it could be safely handled and relocated to undergo a controlled detonation [28]. In Texas City, Texas, an explosion occurred in an apartment on July 19, 2006 that killed one man and injured his roommate. Matthew Rugo was killed after a homemade explosive he had been working with detonated; it was later discovered that he had been synthesizing TATP and after an initial investigation, authorities determined that the explosive material was too dangerous to move, so an evacuation of the apartment complex and a neighboring complex took place and a controlled detonation was conducted [29]. Most recently, terrorist suspect Najibullah Zazi was charged with plotting to use explosive material in an Al Qaeda terrorist plot against the United States. Zazi had purchased large quantities of chemicals used to create TATP from beauty supply stores, and was searching the website of a local hardware store for muriatic acid before his arrest. Zazi was preparing the chemicals in a hotel suite and sent out repeated urgent messages asking for help on the proper synthesis procedure. Websites on "lab safety for hydrochloric acid" were also found bookmarked on his laptop [30].

Recipes to synthesize TATP can be found all over the internet and all starting materials can be picked up at a local hardware store. Acetone, hydrogen peroxide, and acid can be found in a wide range of products from paint thinners to wood bleaching kits to drain cleaners.

Acetone can be purchased relatively pure, hydrogen peroxide varies in concentration from 3-35%, and acid can typically be purchased in concentrations ranging from 40-95%.

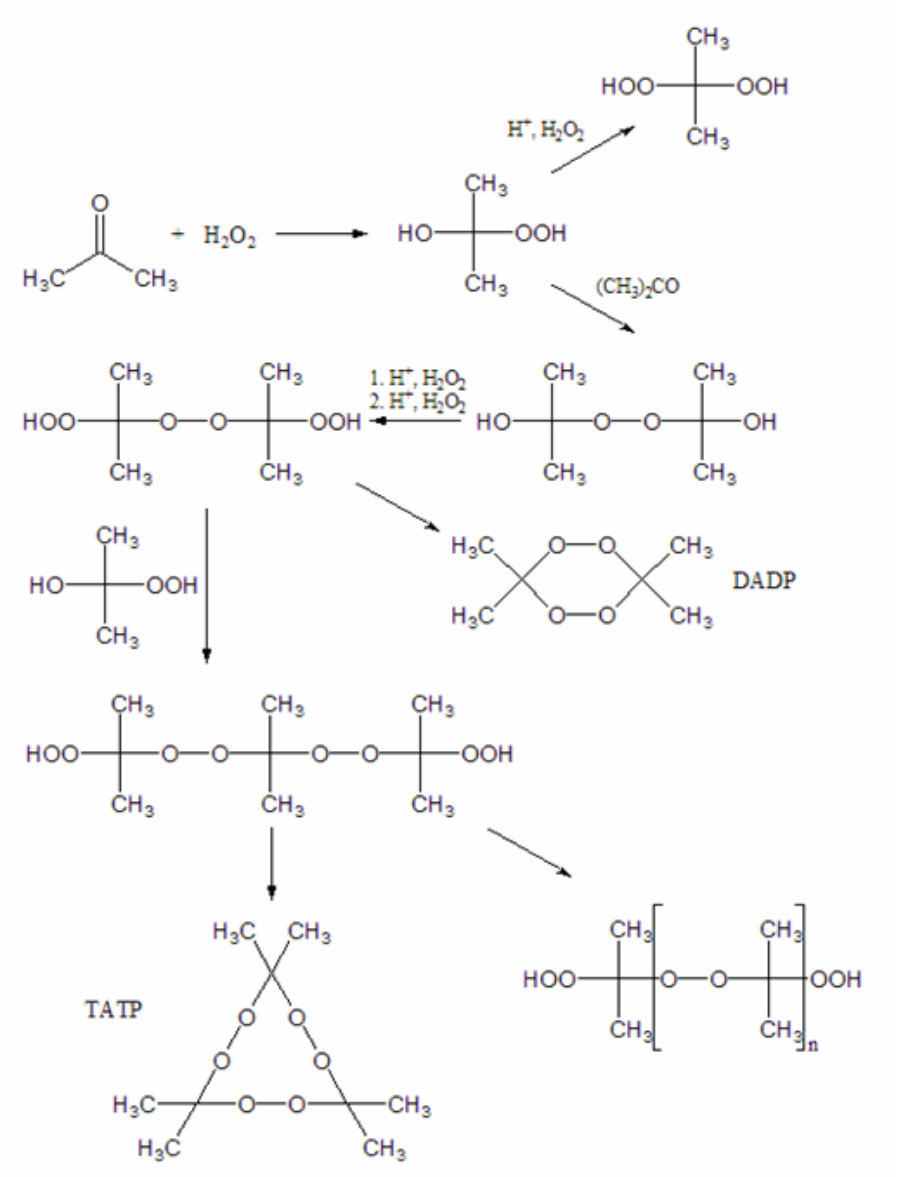


Figure 4: Synthetic mechanism for the formation of TATP

Figure 4 shows the mechanism for the synthesis of TATP. The synthesis of TATP dates back to 1895 when Wolffenstein first made the discovery by reacting a mixture of acetone and hydrogen peroxide for four weeks and collecting the solid material which was recrystallized by ether [8]; it was not until 1959 that Milas reported the first acid catalyzed synthesis of TATP by adding chilled acetone to a mixture of hydrogen peroxide and sulfuric acid [19]. Proven to be an unsafe synthesis because of the excess amount of acid involved (2.6 mL) [22], modern synthesis methods use catalytic amounts of acid to produce large quantities of TATP [11]. TATP samples are typically a combination of the cyclic trimer (TATP) and the cyclic dimer, diacetone diperoxide (DADP), and often the cyclic tetramer, tetraacetone tetraperoxide (TrATrP), as well as numerous peroxide oligomers [31]. Organic peroxides have been studied extensively in the past [8, 19, 32-37] and are becoming increasingly important due to their presence in TATP samples as intermediate products [31, 38, 39].

Even though there are variations within the syntheses, internet recipes for making TATP are very similar. Some of the recipes call for concentrating the hydrogen peroxide if it is weak by carefully boiling away the water; however, if low concentration peroxide is to be used, the ratio of peroxide to acetone is increased. Acid is added slowly to the mixture of hydrogen peroxide and acetone while keeping the temperature of the reaction mixture below 10°C in an ice bath. After the reaction has gone for 24 hours, the precipitate is filtered (internet recipes suggest the use of a coffee filter or paper towel), washed with water to neutralize the acid, and set aside to dry.

Because TATP does not contain any nitro groups or metals, analytical methods that are used to detect other explosives such as TNT and RDX are less sensitive to TATP or are not

applicable, such as thin layer chromatography (TLC), gas chromatography-thermal energy analysis (GC-TEA), liquid chromatography-thermal energy analysis (LC-TEA), high performance liquid chromatography with an ultraviolet detector (HPLC-UV), and ion chromatography (IC) [2]. Due to the danger that this explosive presents to investigators and analysts, methods that can positively identify TATP are most desired. Methods with low limits of detection are also necessary to analyze TATP post-blast residue because the high volatility of the explosive can result in minimal post-blast residue [40].

Numerous analytical methods have been reported for the analysis of TATP. Some of the earlier techniques included IR spectroscopy, NMR spectroscopy, electron ionization-mass spectrometry (EI-MS), chemical ionization-mass spectrometry (CI-MS), and melting point analysis [41, 42]. More recent techniques include ion mobility spectrometry (IMS) [43] and, desorption electrospray ionization-mass spectrometry (DESI-MS) [14, 44]. Most commonly, however, analytical methods involving chromatography are employed because they allow for the simultaneous analysis of both TATP and HMTD. Gas chromatography-mass spectrometry (GC-MS) analysis has been reported using EI-MS [40, 45, 46] and both positive and negative CI-MS [42, 46, 47]. For the analysis of post-blast residue, solid-phase microextraction (SPME) sampling followed by GC-MS analysis has been reported [40]. Liquid chromatography-mass spectrometry (LC-MS) analysis is becoming increasingly popular due to the volatility of TATP and its degradation in the injector port of the GC. A few methods for the detection of TATP using atmospheric pressure chemical ionization-mass spectrometry (APCI-MS) have also been reported [48-50].

Improvised Explosive Devices

IEDs are the most common weapon of choice among terrorists today. They are frequently employed in suicide bomber missions. The sole purpose of an IED is to cause death, injury, and destruction. They can be created from a wide variety of explosives and containers and often include other pieces of metal to act as shrapnel, deadly toxins, or radiological material. Even though the variation of IEDs is great, they typically contain a trigger attached to a fuse which is attached to the main charge [6]. The types of explosives that are often found in IEDs vary widely from the use of military or commercial explosives to a variety of homemade explosives (HMEs), which are becoming increasingly popular due to the greater availability of resources. The most commonly encountered IED is the pipe bomb which is a steal pipe enclosed on both ends, housing the energetic material inside, but IEDs can also be as elaborate as Vehicle Born Improvised Explosive Devices (VBIEDs) which are a car or truck driven by a suicide bomber containing the explosive device.

Instrumentation for Explosives Analysis

The analysis of explosives can be accomplished using a variety of analytical techniques; the instrumentation employed in this research includes gas chromatography-mass spectrometry (GC-MS), electrospray ionization-mass spectrometry (ESI-MS), atmospheric pressure chemical ionization-mass spectrometry (APCI-MS), and ion mobility spectrometry (IMS).

Gas Chromatography

Gas chromatography is one of the most widely used chromatographic methods of analysis and functions on the basis of separation using a gaseous mobile phase and a liquid stationary phase. Analysis of a sample begins with the sample being introduced through a heated injector port, which vaporizes the sample that is then carried to the column by the carrier gas. The components in a sample are separated on the column based on their chemical interactions with the stationary phase, and the temperature programming controls how quickly the components will be eluted out of the column; a higher temperature will shorten the analysis time, and often temperature ramps are employed to separate components in a mixture that vary greatly in molecular weight and/or polarity [51]. There are numerous detectors available to interface to a GC with the most common being thermal conductivity detectors (TCD), flame ionization detectors (FID), electron capture detectors (ECD), and mass spectrometers (MS).

Mass Spectrometry

Mass spectrometry allows for the determination of the elemental composition of a sample and can also provide results that are used to generate molecular structures based on the fragmentation patterns of a molecule. Once the sample enters the mass spectrometer, it becomes ionized by an ion source. The mass analyzer sorts the ions based on their mass to charge ratio (m/z) by moving them through an electromagnetic field to the detector that responds in proportion to the abundance of ions. Figure 5 shows a basic set up of a GC-MS.

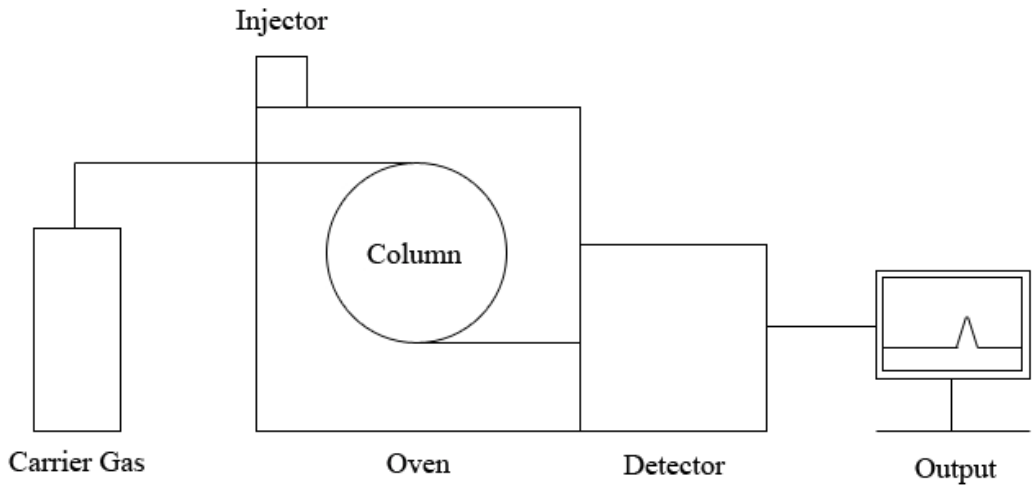


Figure 5: Simple GC diagram

Quadrupole

The quadrupole mass analyzer is commonly found in mass spectrometers, due to its durability, smaller size, cheaper cost, and high scan rate [52]. The four cylindrical rods function as electrodes with both ac and dc currents applied to them. When ions enter the space between the rods, the ac and dc voltages increase and only ions with stable trajectories are allowed through; the remaining ions impact the rods and lose their charge to revert back to neutral molecules. Only the ions whose m/z values fall within the range of the high and low mass filters will have a trajectory stable enough to reach the detector. Figure 6 is an example of a quadrupole mass analyzer.

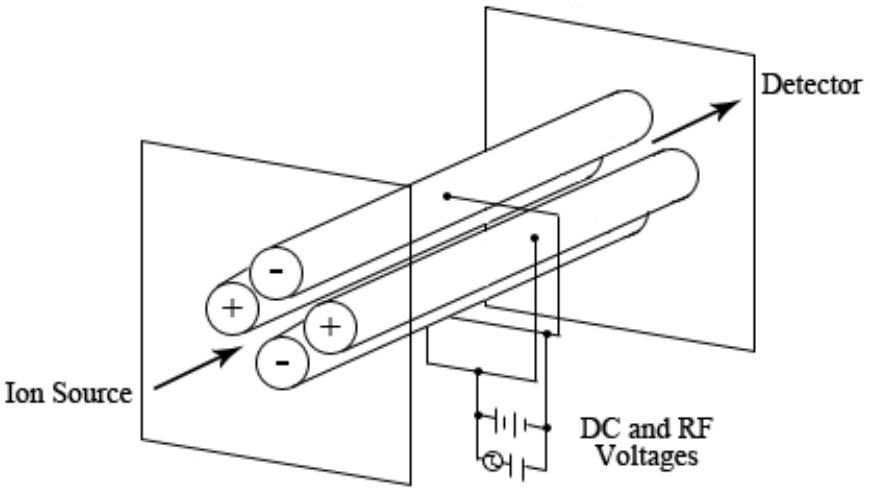


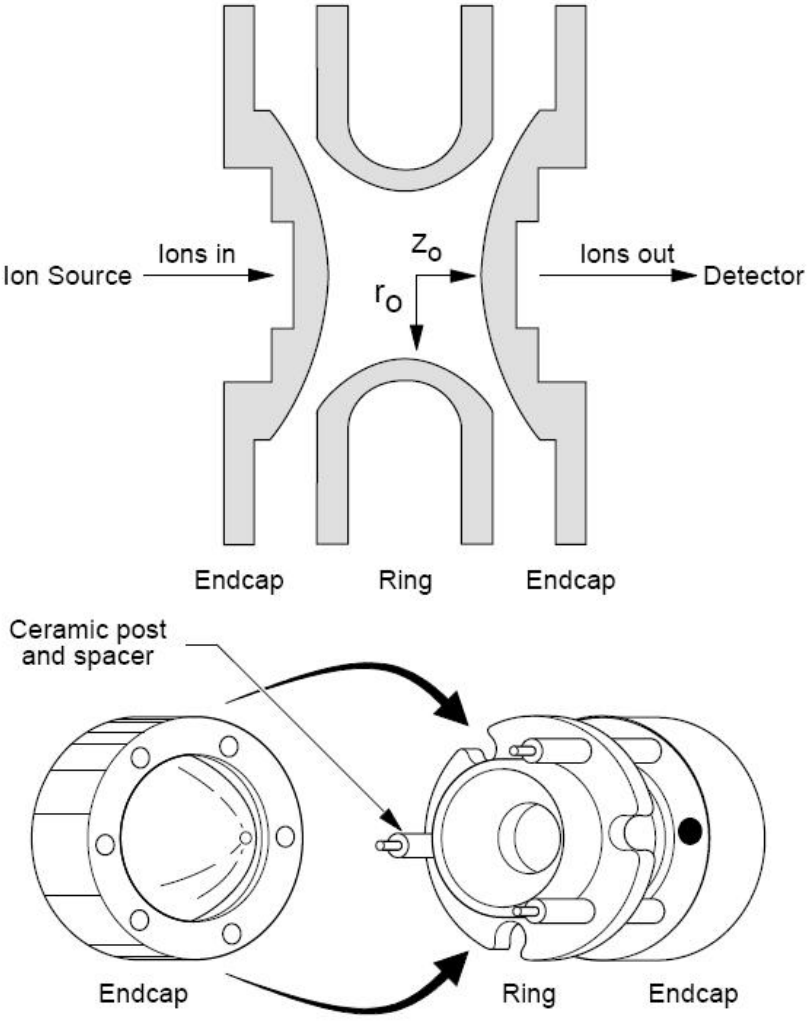
Figure 6: Quadrupole mass analyzer

Ion Trap

An ion trap mass analyzer (shown in Figure 7) can also function as a storage unit for ions for a certain period of time; because of its ability to house ions, tandem mass spectrometry (MS/MS) experiments can be performed with ease. After ions become trapped, their m/z ratios can be measured by applying an RF voltage to the end-cap electrodes which tips the well where they are housed allowing the ions to reach the detector starting with the low mass ions, thereby generating a mass spectrum. The trap is made up of three electrodes – two end-cap electrodes and a ring electrode. The end-cap electrodes either both contain a single aperture which ions pass through if there is an external ion source, or one of the electrodes contains multiple apertures in the case of an internal source. The ring electrode is situated in the center of the two end-cap electrodes; all three electrodes are hyperbolic in shape. Whether an ion is lost or

detected is determined by its stability within the quadrupole field; if the m/z ratio of an ion is below the low-mass cutoff (LMCO) it will not be held in the trap.

Tandem mass spectrometry (MS/MS) can be used to isolate a specific ion in a sample, known as the parent ion, and perform an MS analysis on it, causing it to fragment into ions of lower m/z ratios, known as product ions. Although it is possible to perform MS/MS analysis by setting up two mass analyzers in sequence, a quadrupole ion trap has its advantages; it operates in pulsed mode rather than continuous mode, a specific ion can be selected for analysis and can be fragmented into ions of lower m/z ratios, and those fragment ions can be retained within the trap for subsequent MS^n analysis.



Source: Cooks R., Wong S.H., *Ion Trap Mass Spectrometry.* Current Separations, 1997. 16(3)

Figure 7: Ion trap mass analyzer

Types of Ionization

There are two different types of ionization that are typically used in the source of a mass spectrometer – electron ionization (EI) and chemical ionization (CI).

Electron Ionization (EI)

EI is beneficial when the mass-to-charge ratio of an ion needs to be determined or if the structure of an ion needs to be known [53]. Electrons interact with neutral molecules from the sample in the ion source which causes the neutral molecule to lose an electron and become a radical cation, with the molecular ion designated as $M^{\bullet+}$. The ion source is kept under vacuum and after the molecule undergoes ionization, it reaches the mass analyzer without undergoing subsequent collisions with any other molecules.

$$e^- + M \rightarrow M^{\cdot+} + 2e^- \quad (1)$$

Another common occurrence in EI is the production of charged fragments from the neutral molecule because of the excess amount of energy imparted to it. These fragments typically produced under a current of 70eV, are reproducible from one instrument to another and can be viewed as a fingerprint for the molecule [54].

$$e^- + M \rightarrow M^{\cdot+} + 2e^- + A^+, B^+, \text{etc.} \quad (2)$$

Although it is not as commonly observed, radical anions can be produced in EI as well, however, due to the polarity of the repeller voltage and ion optics, these ions are not observed in normal EI analysis.

$$e^- + M \rightarrow M^{\cdot -} \quad (3)$$

Chemical Ionization (CI)

Chemical ionization (CI) is similar to EI in that the neutral molecules become charged the same way; however, the resulting ions are different. The pressure in the ion source is higher due to the presence of a reagent gas in the ion volume generally around 10^{-3} mbar [54]. Because the sample molecules are not as abundant as the reagent gas molecules, the electrons interact with the reagent gas molecules instead, creating positively charged reagent gas ions. Multiple collisions of the reagent gas ions with the neutral reagent gas molecules occur due to the higher pressure in the source, which then creates protonated reagent gas ions. These ions typically collide with the sample molecules and undergo proton exchange to create a protonated molecular ion, $[M + H]^+$, that does not typically undergo further fragmentation, unlike in EI, and can be detected by the mass analyzer. In negative CI, thermalyzed electrons are captured by the analyte to create an $M^{\cdot -}$ ion which is detected and sometimes exhibits fragmentation.

$$CH_4 + e^- \rightarrow CH_4^+ + 2e^- \quad (4)$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \quad (5)$$

$$CH_5^+ + M \rightarrow CH_4 + MH^+ \quad (6)$$

Another common reaction that can take place between the sample molecules and the reagent gas molecules is adduct formation, $[M + X]^+$ or $[M + X]^-$. Instead of undergoing proton exchange, the reagent gas ion attaches itself to the sample molecule; the use of ammonia as a reagent gas often leads to the formation of a protonated molecular ion or the ammonium adduct, $[M + NH_4]^+$, and sometimes even both.

$$M + NH_4^+ \rightarrow [M+H]^+ + NH_3 \quad (7)$$

$$M + NH_4^+ \rightarrow [M+NH_4]^+ \quad (8)$$

In cases where the molecular ion cannot be determined in EI due to fragmentation, CI is often used as a complimentary analysis because it can provide additional information about the molecular ion; however, little fragmentation occurs in CI, so molecular structures cannot typically be determined from CI data alone.

Liquid Chromatography-Mass Spectrometry (LC-MS)

LC-MS has become a useful instrument for separating and identifying components contained in a sample in recent years due to some of its advantages like speed, reproducibility, and sensitivity [55]. A sample is introduced into the instrument through the injector by a syringe. The sample enters a continuous flow of solvent that serves as the mobile phase. The

mobile phase generally runs through a column which contains a coating that acts as the stationary phase, and the separation of the analytes depends on the interaction with these two phases. Before the separated compounds can be sent to the detector, the solvent and any additives within the solvent need to be evaporated and the analytes ionized; this is accomplished in an interface. The most common interfaces used in conjunction with LC-MS are the electrospray ionization (ESI) interface and the atmospheric pressure chemical ionization (APCI) interface.

Electrospray Ionization (ESI)

ESI is ideal for the analysis of very polar and non-volatile compounds, samples that are already ionized, and compounds with high molecular mass [56]. It is a soft ionization technique, so there is little fragmentation, and often protonated or deprotonated molecular ions are produced; analytes within the sample can also form adducts with the mobile phase solvent. Samples from the LC are introduced through a capillary that is kept under a high potential. At the end of the capillary, the solution is vaporized, creating a fine spray of charged microdroplets. The droplets evaporate with the aid of a countercurrent flow of drying gas which decreases the droplet size, and finally produces ions in the gaseous phase, which are then sent to the detector [56].

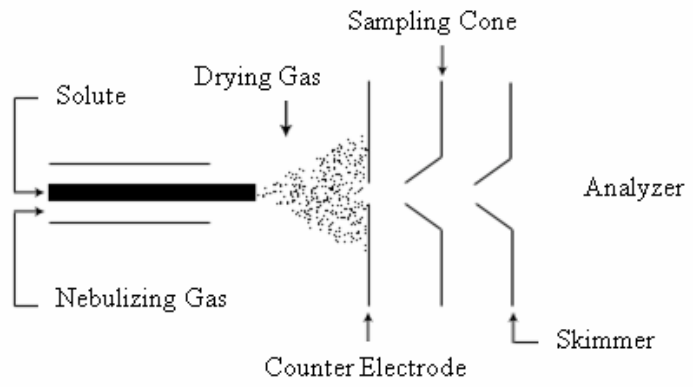


Figure 8: Schematic of an ESI interface

Atmospheric Pressure Chemical Ionization (APCI)

An APCI interface (Figure 9) uses a heated nebulizer and a nebulizer gas to produce droplets from the solvent which is eluted from the column. A combination of heat and gas desolvate the droplets, which produces a vapor containing both solvent and analyte molecules. A high voltage corona discharge needle is used to ionize the solvent molecules in the vapor; these ionized solvent molecules then form adducts with the analyte molecules to ionize the analyte. The ions pass through a drying gas which causes the cluster of ions to separate and subsequently pass to the mass spectrometer. APCI is advantageous because it allows for the analysis of less polar and even neutral analytes with good detection limits. Other advantages of using APCI are that both polar and non-polar solvents can be used for the mobile phase, and concentrated additives can be used as well. APCI follows the basic principles of chemical ionization (CI) – proton transfer, charge exchange, and adduct formation [57].

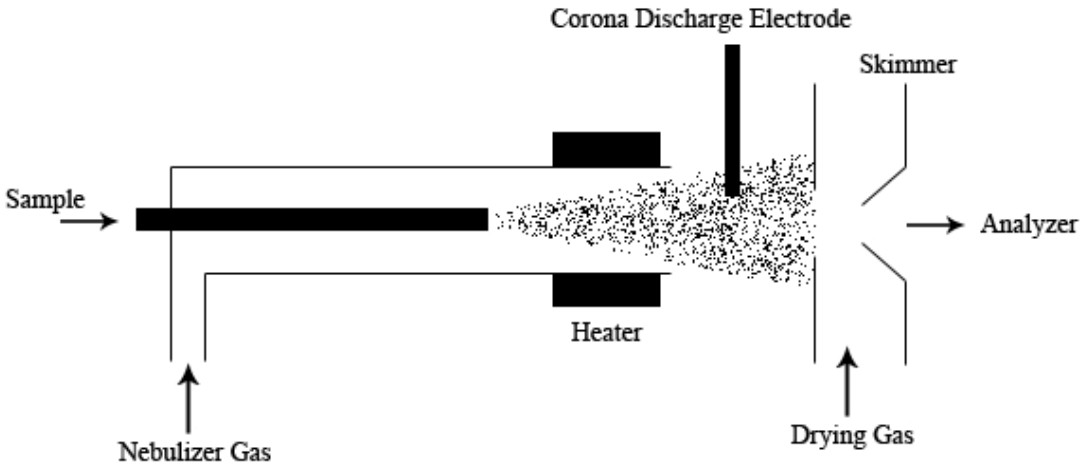


Figure 9: Schematic of an APCI interface

Ion Mobility Spectrometry (IMS)

Ion Mobility Spectrometry (IMS) characterizes compounds based on the drift velocity of their ions through an electric field [58]. A sample is volatilized by a desorber heater and enters the ionization chamber via the inlet where it becomes ionized. The ions are then introduced into the drift region through an ion gate. The ions move through the drift region of the drift tube which has an electric field applied to it and are collected on a detector plate; the amount of time it takes for the ions to reach the detector is the drift time. Once at the detector, the ions are neutralized and a plot of the detector response versus the drift time is generated, known as the mobility spectrum. Positive or negative ions can be collected by varying the direction of the electric field within the drift tube. The IMS is operated in the positive mode for narcotics detection and the negative mode for explosives detection. A simple IMS schematic is shown in Figure 10.

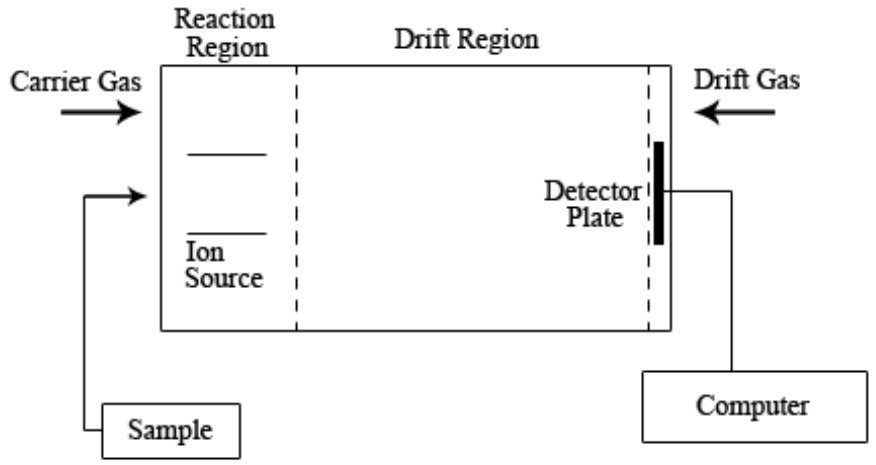


Figure 10: Schematic of an IMS

Sampling Techniques for Explosives Analysis

Solid Phase Microextraction (SPME)

SPME was first introduced by Pawliszyn in 1989 as a simple and rapid technique for the analysis of organic compounds [59]. The SPME fiber assembly is a needle housing a fiber with a sorbent coating. The basic principle behind SPME lies within the attraction between the coating on the fiber and the analytes in a solution, and the small area of the fiber is beneficial for concentrating trace amounts of a compound in a sample [60]. The fiber assembly is placed into a holder with a plunger that exposes and retracts the fiber from the needle where the fiber is located. After the SPME fiber has been exposed to a sample by direct immersion or headspace

absorption, it is subsequently thermally desorbed, usually in the injector port of a GC. The main advantage to using SPME is the simplification of the analysis by combining sampling, extraction, concentration, and sample introduction into just one process [61].

CHAPTER 2: SAMPLE PREPARATION AND INSTRUMENTAL METHODS

Twenty-seven commercially available acetone sources were used to determine if additives present in the acetone source carried through the TATP synthesis and could be detected pre- and post-blast. TATP samples were prepared both in the laboratory and on a larger scale for field analysis.

Sample Preparation

Preparation for the Analysis of Acetone Samples

The acetone sources were analyzed by GC-MS via a direct injection of the acetone sample onto the GC column and by SPME sampling the headspace above the acetone with subsequent desorption in the injector port. A 0.25 µL injection was used for direct injection samples. A 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME was used to sample the headspace over approximately 200 µL of acetone in a 4 mL glass vial with a Teflon septum cap for 10 minutes at room temperature.

TATP Synthesis

TATP samples were synthesized in small batches by licensed personnel in the laboratory at the National Center for Forensic Science. Because the research focuses on the analysis of additives in TATP samples, they were not recrystallized, and coffee filters were used in place of

laboratory filter paper to mimic internet syntheses for all laboratory experiments relating to the impurity analysis. All starting materials were chilled prior to use. 200 µL of acetone was added to a 2 mL plastic microcentrifuge tube suspended in an ice bath. 200 µL of 35% (w/w) hydrogen peroxide was added to the acetone. In 10 µL aliquots, 20 µL of 96% (w/w) sulfuric acid was added slowly to the acetone/hydrogen peroxide mixture. The tube was capped, gently shaken, and submerged in an ice bath for 24 hours. After 24 hours, the precipitate was collected by adding DI water to the microcentrifuge tube, gently stirring the solid with a spatula, and pouring it into a glass funnel lined with a coffee filter. The solid sample was washed repeatedly with DI water until a filtrate pH of 5-5.5 was obtained. The precipitate was carefully transferred to a piece of filter paper where it was dried for 30 minutes behind a blast shield.

Preparation for the Analysis of Pre-blast TATP Samples

Pre-blast samples were analyzed by solution and by SPME. After the TATP had dried for half an hour, approximately 10-12 mg of the material was placed in a 4 mL glass vial with a Teflon lined screw cap. The solid was dissolved in 200 µL of acetonitrile, and a 1 µL injection was used for all pre-blast solution samples. For SPME analysis, 10-12 mg of TATP was placed into a 4 mL glass vial with a Teflon septum cap. A 65 µm PDMS/DVB SPME fiber was used to sample the headspace directly above the solid for 30 minutes at room temperature.

Determining the Concentration of Acetone Additives

Standard solutions containing a mixture of the carry-over additives, including 4-tert-butylcyclohexyl acetate isomers, diethyl phthalate, methyl dihydrojasmonate and benzyl benzoate, were prepared and dilutions ranging from 6.25-100 ng/μL in concentration were made. Calibration curves were generated for each of the components in the solution. A larger batch of TATP was synthesized for some of the samples in this set of experiments to create more concentrated solutions. The synthesis procedure is the same as described above, however, 400 μL of acetone, 400 μL of hydrogen peroxide, and 40 μL of sulfuric acid were used. After drying the solid for 30 minutes, 10-75 mg of TATP was placed in a 4 mL glass vial and dissolved in 200-500 μL of acetonitrile. These samples were directly injected into the GC using 1-2 μL injections; the injected amount was increased to 3-4 μL if the analyte of interest was not concentrated enough and fell below the lowest concentration in the calibration curve.

Determination of the Lifetime of Carry-Over Impurities

Samples were periodically taken from a batch of TATP that was allowed to air dry in a fume hood over a period of time, and the samples were analyzed to determine how long the additives could be detected. For the TATP batches, four to six sub-samples were taken up to 24 hours if possible; approximately 10 mg of TATP was placed into a 4 mL glass vial with a Teflon septum cap. The headspace was sampled by a 65μm PDMS/DVB SPME for 30 minutes at room temperature. The SPME fiber was desorbed in the inlet of the GC. The amount of carry-over

present in the samples was determined by plotting the integrated areas of the peak corresponding to the impurity from the chromatogram divided by the sub-sample weight.

Analysis of TATP Samples for the Presence of Oligoperoxides

TATP samples were synthesized in accord with methods previously reported in the literature [8, 62]. Some of the TATP samples were sublimed by placing TATP crystals in a microscope well slide, covering the slide with a flat microscope slide, and heating the samples on a dry bath at 50-85°C until TATP crystals formed on the microscope slide.

TATP samples that were analyzed by ESI-MS were dissolved in methanol and samples that were analyzed by GC-MS were dissolved in either pentane or methylene chloride and subsequently dried with anhydrous sodium sulfate before being injected into the GC.

Analysis of TATP Samples Synthesized with Different Acids

TATP samples were synthesized using sulfuric acid (H_2SO_4), hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and nitric acid (HNO_3). After synthesis, the samples were gravity filtered and washed up to a pH of greater than 7 with a sodium bicarbonate solution and allowed to dry for 30 minutes. Samples were washed to a pH greater than 7 to ensure that any acid was removed from the outside of the crystals. A portion of the synthetic samples was recrystallized to allow removal of any acid potentially trapped in the crystals. TATP samples were dissolved in methanol with gentle heating to give concentrated solutions that were cooled at 0°C for 24-48

hours. Samples were recrystallized multiple times. The recrystallized TATP was filtered using vacuum filtration and was washed repeatedly with DI water.

Approximately 10-12 mg of non-recrystallized and recrystallized TATP were placed in 4 mL vials with Teflon septum caps. The headspace was sampled for 20 minutes at room temperature using a 65 μm PDMS/DVB SPME and was desorbed in the GC inlet. A second set of samples comprised of 10-12 mg of non-recrystallized and recrystallized TATP were placed in 4 mL vials with septum caps. The vials were heated at 50°C for 20 minutes and the headspace was sampled with a 65 μm PDMS/DVB SPME for 10 minutes. These samples were also analyzed by GC-MS.

The behavior of the non-recrystallized and recrystallized TATP at room temperature and upon heating was compared based on the GC-MS analysis. Crystals of the non-recrystallized and recrystallized TATP samples were placed in a glass capillary tube and analyzed using a Meltemp device to determine the melting point of the non-pure and pure material. Crystals from the same material were also directly desorbed into the IMS and analyzed in the negative mode.

Sample Preparation for Post-Blast TATP Samples

TATP samples that were to be used for detonation followed the same synthetic procedure, but the analysis of the samples after detonation varied in order to try and determine if solution or SPME sampling produced the best results for the detection of the carry-over impurities.

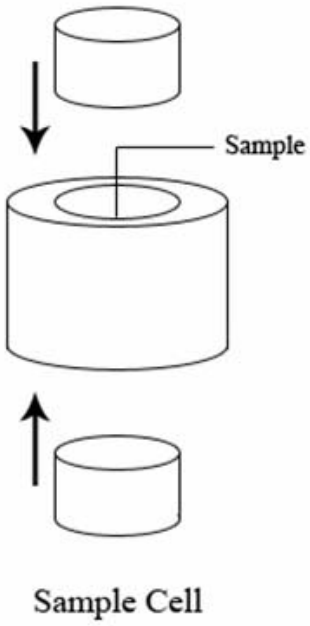


Figure 11: Fallhammer and a schematic of the cell

Approximately 10 mg of TATP was detonated using a Bam Fallhammer device (Figure 11) by dropping a 5 kg weight from a height of 20 cm to impart 10 J of energy into the TATP. Immediately after detonation, the sample cell components were collected and placed into a 22 mL vial with a Teflon septum cap. Products were analyzed in one of two ways. (1) For solution analysis, 300 µL of pentane was washed over the Fallhammer cell to extract any compounds present. A 2 µL injection was analyzed by GC-MS. (2) The cell was collected and placed into a 22 mL vial with a Teflon septum cap. The vial was placed onto a dry bath and heated at 60°C

while sampling the headspace above the pieces with a 65 µm PDMS/DVB SPME for 15 minutes. After sampling, the SPME fiber was desorbed in the injector port of the GC.

Large Scale TATP Sample Preparation for Pre- and Post-blast Analysis

TATP Synthesis

The syntheses of the larger batches of TATP were handled by specially trained and licensed personnel using extreme caution. Six different samples were synthesized using a variety of acetones, a few different peroxide sources with varying concentrations, and sulfuric acid to produce samples weighing 2-90 grams.

Table 1: Synthesis materials

Sample	Acetone Source	Peroxide Source
Control #1	HPLC grade	30% CCI
Control #2	HPLC grade	35% Acros
Sample #3	Acetone #21	35% Acros
Sample #4	Acetone #3	35% Acros/30% CCI
Sample #5	Acetone #22	5-20% Hair Developer
Sample #6	Acetone #27	30% CCI

All samples were synthesized using small amounts of sulfuric acid. Sample 1 was synthesized using 30 mL of acetone and 50 mL of 30% (w/w) hydrogen peroxide. Sample 2 was synthesized from 60 mL of acetone and 100 mL of 35% (w/w) peroxide. Two batches of TATP from the large scale synthesis of Samples 3-5 were combined for detonation. Sample 3 was prepared by mixing 60 mL of acetone with 100 mL of 35% (w/w) peroxide. The Sample 4 batch

was synthesized using 60 mL of acetone and 100 mL of a 60:40 mixture of 30% and 35% (w/w) peroxides respectively. The Sample 5 batch was prepared from 60 mL of acetone and 100 mL of a hair developer containing 5-20% (w/w) hydrogen peroxide. Sample 6 was synthesized using 210 mL of acetone and 350 mL of 30% (w/w) peroxide.

Samples were synthesized in a flask that was submerged in an ice bath. The acetone and hydrogen peroxide were combined in the flask and allowed to cool to below 5°C. The acid was added dropwise with constant stirring and monitoring the temperature to keep it below 10°C. The samples were placed in a freezer to react for 12-24 hours. The precipitate was carefully collected by gravity filtration and washed repeatedly with DI water until the pH was 5 or greater. The material was placed onto filter paper and allowed to air dry.

Sample Preparation for Pre-blast Analysis

After 30 minutes of drying the solid, samples were collected for analysis of the melting point of the material, analysis for carry-over products by solution and SPME, and analysis for the presence of peroxide oligomers. Solution samples were prepared by placing approximately 12mg of TATP in a 4 mL glass vial and adding 200 µL of acetonitrile. TATP (12 mg) was placed into a second 4 mL glass vial with a septum cap, and the headspace was sampled with a 65 µm PDMS/DVB SPME fiber for 30 minutes at room temperature. For the analysis of the oligoperoxides, approximately 10 mg of TATP was dissolved into 300 µL of methanol. The solution samples and the SPME fibers were kept in a freezer and frozen until analysis by GC-MS or APCI-MS could be performed. For GC-MS analysis, a 1 µL injection was used for all solution samples.

Sample Preparation for Post-blast Analysis

The samples to be detonated were placed on 25.4 cm x 25.4 cm x 0.48 cm aluminum plates that were set on top of 30 cm x 30 cm x 2.54 cm steel plates. Following detonation, the aluminum plates were swabbed with two 2 cm^2 cotton swabs and were placed into 8 mL glass vials with Teflon septum caps. One swab was to be sampled by SPME and analyzed by GC-MS and the other was immediately analyzed by IMS. Each aluminum plate was sealed in a K-pak bag and placed on ice in a cooler until sampling and analysis could be performed. The vials with the cotton swabs were heated on a dry bath at 40°C and the headspace was simultaneously sampled with a 65 μm PDMS/DVB SPME for 30 minutes, followed by desorption of the fiber in the inlet of the GC. The K-pak bags containing the aluminum plates were heated for 10 minutes in an oven at 40°C. The bags were then removed and the headspace in the bag was sampled by SPME for 30 minutes with a 65 μm PDMS/DVB fiber and was subsequently analyzed by GC-MS.

Instrumental Methodology

Gas Chromatography-Mass Spectrometry

Experiments pertaining to the analysis of acetone carry-over products in TATP syntheses both in the laboratory and for the large-scale tests were performed by gas-chromatography-electron ionization-mass spectrometry [GC-(EI)MS]. An Agilent 6890 GC interfaced to an Agilent 5973 MS was used for all GC-(EI)MS experiments. An HP-5MS capillary column 30 m

in length, 0.25 mm in internal diameter, with a 0.25 μm coating was used, and was interfaced to the single quadrupole mass spectrometer, with the helium carrier gas flow rate at 1.2 mL/min. Injections were made manually and performed in a splitless mode for every experiment. The temperature programming of the GC was optimized for the analysis of the carry-over products and differs from the previously reported optimized methodology for the detection of TATP using the same instrument [16]. The injector port temperature was set at 225°C, with an initial oven temperature of 50°C held for 3 minutes, followed by a temperature ramp of 10°C/min until 180°C, followed by a second temperature ramp of 20°C/min until a final temperature of 280°C, which was held for 5 minutes. The MS source was operated at a temperature of 200°C at 70eV.

The same GC-MS was used for the analysis of TATP synthesized with different acids, but with a slightly different method. The helium flow rate was increased to 1.6 mL/min and the injector port temperature was lowered to 110°C. The initial oven temperature was 50°C and was held for 3 minutes before being ramped 10°C/min to 180°C. The temperature was held at 180°C for one minute and then ramped at 20°C/min until the oven reached 250°C, which was held for 5 minutes. Both the MS source and the quadrupole were operated at 100°C.

All GC-(CI)MS analyses of TATP samples for the presence of oligomeric peroxides were performed using a Trace GC 2000 interfaced to a Polaris Q Ion Trap mass spectrometer utilizing a RTX-5MS capillary column 27 m in length, with a 0.25 mm internal diameter, and with a 0.25 μm coating. All experiments were performed using a 1 μL splitless manual injection with a helium gas flow rate of 1.2 mL/min. The injector port temperature was set at 110°C, and the oven temperature was held for 3 minutes at 50°C and then ramped for 8°C/min until it reached 180°C. Positive chemical ionization was performed using ammonia gas at a flow rate of 2

mL/min. The source of the mass spectrometer was operated at 100°C and in full scan mode (m/z 30-300).

Direct Insertion Probe

A Direct Insertion Probe (DIP) was also used for the analysis of TATP samples for the presence of oligoperoxides. Solid samples of TATP were analyzed by ammonia positive ion GC-(CI)MS using a DIP with the Polaris Q ion trap mass spectrometer as mentioned in the previous section. Solid samples were placed in a sample cup and introduced directly into the mass spectrometer. The probe started at a temperature of 30°C and was held for 30 seconds before being ramped 100°C/min to reach a final temperature of 180°C which was then held for 2 minutes.

Liquid Chromatography-Mass Spectrometry

ESI-MS was used for the analysis of oligoperoxides in TATP samples synthesized in the laboratory. A Spectra System SCM 1000 pump was coupled to an LCQ Duo ion trap mass spectrometer with an ESI interface. A 75:25 methanol/water solution was pumped at a flow rate of 200 μL/min and a 5 μL/min flow of either 4 mM sodium acetate or ammonium acetate was added to the flow by a syringe pump as a complexing additive. Samples were injected through a 5 mL sample loop. Some ESI-MS experiments utilized an Agilent 1100 HPLC coupled with an Agilent 1100 MSD quadrupole mass spectrometer equipped with an ESI interface and was operated using a previously reported methodology [39].

APCI-MS was used for the analysis of oligomers present in the large scale TATP samples and for the analysis of oligomers present in samples synthesized with various acids. The same LCQ Duo ion trap mass spectrometer was used but was coupled with an APCI interface and operated in the positive mode. The flow rate of the mobile phase was set at 106 μL/min and consisted of a 75:25 methanol/water solution with a 5 μL/min flow of 4 mM ammonium acetate complexing additive. The capillary was operated at 36.81 V at 100°C, and the corona discharge was operated at 4.81 kV with a current of 5.17 μA. An optimal vaporizer temperature of 360°C was also employed.

Ion Mobility Spectrometry

An Ionscan 400B IMS was operated in the positive mode for the analysis of the swabs of post-blast TATP residue sampled during the large-scale field tests. The drift heater was set at 212°C with an inlet heater of 285°C. The desorber heater temperature was 205°C and the drift flow rate was 300 mL/min. The analysis time for a sample was 15 seconds with 47 segments per analysis.

The IMS was used in the negative mode for the analysis of TATP samples synthesized using various acids. The temperatures for the drift, inlet, and desorber heaters were 112°C, 240°C, and 230°C respectively. The drift flow rate was set at 351 mL/min. The total analysis time for samples was 6.6 seconds with 15 segments per analysis.

TATP can be detected in both the positive and negative mode, but it can be detected with greater sensitivity in the positive mode.

CHAPTER 3: RESULTS

Some of the trace-level organic additives identified in the acetone sources were detected in pre- and post-blast samples of TATP. Studies were conducted to determine how long these additives could be detected in a given sample of TATP that was allowed to air dry and in what concentration they were present. Investigations were also conducted into the presence of peroxide oligomers in TATP samples and possible effects from synthesizing TATP with different acids. Detection of the carry-over impurities in TATP was also investigated after detonation.

Analysis of Acetone Sources for the Presence of Additives

Table 2 lists the acetone sources used in this research by name and the number used to identify them. The chromatograms resulting from the analysis of each of the industrial and commercial acetone sources were analyzed for the presence of any organic additives that were in the acetone. Listed ingredients from the bottle were identified when possible but numerous other compounds were present in a majority of the acetone sources. These compounds were identified by a greater than 90% match with the National Institute of Standards and Technology (NIST) Electron Ionization Mass Spectral (EI-MS) library and had to share at least 4 major ions. Standards were purchased for the most common additives identified in the acetone samples. Mixtures of these standards were created and were analyzed via direct injection into the GC-MS using the same methodology as the analysis of the acetone samples. The retention times and the mass spectral data for the standards were compared to the same data obtained for the compounds

from the analysis of the acetone sources. The compounds were confirmed with a retention time match of ±0.1 minutes and the presence of at least 4 of the major ions. Table 3 lists the common additives identified in the acetones and the letters used to identify them, along with the International Union of Pure and Applied Chemistry (IUPAC) name and Chemical Abstracts Service (CAS) number. The compounds in which standards were purchased for are also indicated.

Table 2: Acetone sources

Acetone Number	Acetone Product Name
1	Home Depot
2	Beauty Secrets Clear
3	Beauty Secrets Red
4	Sally Hansen Yellow
5	Perfection Yellow
6	Sally Hansen Blue
7	Perfection Purple
8	Cutex Gold
9	Publix Clear
10	Publix Yellow
11	Publix Green
12	ONYX Professional
13	Clear "Professional Use Only"
14	CVS Blue
15	Scented "Professional use only"
16	CVS Purple
17	Cutex Blue
18	Cutex Purple
19	Diamond Acetone
20	Studio 35 Regular
21	Studio 35 Mango Mandarin
22	Studio 35 Coconut Lime
23	Crown
24	Sunnyside
25	USA
26	Ace
27	Beauty Secrets Red #2

Table 3: IUPAC names and CAS numbers for common acetone additives

Analyte ID	CAS #	IUPAC Name	Common or Other Name
A	108-38-3	1,3-dimethyl-benzene	m-xylene
B	98-82-8	(1-methylethyl)-benzene	cumene
C*	108-32-7	4-methyl-1,3-dioxolan-2-one	propylene carbonate
D	138-86-3	1-methyl-4-isopropenylcyclohexene	limonene
E	124-18-5	decane	
F*	106-65-0	dimethyl butanedioate	butanedioic acid, dimethyl ester
G*	1119-40-0	dimethyl pentanedioate	pentanedioic acid, dimethyl ester
H	140-11-4	phenylmethyl acetate	acetic acid, phenylmethyl ester
I	106-32-1	ethyl octanoate	octanoic acid, ethyl ester
J	112-40-3	dodecane	
K	1731-84-6	methyl nonanoate	nonanoic acid, methyl ester
L*	627-93-0	dimethyl hexanedioate	hexanedioic acid, dimethyl ester
M	100-86-7	2-Methyl-1-phenyl-2-propanol/alpha-alpha-dimethyl-benzeneethanol acetate	
N(i-ii)*	32210-23-4	4-tert-butylcyclohexyl acetate	vertenex
O	103-37-7	phenylmethyl butanoate	butanoic acid, phenylmethyl ester
P	104-61-0	(5S)-5-pentyloxolan-2-one	dihydro-5-pentyl-2(3H)-furanone
Q	2705-87-5	prop-2-enyl 3-cyclohexylpropanoate	cyclohexanepropanoic acid, 2-propenyl ester
R	103-95-7	3-(4-isopropylphenyl)-2-methylpropionaldehyde	cyclamen aldehyde
S	103-60-6	2-methyl-propanoic acid, 2-phenoxyethyl ester	phenoxy ethyl isobutyrate
T	51115-63-0	2-methylbutyl 2-hydroxybenzoate	2-hydroxy-benzoic acid, 2-methylbutyl ester
U*	80-54-6	3-(4-tert-Butylphenyl)-2-methylpropanal	lilial
V	90-17-5	(2,2,2-trichloro-1-phenylethyl) acetate	alpha-(trichloromethyl)-benzenemethanol acetate
W	104-67-6	5-heptyloxolan-2-one	5-heptyldihydro-2(3H)-furanone
X	2050-08-0	pentyl 2-hydroxybenzoate	2-hydroxy-benzoic acid, pentyl ester
Y*	84-66-2	diethyl benzene-1,2-dicarboxylate	diethyl phthalate
Z*	24851-98-7	2-(3-oxo-2-pentylcyclopentyl)acetate	methyl dihydrojasmonate

Analyte ID	CAS #	IUPAC Name	Common or Other Name
AA	101-86-0	2-Hexyl-3-phenyl-2-propenal	2-(phenylmethylene)-octanal
BB*	120-51-4	phenylmethyl benzoate	benzyl benzoate
CC*	1222-05-5	4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]isochromene	galaxolide
DD	88-29-9	7-acetyl-6-ethyl-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene	musk 36A

(i-ii) Mixture of cis and trans isomers

* Standard available

As mentioned above, some of the acetone sources contained numerous organic additives that were identified; however, additives were not present in every acetone source. All acetones were analyzed via a direct injection of the acetone and by sampling the headspace above the acetone with a SPME fiber to compare the two methods and see if the same components were identified.

An example of the total ion chromatogram of an acetone that was determined to contain no additives is shown in Figure 12 (direct injection and SPME) and an example of the total ion chromatogram of an acetone that contains numerous additives is shown in Figure 13 (solution and SPME), but not all additives that were identified in the sample are labeled.

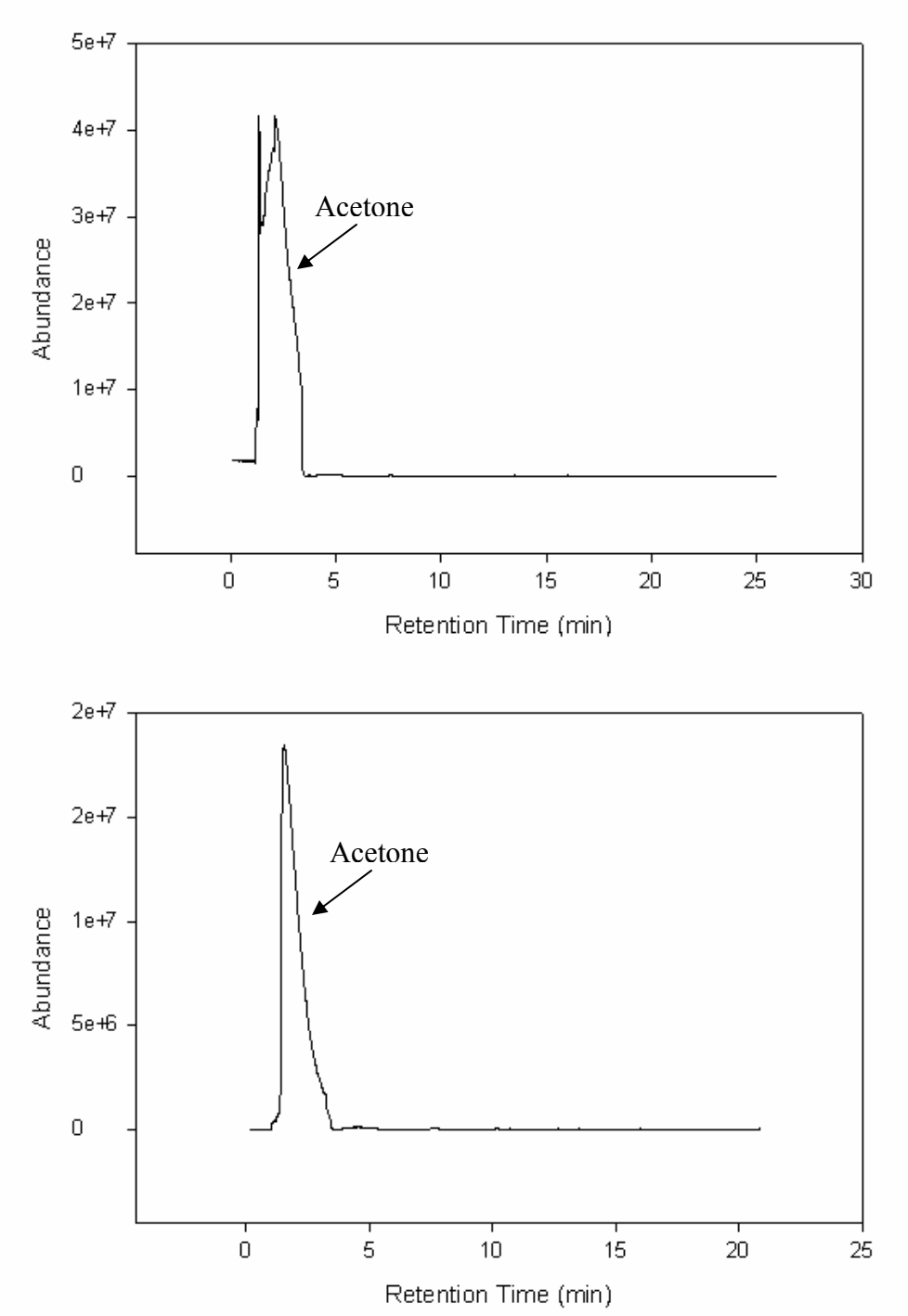


Figure 12: Acetone #12 analyzed via direct injection (upper) and SPME (lower) by GC-MS that did not contain additives

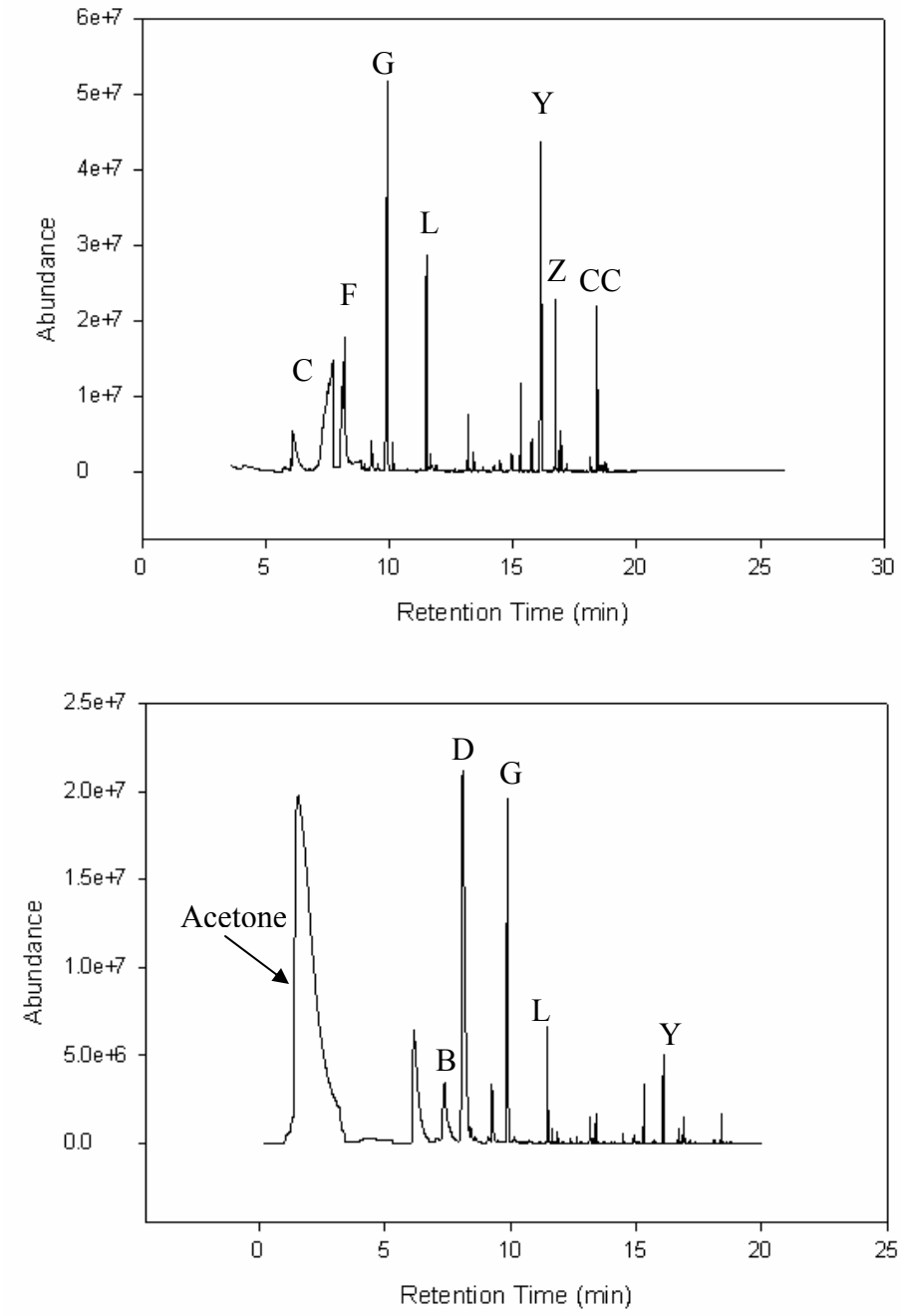


Figure 13: Acetone #22 analyzed via direct injection (upper) and SPME (lower) by GC-MS that contained numerous carry-over additives. (C) propylene carbonate, (F) butanedioic acid, dimethyl ester, (G) pentanedioic acid, dimethyl ester, (L) hexanedioic acid, dimethyl ester, (Y) diethyl phthalate, (AA) methyl dihydrojasmonate, (CC) galaxolide, (B) cumene, (D) limonene. Acetone elution not shown in the first chromatogram.

Analysis of Pre-blast TATP Samples

Analysis of TATP Samples for the Presence of Acetone Carry-Over

All twenty-seven of the acetone sources were used to synthesize two separate batches of TATP to be used for the analysis of carry-over products. The total ion chromatograms for all of the TATP samples, analyzed by both SPME and solution, were carefully compared for the presence of any impurities that were also identified in the acetone samples. Additives that carried over through the TATP synthesis could be identified in 14 out of the 27 solution samples and 18 out of the 27 SPME samples; additives identified in some acetone sources did not carry-over to the TATP. Tables 4 and 5 list the impurities identified in the TATP (listed by letter) and in which acetone (listed by number) they were detected in. Table 4 lists the additives that carried over from the acetone sources by analyzing a solution of TATP and Table 5 lists the additives identified by SPME sampling the headspace above the TATP.

Table 4: TATP solution samples with carry-over impurities from the acetone source

	Acetone																										
Analyte	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
B							x		x	x	x			x			x	x			x	x					
L																x											
N (i)							x	x									x	x									
N (ii)							x	x						x			x	x									
R											x																
U																						x					
Y				x						x											x	x					
Z																						x					
BB			x								x										x						x
DD				x																							

Table 5: Acetone carry-over identified in TATP sampled by SPME

	Acetone																										
Analyte	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
A																									x		
B					x		x	x	x	x	x			x		x	x	x		x	x	x					
C					x	x		x		x	x			x			x	x				x					
E																										x	
F				x		x		x						x			x	x									
H				x		x								x													
I															x												
J																										x	
K																	x										
L				x		x		x						x			x	x									
M																					x						
N (i)					x		x	x						x		x	x	x		x	x						
O			x																								
P																						x					
N (ii)					x		x	x						x		x	x	x		x	x	x					
Q															x												
S							x																				
V				x		x																					
W																					x						
X							x																				
Y				x	x			x		x	x			x		x	x	x			x	x					
Z																					x	x					
BB			x		x		x				x			x			x			x	x						x
CC																						x					

The following chromatograms are representative of some of the results achieved during the analysis of the pre-blast material. The major analytes that were identified in the pre-blast samples that carried over from the acetone source are labeled, along with acetone, DADP, and TATP if present. Chromatograms for TATP solution and SPME samples synthesized with the same acetone source are given to compare the two sampling methods. Figure 14 is an example of a TATP sample that was synthesized with an acetone that contained additives but the additives failed to carry over through the TATP synthesis. Figure 15 is an example of a TATP sample where multiple additives carried through the synthesis.

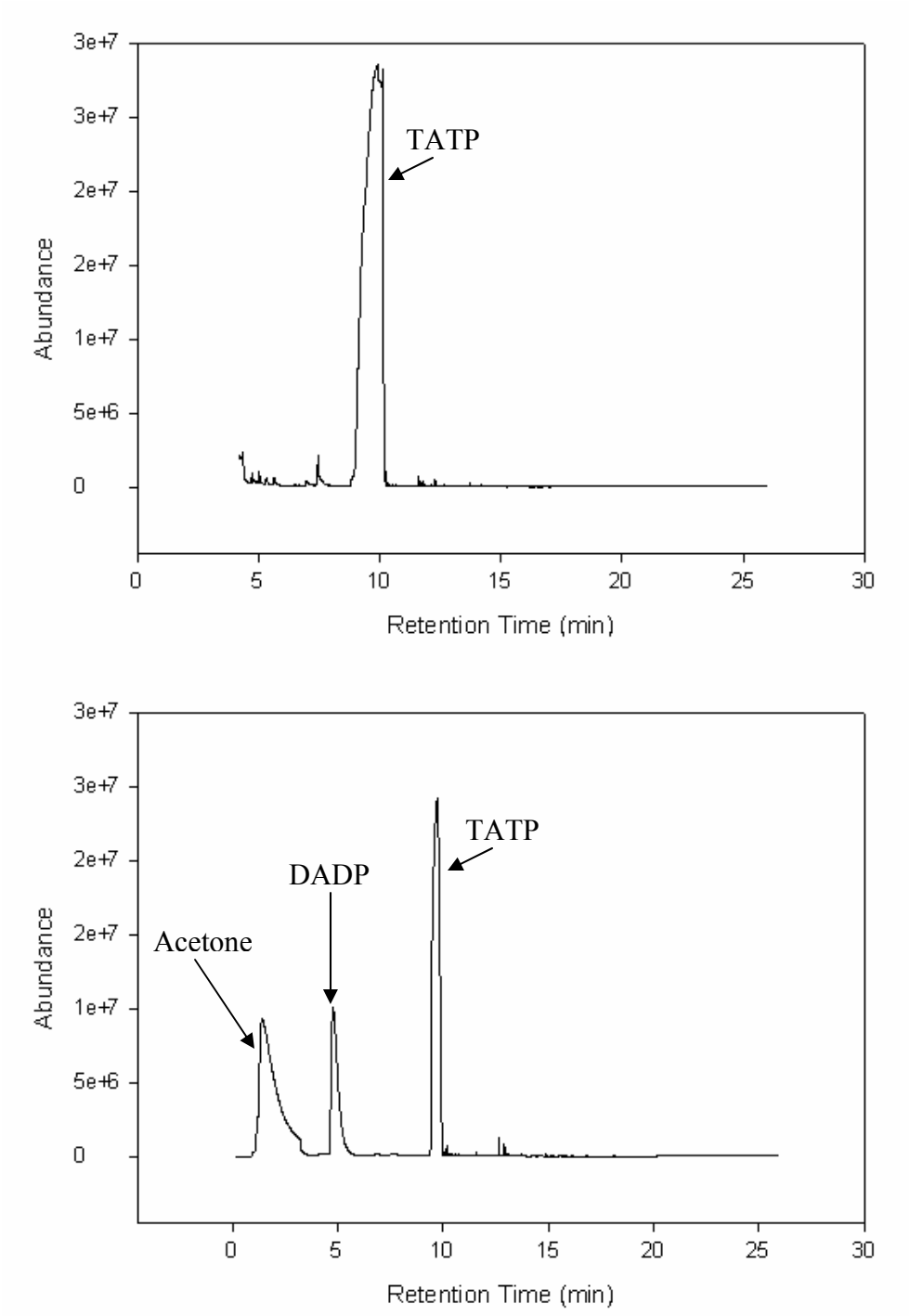


Figure 14: Solution (upper) and SPME (lower) TATP samples analyzed by GC-MS that did not contain any impurities from acetone #1. Acetone and DADP elution not shown in the first chromatogram

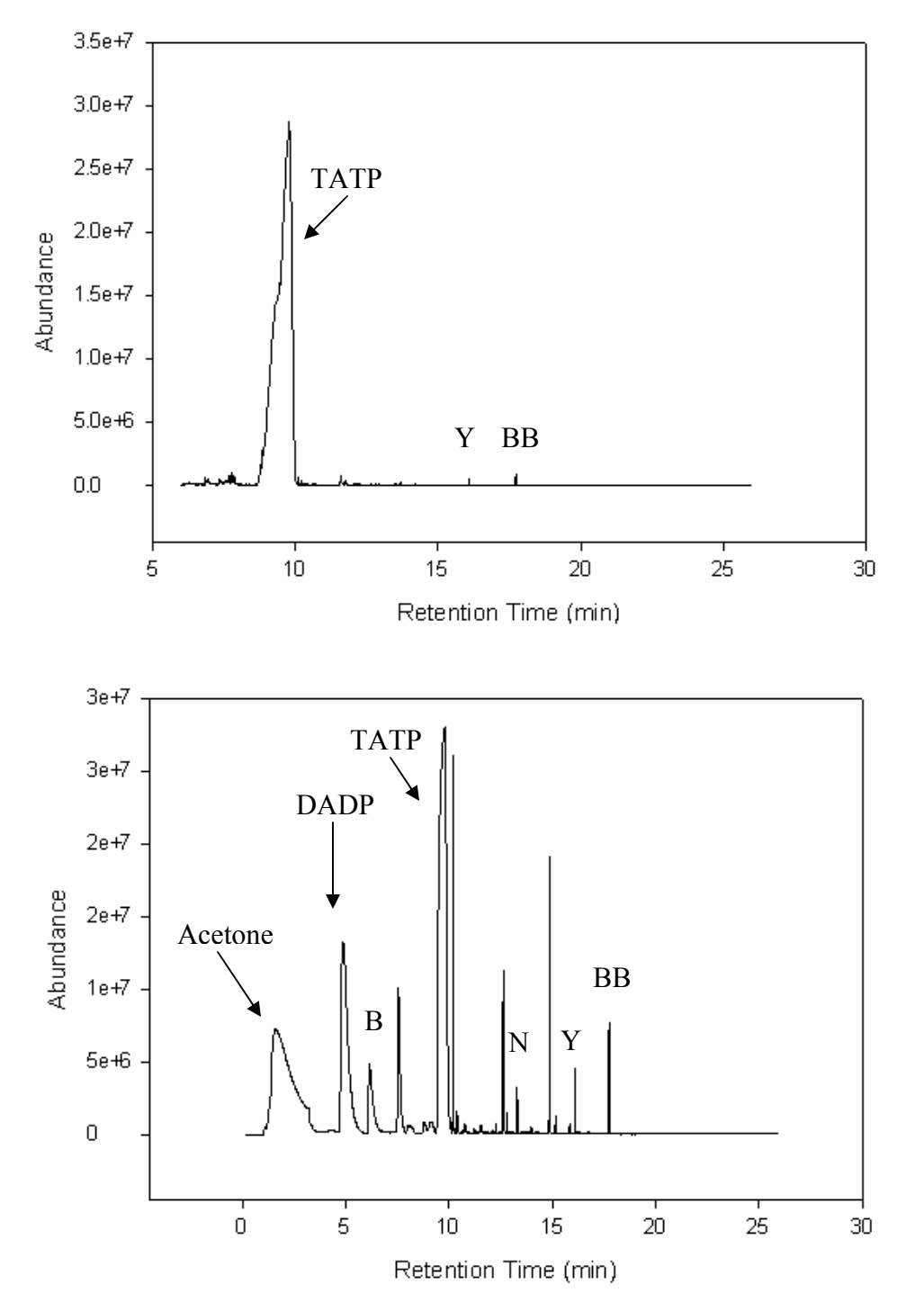


Figure 15: Solution (upper) and SPME (lower) TATP samples analyzed by GC-MS with multiple analytes that carried over from acetone #21. (Y) diethyl phthalate, (BB) benzyl benzoate, (B) cumene, (N) 4-tert-butylcyclohexyl acetate (ii)

Analysis of the Concentration of the Impurities in TATP Samples

Solutions of some of the standards from Table 3 were analyzed by GC-MS, and the areas of the peaks corresponding to the carry-over additives were integrated. These areas were plotted against the concentration of the standard solution. The calibration curve for the dilutions of the benzyl benzoate standard is given in Figure 16, and is representative of the calibration curves for the other standards. The values given in Table 6 contain the slope and intercept from the regression line from the calibration curves for each standard analyte, along with the number of points along the calibration curve (n), the correlation coefficient (r), the concentration range of the solutions, the limits of detection (LOD), and the limits of quantitation (LOQ).

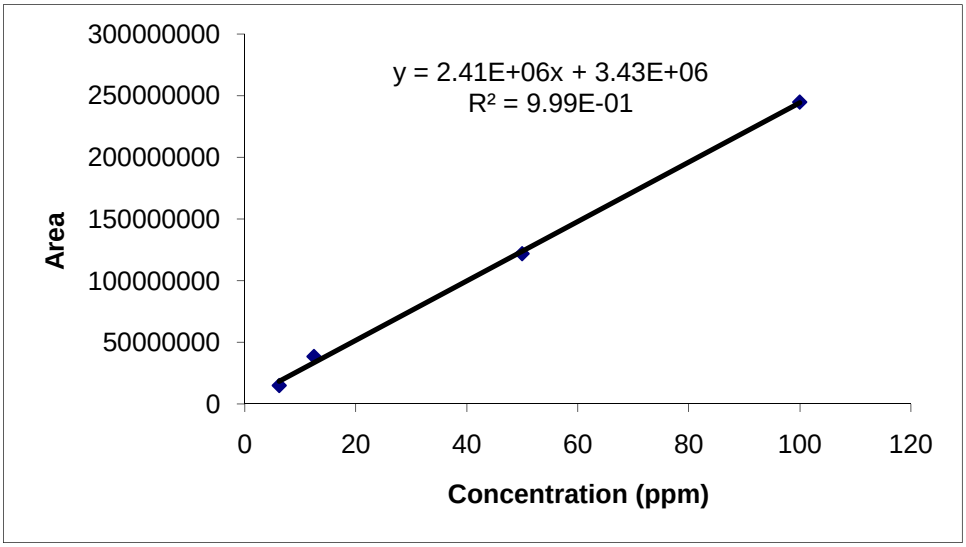


Figure 16: Benzyl benzoate calibration curve

Table 6: Calibration curve values for each analyte.

Analyte	Slope	Intercept	n	r	Concentration (ppm)	LOD (ppm)	LOQ (ppm)
4-tert-butylcyclohexyl acetate (i)	5.64E+05	2.68E+06	4	0.998	6.25-100	0.120	0.400
4-tert-butylcyclohexyl acetate (ii)	1.18E+06	4.50E+06	4	0.959	6.25-100	1.69	5.63
diethyl phthalate	2.19E+06	5.39E+06	4	0.998	6.25-100	2.34	7.78
methyl dihydrojasmonate	4.08E+05	2.00E+06	4	0.999	6.25-100	2.37	7.89
benzyl benzoate	2.41E+06	3.43E+06	4	0.999	6.25-100	1.73	5.77

The LOD and LOQ values were calculated using Equations 9 and 10. The slope of the regression line is represented by "b" and the standard deviation of the slope is "s_b." The intercepts were determined to be statistically significant for each analyte except methyl dihydrojasmonate through the use of a parametric t-test at the 95% confidence level.

$$LOD = (3s_b)/b \quad (9)$$

$$LOQ = (10s_b)/b \quad (10)$$

The TATP samples synthesized for the quantitative analysis of selected acetone impurities in TATP used acetones #3, #8, #11, #21, and #22. From the total ion chromatograms of the TATP samples, the peaks of the impurities were integrated. Those areas were used to calculate the concentration of the impurity in the TATP sample from the calibration curves. The

concentration of the TATP sample and the concentration of the impurity in the TATP solution were used to calculate the percent (w/w) of the impurities. The results are given in Table 7.

Table 7: Weight percent of the impurities relative to a sample of TATP

Carry-Over Additive	Acetone Source	(w/w)%
4-tert-butylcyclohexyl acetate (i)	8	0.00227
4-tert-butylcyclohexyl acetate (ii)	8	0.00281
diethyl phthalate	21	0.0225
	22	0.0206
methyl dihydrojasmonate	21	0.00325
benzyl benzoate	3	0.085
	11	0.017
	21	0.062

Analysis of the Lifetime of the Impurities in Samples of TATP

Acetones #3, #5, #16, and #17 were used to synthesize TATP for the determination of the lifetime of the impurities in air dried samples of TATP. Figure 17 shows the expanded retention time area from 10 to 15 minutes of the chromatograms from the analysis of TATP synthesized with acetone #16. The solid TATP was sampled over the course of 24 hours and the chromatograms show the visible decrease in abundance of the 4-tert-butylcyclohexyl acetate isomers (N) up to 5 hours. After 24 hours of sampling, the carry-over additives were not identified in the total ion chromatogram even upon ion extraction (data not shown).

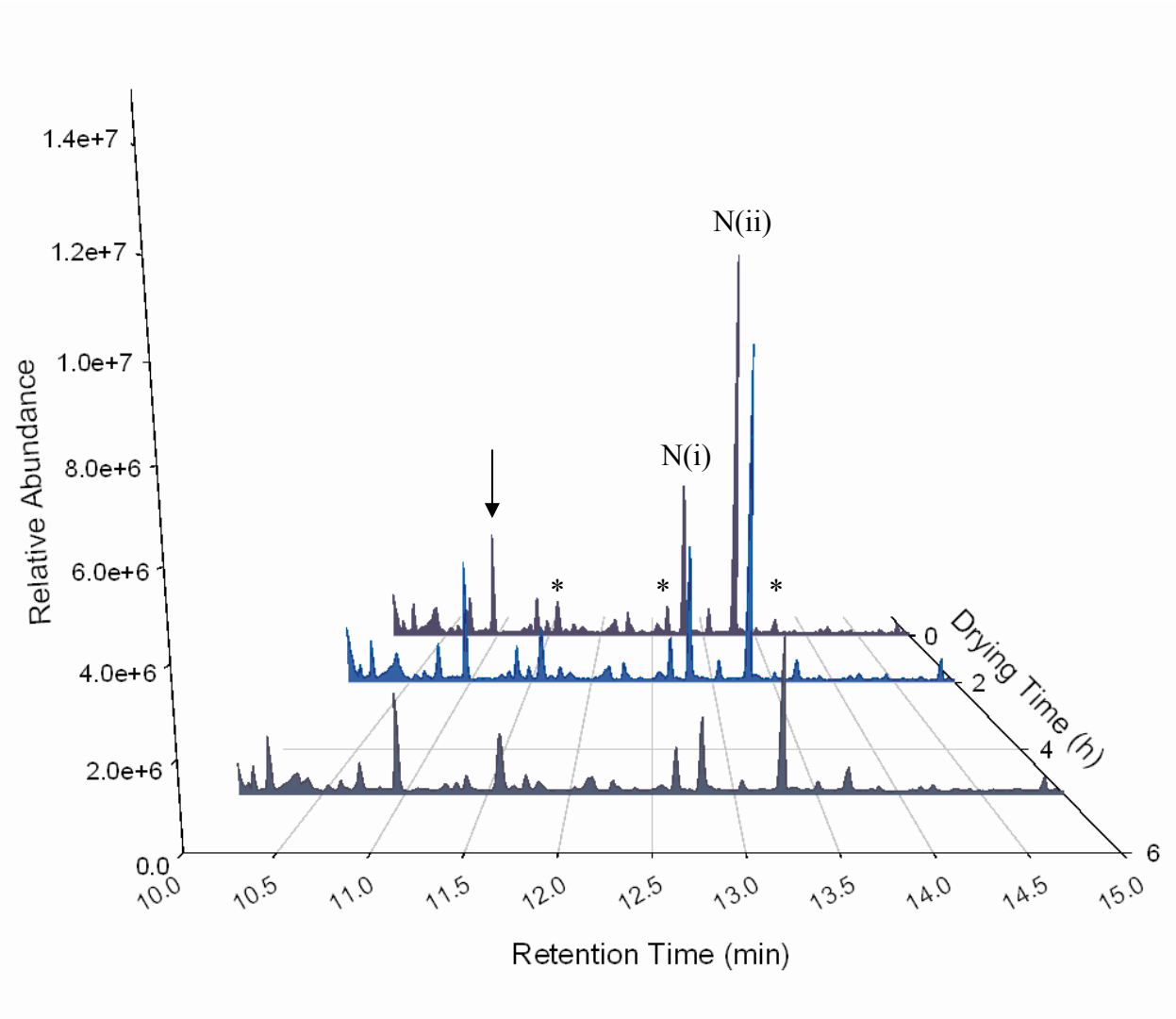


Figure 17: A series of chromatograms showing the general decrease of the impurities in a TATP sample. The major carry-over components identified in the total ion chromatograms are: (N) 4-tert-butylcyclohexyl acetate (i) and 4-tert-butylcyclohexyl acetate (ii). The * represents siloxane peaks, and the peak that the arrow is pointing to shares ions (m/z 43, 59, 75) common to peroxide

Integrated areas corresponding to the carry-over peaks of interest were obtained from the total ion chromatograms from each sample of TATP analyzed, and those areas were divided by the weight of the TATP that was sampled. The weight-normalized areas for each analyte were

divided by the time-zero weight-normalized area and plotted against the length of time the TATP was dried. Over a period of up to 24 hours, the amount of carry-over present in the TATP samples synthesized with acetones #3, #5, #16, and #17 all decreased with increasing drying time. Figure 18 shows the plots of the carry-over analytes from acetones #5, #16, #17 normalized to time-zero to show the general decrease in the amount of analyte present in the TATP samples over time.

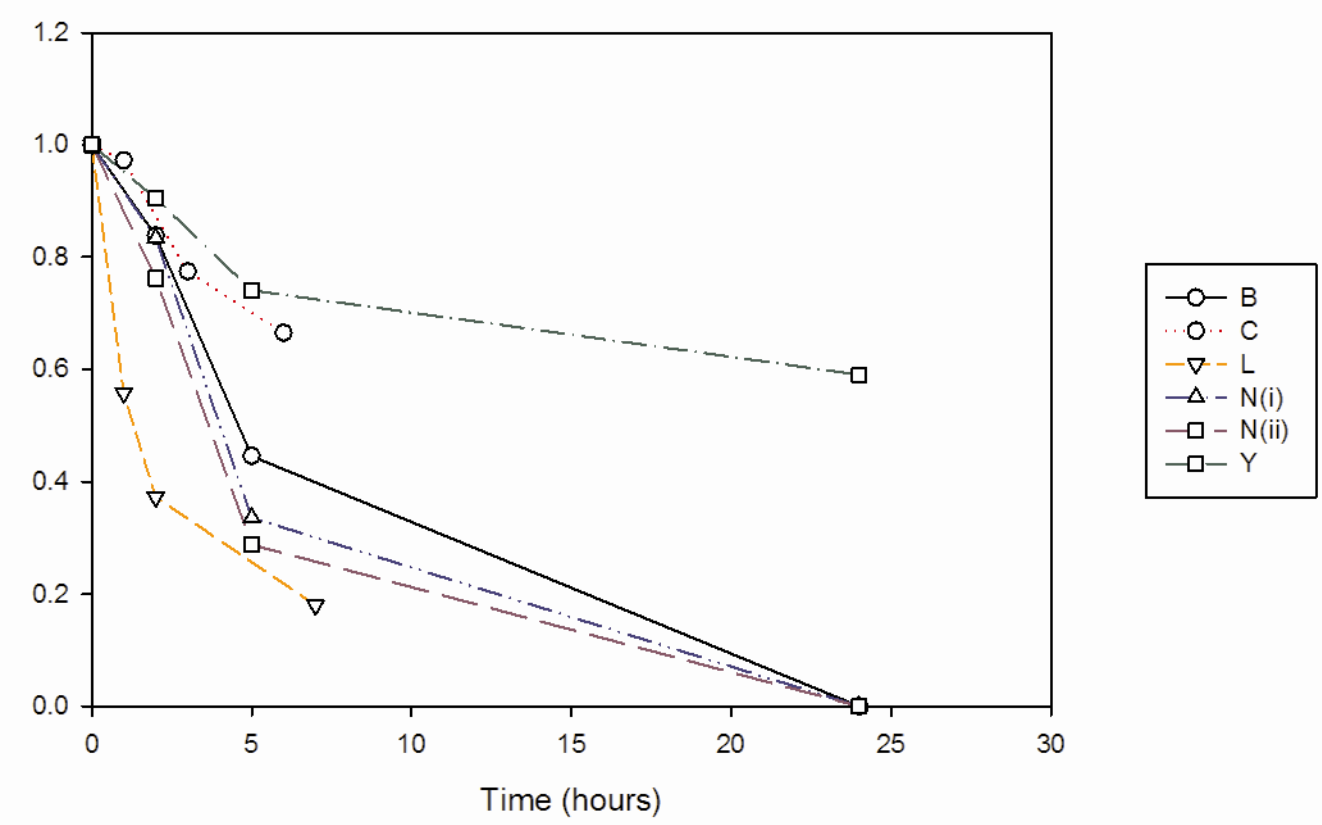


Figure 18: General lifetimes of impurities in samples of TATP. The analytes identified are (B) cumene in acetone #16, (C) propylene carbonate in acetone #5, (L) hexanedioic acid, dimethyl ester in acetone #5, (N(i)) 4-tert-butylcyclohexyl acetate (i) in acetone #16, (N(i)) 4-tert-butylcyclohexyl acetate (ii) in acetone #16, (Y) diethyl phthalate in acetone #16

Analysis of TATP for the Presence of Peroxide Oligomers

Pre-blast TATP samples were analyzed by ESI-MS for the presence of oligoperoxides using either sodium or ammonium acetate as the complexing additive to positively identify the oligomers. Figures 19 and 20 compare TATP samples that contain oligomers using sodium and ammonium acetate as the additive. The distributions of the oligoperoxides in both samples are similar. There is a difference of 5 mass units between successive oligomers in the sample using ammonium acetate as the additive, $[H(O_2C(CH_3)_2)_nOOH + NH_4]^+$ (n = 2, 3,…), and the sample using sodium acetate, $[H(O_2C(CH_3)_2)_nOOH + Na]^+$ (n = 2, 3,…). TATP is not identified in Figure 19, but it is shown in Figure 20. Also shown in both figures are the ammonium and sodium complexed hydroperoxy/acyl terminated oligomers, $[H(O_2C(CH_3)_2)_nOOC(O)CH_3]$ (n = 2, 3,…).

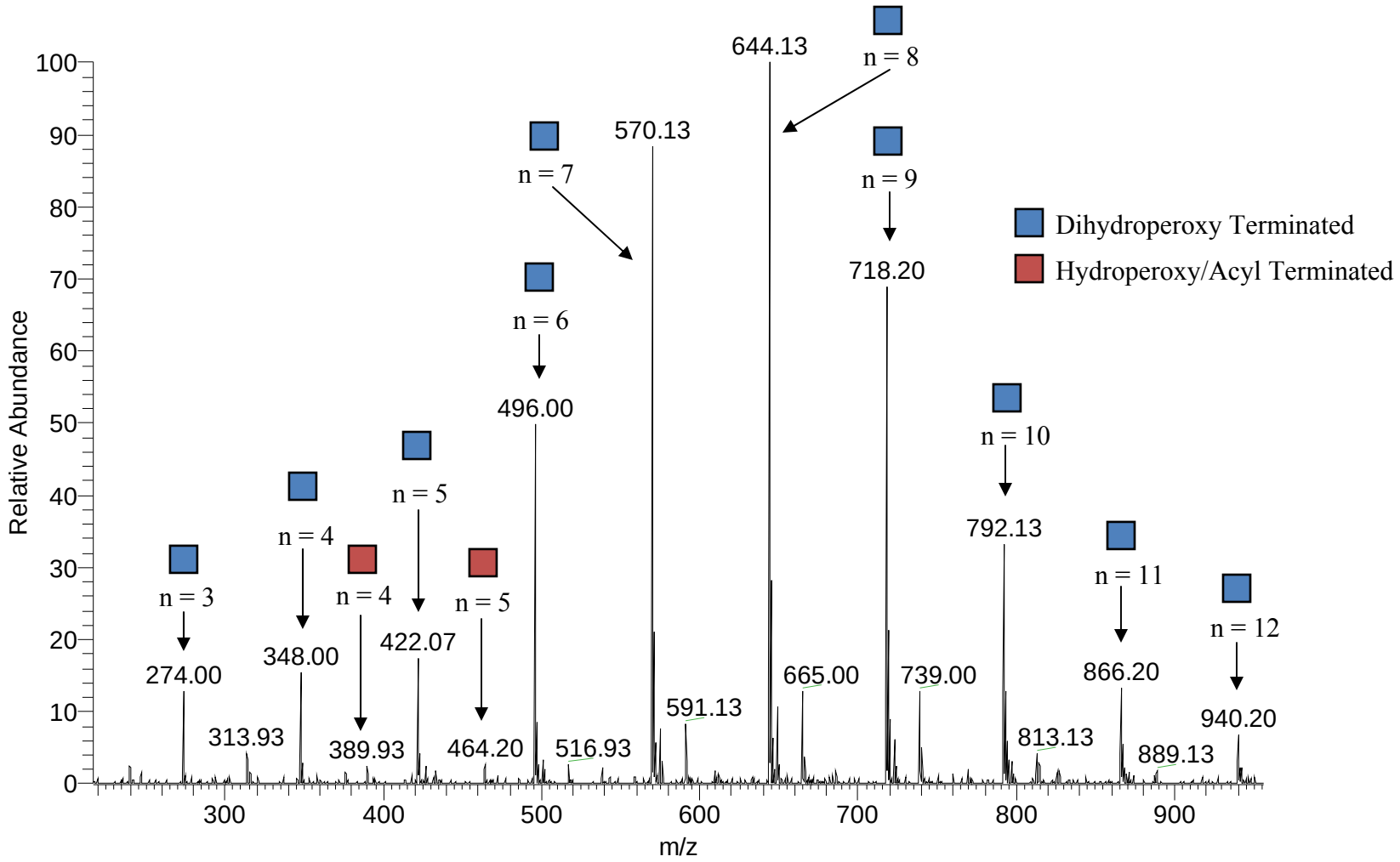


Figure 19: TATP sample showing the oligomers with ammonium adducts analyzed by ESI

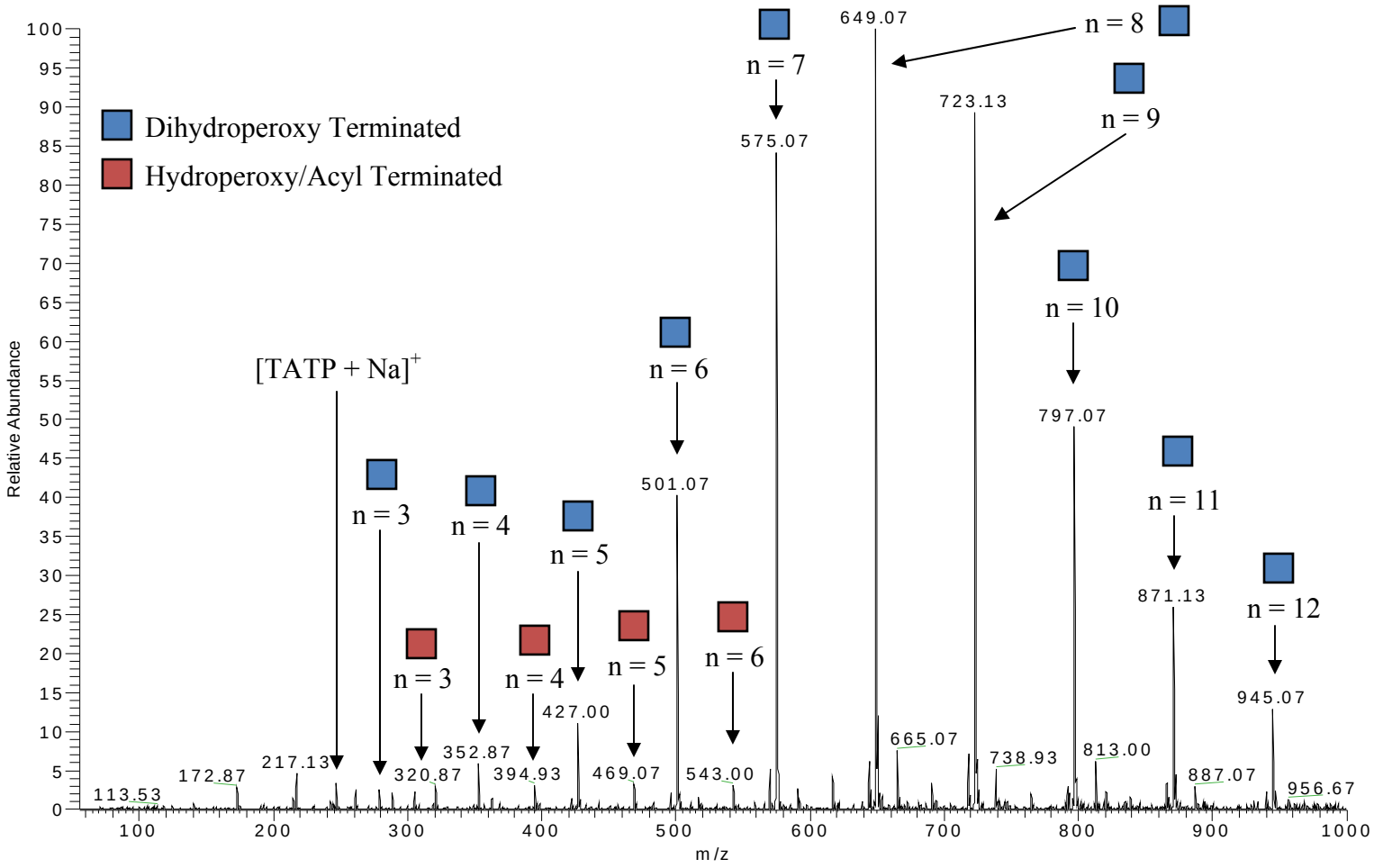


Figure 20: Sodium adduct oligomers in a sample of TATP analyzed by ESI

ESI tandem MS experiments were conducted on some of the higher mass oligomers to determine the fragmentation patterns and to see if any of those oligomers break down to form TATP, DADP, or lower mass oligoperoxides, which would provide selected reaction monitoring methods for detecting the oligomers. The ammonium or sodium adduct of n = 4, $[H(O_2C(CH_3)_2)_4OOH]$, was isolated in the ion trap mass analyzer then allowed to undergo collision induced dissociation by resonant excitation. Product ions are shown in Figures 21 and 22. Figure 21 shows the fragmentation of the n = 4 oligomer into the cyclic tetramer, TATP, DADP, and a few smaller mass oligomers with ammonium adducts. Figure 22 shows the different fragmentation pattern of the n = 4 oligomer with sodium adducts.

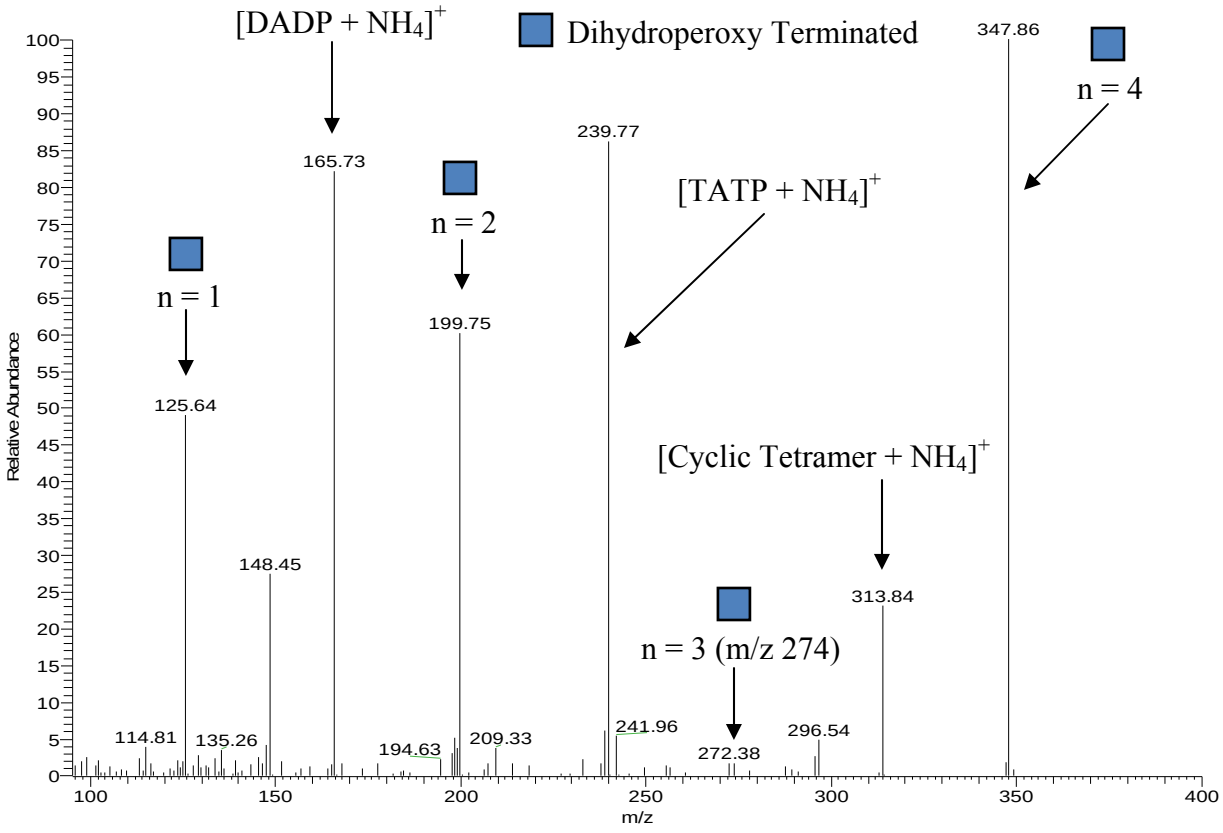


Figure 21: ESI MS^2 of n = 4 (m/z 348) with NH_4^+ adducts at 18% CID

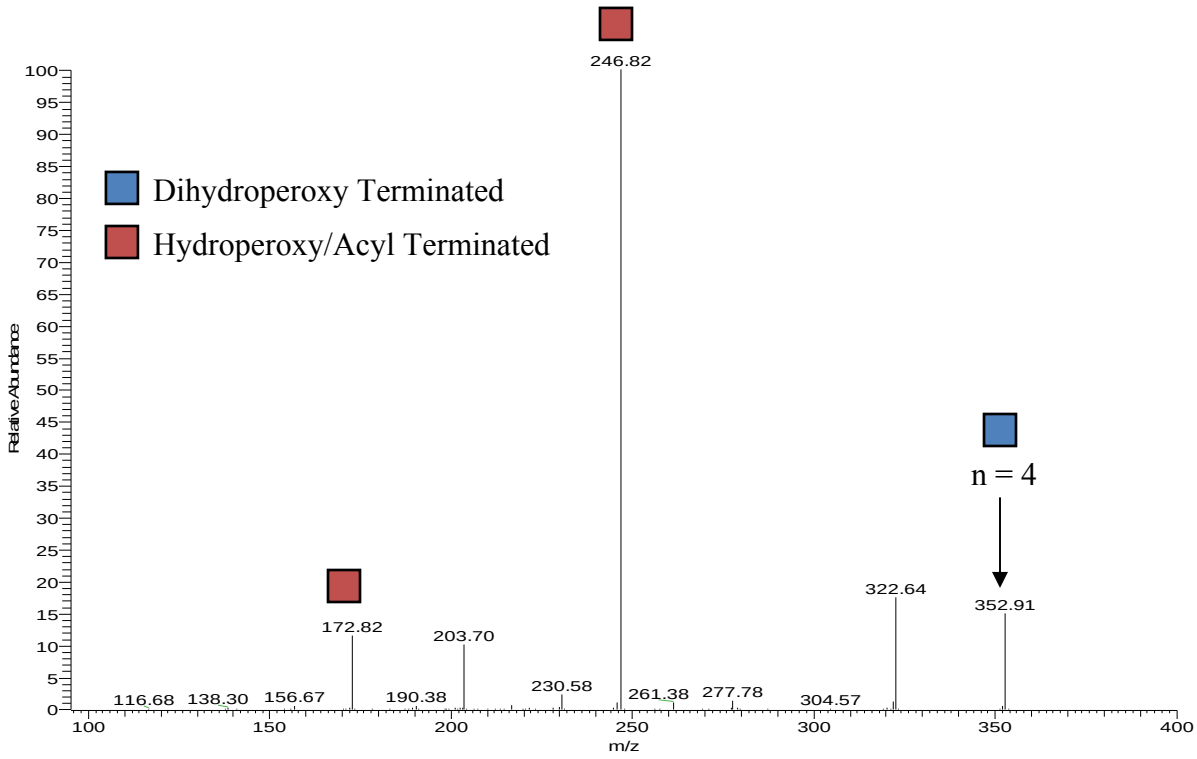


Figure 22: ESI MS^2 of n = 4 (m/z 353) with Na^+ adducts at 20% CID

Analysis of TATP Synthesized With Various Acids

GC-MS Analysis

Headspace samples of TATP that had been synthesized with different acids were analyzed for the presence and relative abundance of acetone and DADP to see if it would be possible to determine the type of acid used in the synthesis of the material. Figure 23 shows the total ion chromatograms from TATP samples synthesized with sulfuric acid and hydrochloric acid. The two syntheses were allowed to react for the same amount of time and were sampled by

SPME at room temperature. The figures show the difference in abundance of DADP in the two samples.

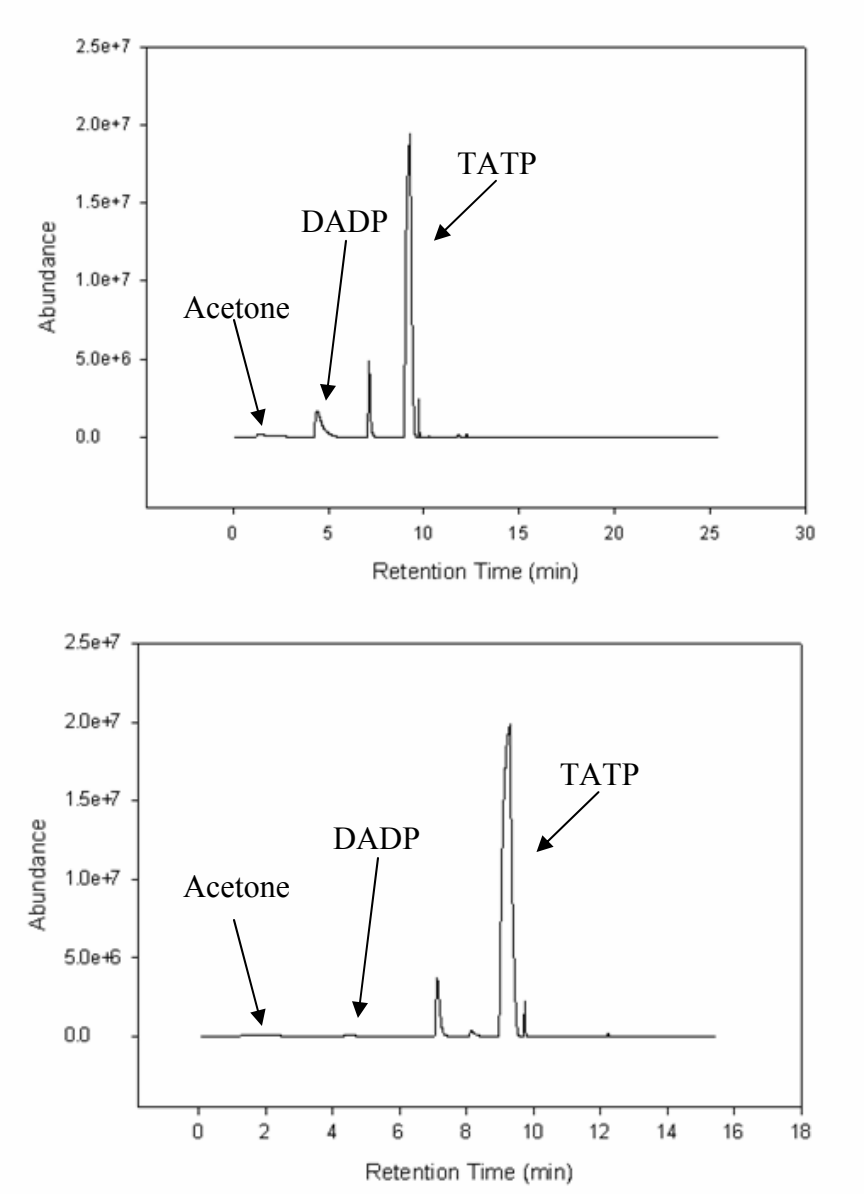


Figure 23: TATP synthesized with sulfuric acid (upper) and hydrochloric acid (lower) to show the difference in abundance of acetone and DADP in the two SPME headspace samples analyzed by GC-MS

In addition to sampling the headspace of the TATP by SPME at room temperature, the headspace was also sampled by SPME while gently heating the material on a dry bath. The results of the room temperature and heated analyses were compared to determine the effects of heat on the abundance of acetone and DADP in the samples. Figures 24 and 25 show an overlay of the total ion chromatograms from the room temperature and heated SPME samples of the headspace above TATP samples that were synthesized with sulfuric, hydrochloric, nitric, and phosphoric acid.

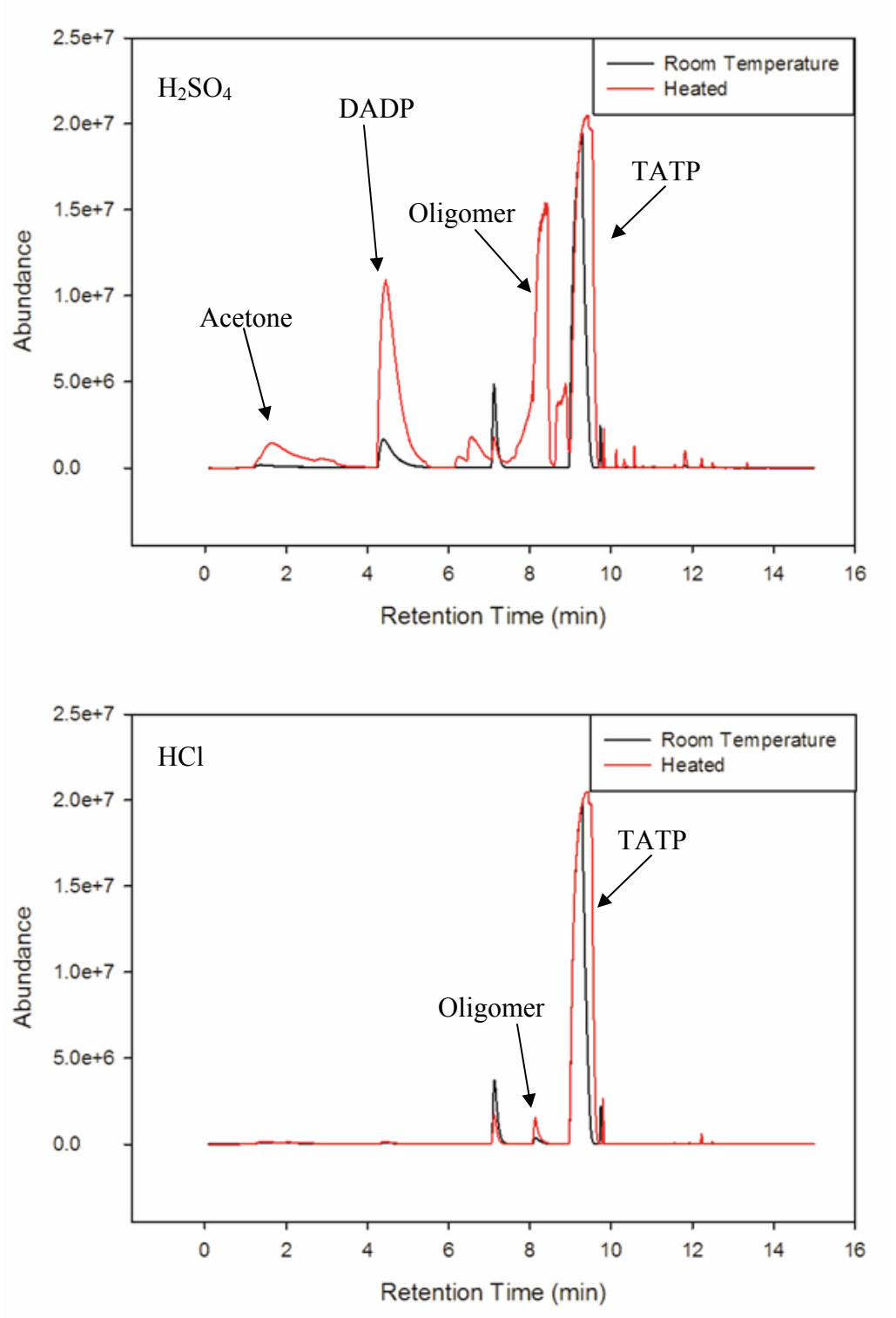


Figure 24: Sulfuric (upper) and hydrochloric (lower) acid TATP room temperature and heated SPME samples analyzed by GC-MS.

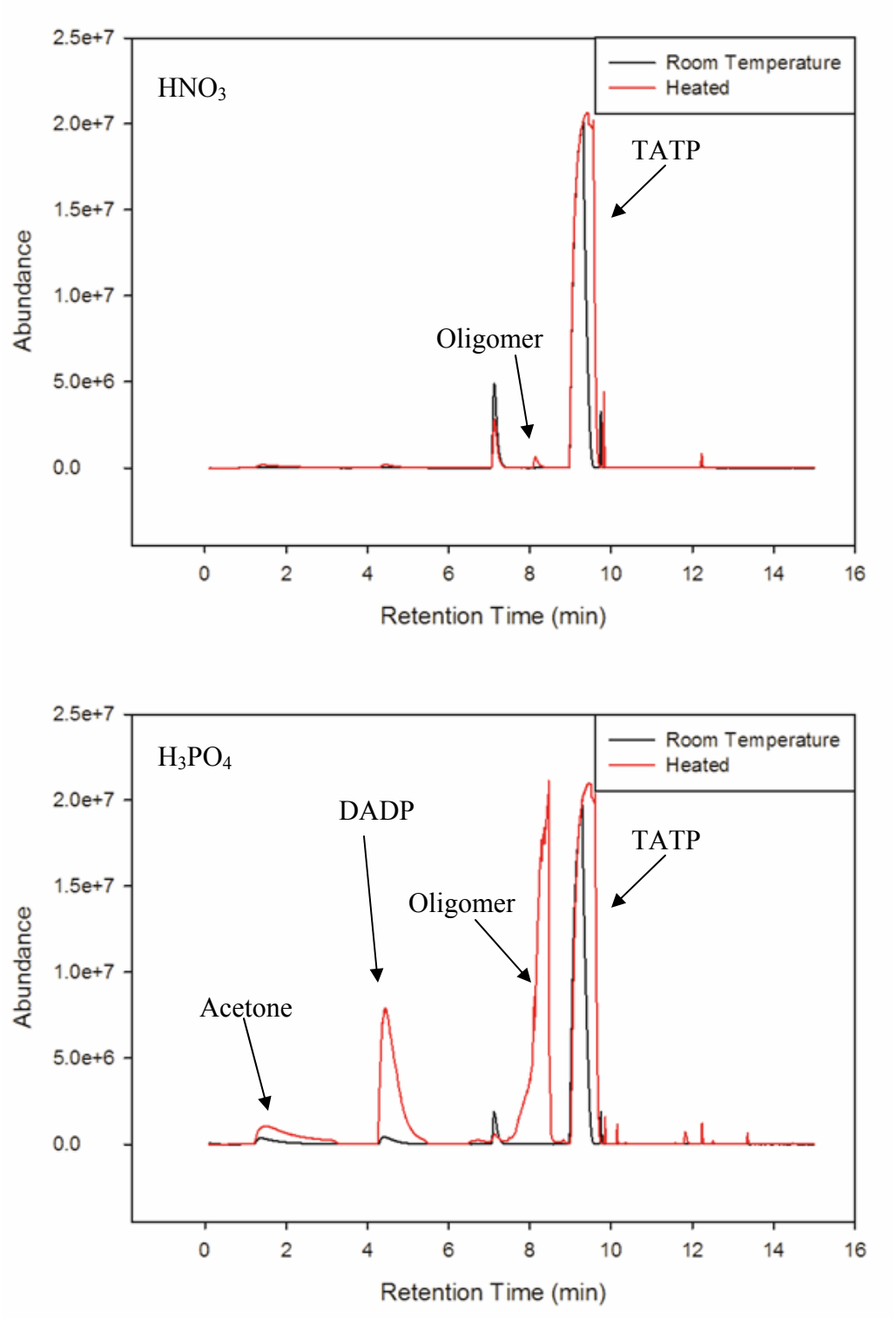


Figure 25: Nitric (upper) and phosphoric (lower) acid TATP room temperature and heated SPME samples analyzed by GC-MS.

APCI-MS Analysis for the Presence of Oligoperoxides

TATP samples synthesized with the different acids were analyzed by positive APCI-MS to see if the oligomer distribution in the samples would differ such that oligomer composition could be used to further identify the acid source. Figure 26 shows samples synthesized by sulfuric acid (upper), hydrochloric acid (middle), and nitric acid (lower) which are mostly TATP but also contain weak oligoperoxides. The composition of oligomers from batch to batch of TATP synthesized with the same acid varied greatly, so these results are only representative.

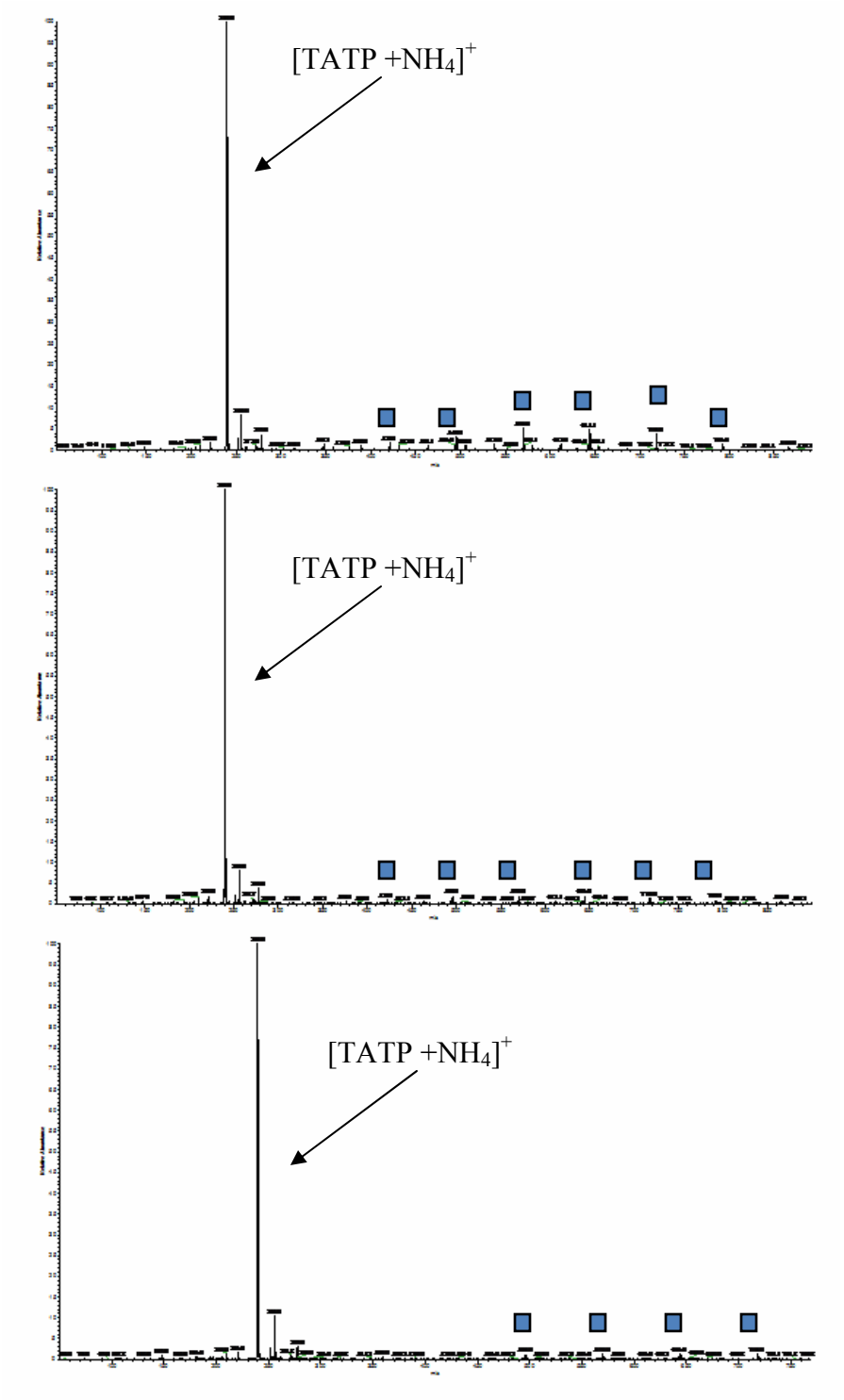


Figure 26: TATP samples synthesized with sulfuric (upper), hydrochloric (middle), and nitric acid (lower) that were analyzed by APCI which show the distribution of the oligomers

Crystals from TATP synthesized with the different acids were directly desorbed in the IMS operating in the negative mode to see if there were any unique peaks or trends in the plasmagrams that were specific to one certain acid. Figure 27 compares the difference between the IMS plasmagrams for TATP synthesized with sulfuric, hydrochloric, and nitric acid. The plasmagrams do differ between the TATP samples with two extra peaks at longer drift times than the TATP and calibrant peaks in the sample prepared with sulfuric acid that are not present in the other TATP samples, and the sample synthesized with nitric acid contains an intense nitrate ion peak.

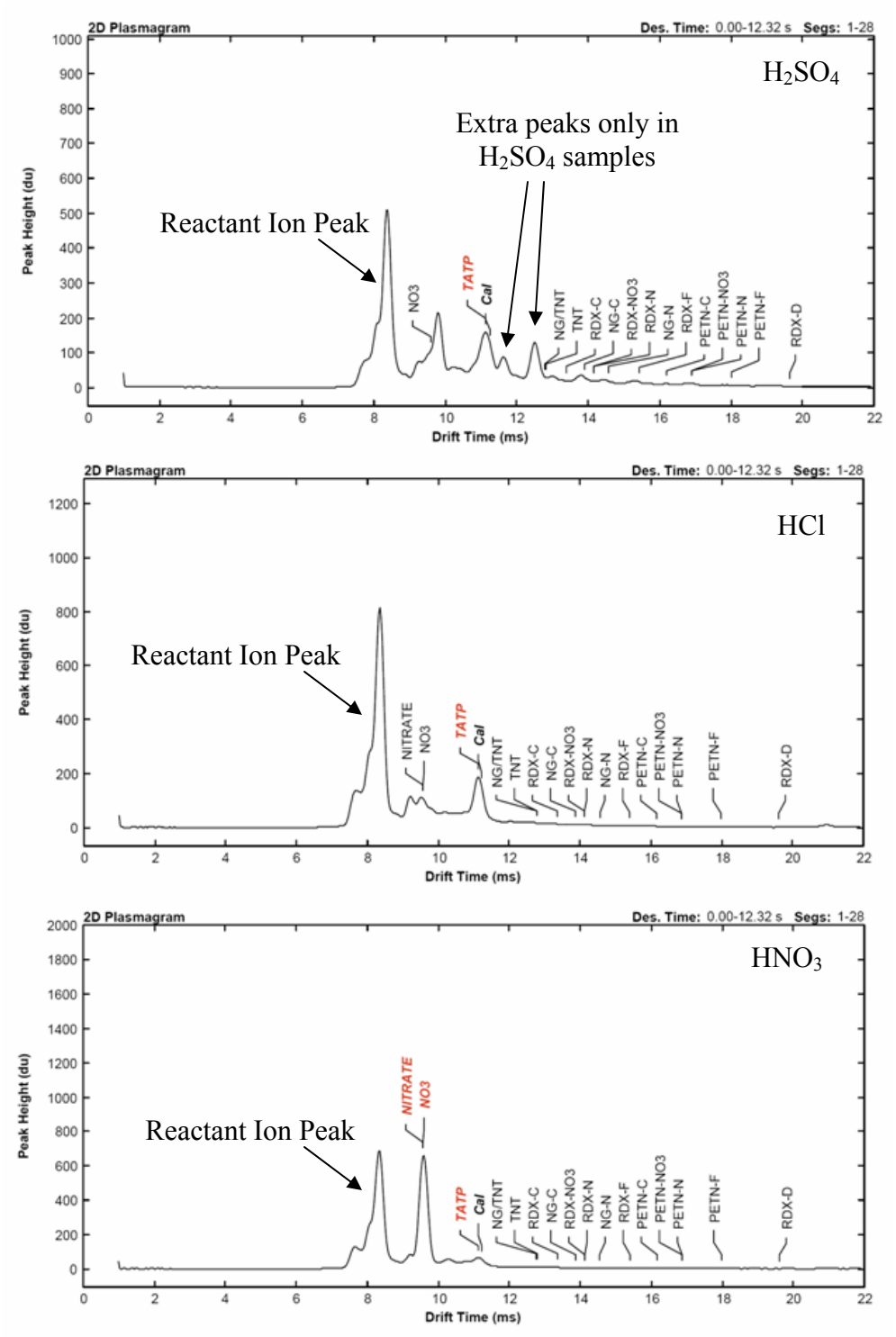


Figure 27: TATP synthesized with sulfuric (upper), hydrochloric (middle), and nitric (lower) to show the differences in the IMS plasmagrams

Laboratory Post-blast Analysis of TATP

Approximately 100 to 200 milligrams of the TATP samples synthesized with the different acetones were detonated using a fallhammer device and the post-blast samples were analyzed by solution and SPME. Even though two different sampling techniques were used, the carry-over additives could not be detected post-blast for the majority of TATP samples; however, benzyl benzoate was weakly detected in a sample of TATP synthesized with acetone #3.

Large-scale Analysis of Pre- and Post-blast TATP

Each pre-blast sample of TATP was weighed and the melting point for the material was determined by placing a few crystals in a Meltemp device and monitoring the range over which the material melted. Table 8 gives the yields for each of the TATP samples along with the corresponding melting point. Control sample #1 and control sample #2 were combined before being weighed. Prior to combining the control samples, each of them was analyzed by solution and SPME and the melting point data was collected.

Table 8: TATP yields and melting points of the pre-blast material

Sample	Weight (g) (% yield)	Melting Point (°C)	Presence of Oligomers
Control #1/#2	13.5 (15%)	58-85	s
		85-92	s
Acetone #21	3.68 (3%)	85-92	w
Acetone #3	18.9 (16%)	84-92	s
Acetone #22	1.98 (2%)	85-92	w
Acetone #27	88.9 (42%)	84-91	s

s = strong
w = weak

Analysis of Pre-blast TATP

Analysis of TATP Samples for the Presence of Acetone Carry-Over

TATP was sampled by both solution and SPME to compare the results from the large-scale pre-blast analysis to the laboratory pre-blast analysis to see if the same impurities or if more impurities could be detected in TATP synthesized on a much larger scale. The total ion chromatograms from the analysis of TATP synthesized with acetone #22, both solution and SPME analyses, are given in Figure 28 to compare the two sampling methods. The chromatograms show that multiple impurities were detected by both sampling methods.

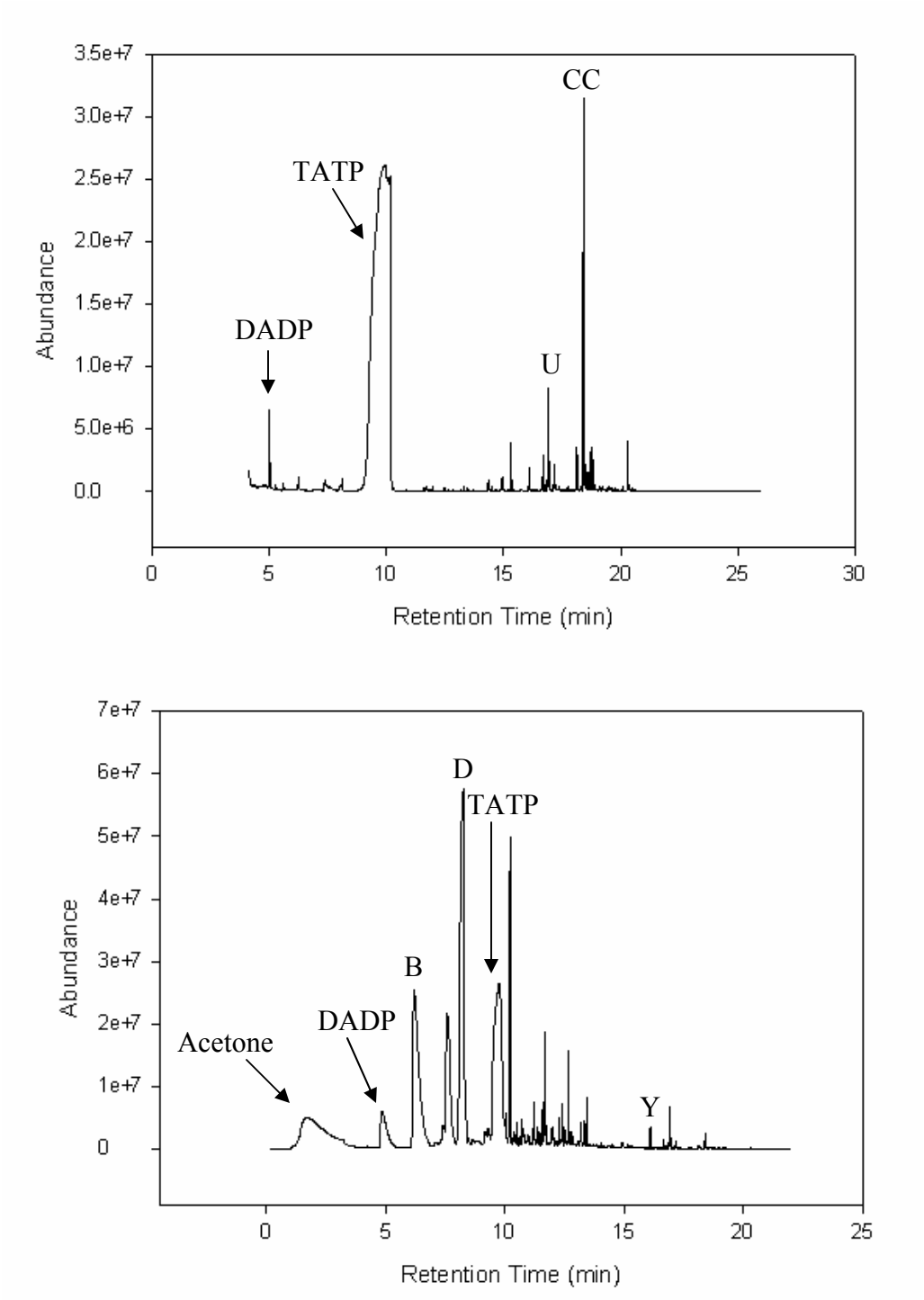


Figure 28: Sample #5 analyzed via solution (upper) and SPME (lower) by GC-MS. Carry-over products labeled: (U) lilial, (CC) galaxolide, (B) cumene, (D) limonene, (Y) diethyl phthalate

The total ion chromatograms for each of the solution and SPME samples were analyzed for the presence of any additives that carried through the synthesis. The results of the analysis of the pre-blast samples for carry-over impurities are given for both solution and SPME samples in Tables 9 and 10. The table lists the acetone sources that were used to synthesize TATP by number and "C" denotes the control samples that were synthesized with lab acetone. Multiple impurities were identified using both methods, but some impurities were only identified via one sampling method. The impurities only identified in solution samples were: (R) 3-(4-isopropylphenyl)-2-methylpropionaldehyde, (W) 5-heptyldihydro-2(3H)-furanone, and (AA) 2-(phenylmethylene)-octanal. The impurities only identified in SPME sampling the headspace of the TATP were (K) nonanoic acid, methyl ester, (L) hexanedioic acid, dimethyl ester, and (O) butanoic acid, phenylmethyl ester.

Table 9: Solution analysis for the presence of carry-over additives

Analyte/Acetone	C 1	C 2	3	21	22	27
cumene (B)				x	x	
limonene (D)					x	
4-tert-butylcyclohexyl acetate [N(i)]				x	x	
4-tert-butylcyclohexyl acetate [N(ii)]				x	x	
3-(4-isopropylphenyl)-2-methylpropionaldehyde (R)					x	
phenoxy ethyl isobutyrate (S)				x		
lilial (U)				x	x	
5-heptyldihydro-2(3H)-furanone (W)				x		
diethyl phthalate (Y)				x	x	
methyl dihydrojasmonate (Z)				x	x	
2-(phenylmethylene)-octanal (AA)				x		
benzyl benzoate (BB)			x	x		x
galaxolide (CC)				x	x	

Table 10: Analysis by SPME for acetone carry-over

Analyte/Acetone	C 1	C 2	3	21	22	27
cumene (B)				x	x	
limonene (D)					x	
nonanoic acid, methyl ester (K)				x		
hexanedioic acid, dimethyl ester (L)					x	
4-tert-butylcyclohexyl acetate [N(i)]				x	x	
butanoic acid, phenylmethyl ester (O)			x			x
4-tert-butylcyclohexyl acetate [N(ii)]				x	x	
phenoxy ethyl isobutyrate (S)				x		
lilial (U)					x	
diethyl phthalate (Y)				x	x	
methyl dihydrojasmonate (Z)					x	
benzyl benzoate (BB)			x	x		
galaxolide (CC)				x	x	x

Analysis of TATP Samples for the Presence of Oligoperoxides

The analysis of the TATP samples by positive APCI-MS for the presence of oligoperoxides showed that some samples contained multiple oligomers (indicated by “s” in Table 8) and others barely contained any (indicated by “w” in Table 8), as well as the presence of some ions that could not be identified. Figure 29 shows the comparison of control sample #1 (upper) that contains multiple oligomers and weak TATP and DADP with TATP synthesized with acetone #3 (lower) that has a high abundance of TATP, oligomers, and benzyl benzoate (BB), one of the carry-over products.

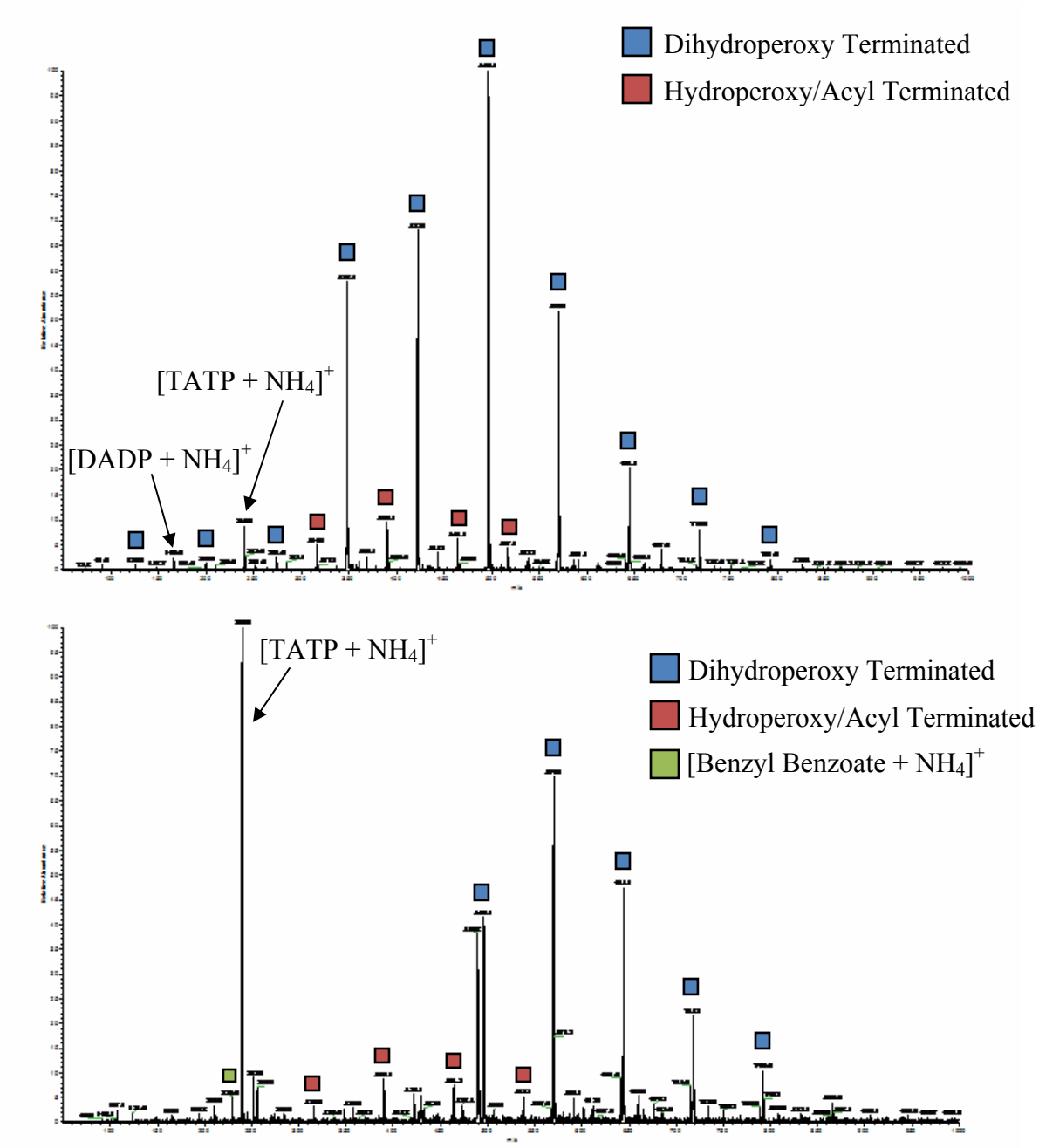


Figure 29: Distribution of oligomers in two different TATP samples analyzed by APCI and the identification of carry-over

Post-blast Analysis

Analysis for the Presence of Carry-Over Products in Post-Blast Debris

Sampling the headspace of the K-pak bags containing the aluminum sheets from the detonation yielded results where TATP was identified in every sample, but carry-over was only identified in three out of the four samples in which impurities had been identified in the pre-blast material. The GC-MS analysis of the cotton swabs that were used to wipe down the aluminum plates after detonation failed to detect TATP in all five samples, but carry-over was still identified in two of the samples. Figure 30 shows the detection of TATP and the benzyl benzoate (BB) carry-over by sampling the headspace of the K-pak bag containing the aluminum plate from the detonation of TATP synthesized with acetone #21.

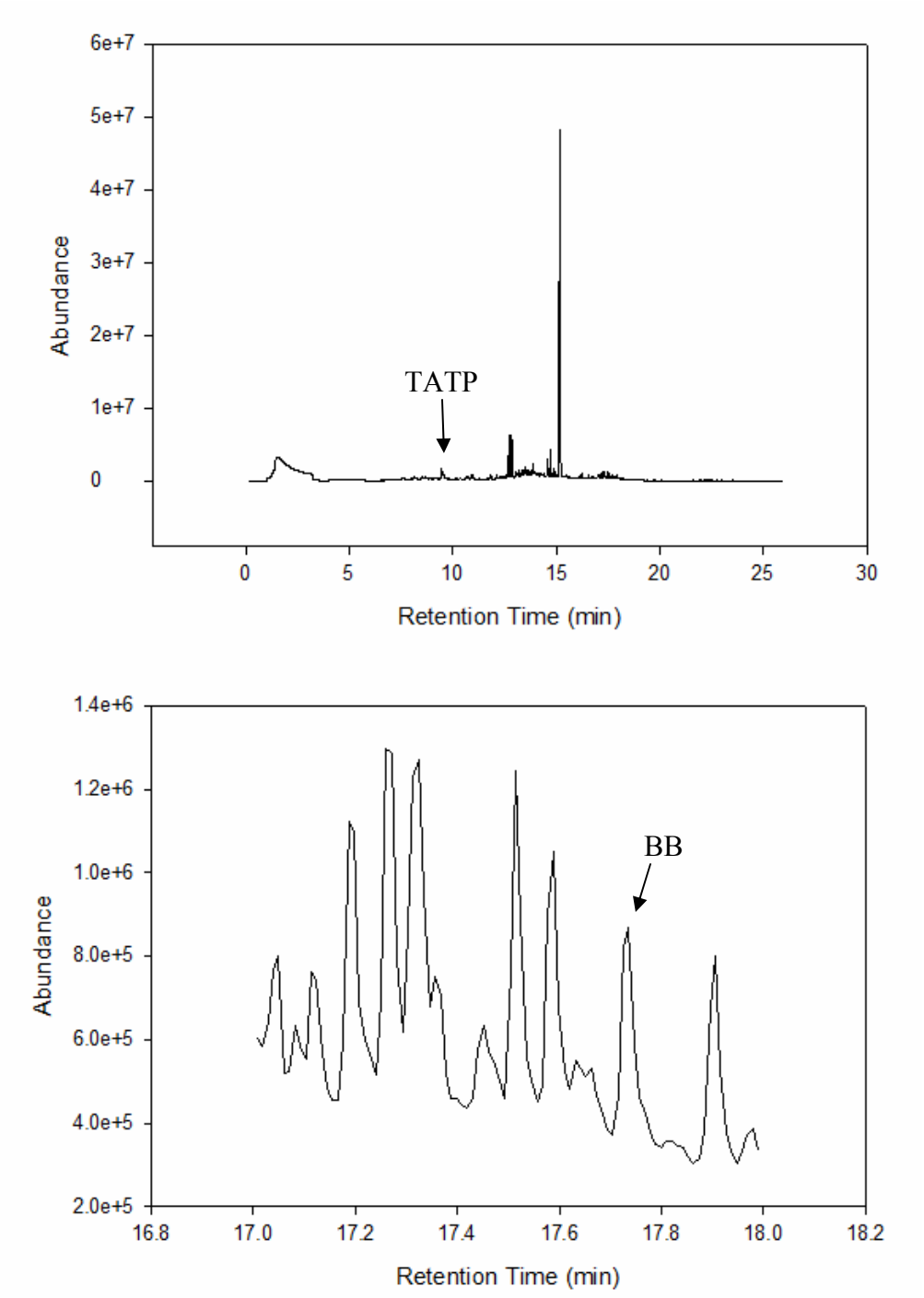


Figure 30: Headspace of the K-pak bag analyzed by GC-MS containing the aluminum plate from the detonation of TATP synthesized with acetone #21 showing the detection of TATP (upper), and the time range from 17-18 minutes is expanded to show the weak detection of the carry-over, (BB) benzyl benzoate (lower)

Similar to laboratory results, benzyl benzoate (BB) was the only additive to be detected post-blast and it was detected in more samples by SPME sampling the headspace of the K-pak bags containing the aluminum plates. Table 11 lists the single carry-over analyte that was identified in the post-blast residue, and in which samples it was detected by listing the acetone number the TATP was synthesized with.

Table 11: Acetone carry-over by SPME sampling the headspace of the K-pak bags and cotton swabs. The control sample is indicated by "C"

	K-Pak Bag Samples				
Analyte	C	3	21	22	27
Benzyl Benzoate		x	x		x
	Swab Samples				
Analyte	C	3	21	22	27
Benzyl Benzoate		x			x

IMS Analysis for the Detection of TATP

The swabs from the post-blast debris were analyzed as soon after the detonation as possible, but TATP was not detected in all five samples. The IMS was operated in the postitive mode, and plasmagrams were generated from the direct desorption of the cotton swabs used to wipe down the aluminum plates after detonation. Figure 31 is an example of a plasmagram generated from the analysis of a swab in which TATP was detected.

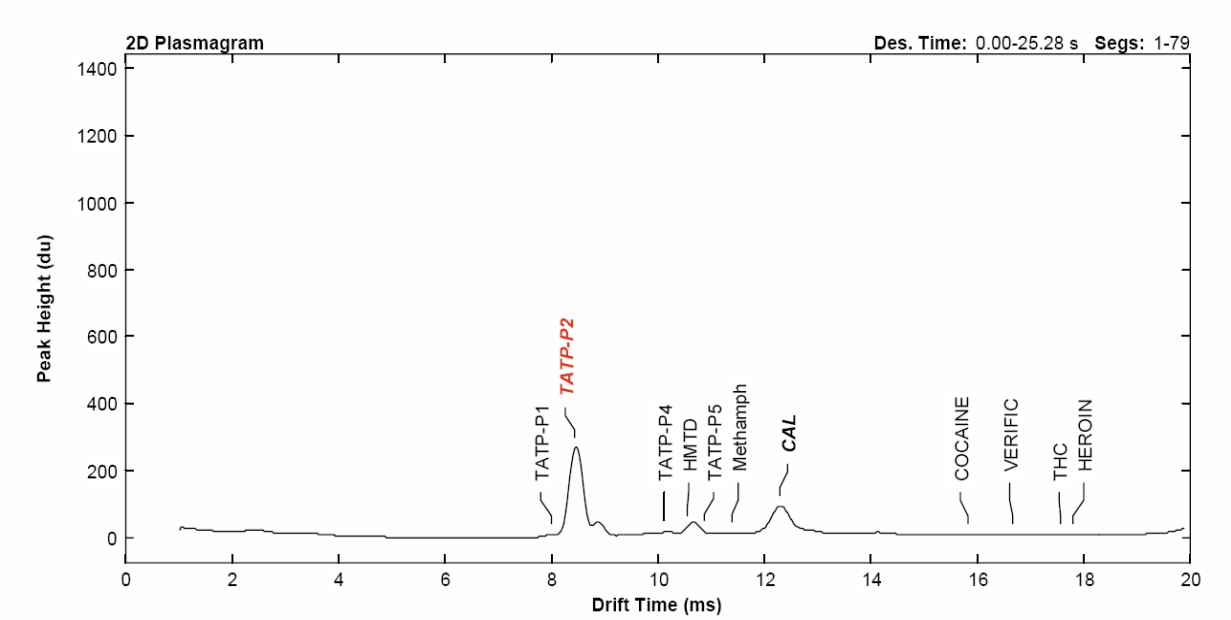


Figure 31: IMS analysis of the cotton swab used to wipe down the aluminum sheet from the detonation of TATP synthesized with acetone #3

CHAPTER 4: DISCUSSION

The results presented in Chapter 3 are discussed in detail in this chapter. In summary, the presence of acetone carry-over products was detected in the majority of TATP samples; however, due to the trace levels of the additives present in the TATP, along with the ability of TATP to sublime at room temperature, the detection of these additives is limited in pre- and post-blast analysis. The presence of the oligoperoxides in TATP varies randomly from batch to batch even when synthesized from the same acetone source. TATP synthesized with sulfuric acid and nitric acid can generally be discriminated from TATP synthesized with other acids by IMS analysis of the crystals. Post-blast analysis of TATP samples from laboratory tests showed only one carry-over product could be detected after detonation. The only carry-over analyte to be detected post-blast in the laboratory samples was also the only additive detected after detonation of the large-scale TATP samples.

Analysis of Acetone for the Presence of Additives

The analysis of each of the acetone sources showed that some acetones contained no detectable additives, many acetones contained numerous additives, and some of the additives were identified in multiple sources. The industrial acetone sources were consistent in that very few organic additives were identified in the samples while the nail polish removers were the sources that contained multiple common additives. Figure 32 provides the chemical structures for some of the most common additives identified in the acetone sources analyzed.

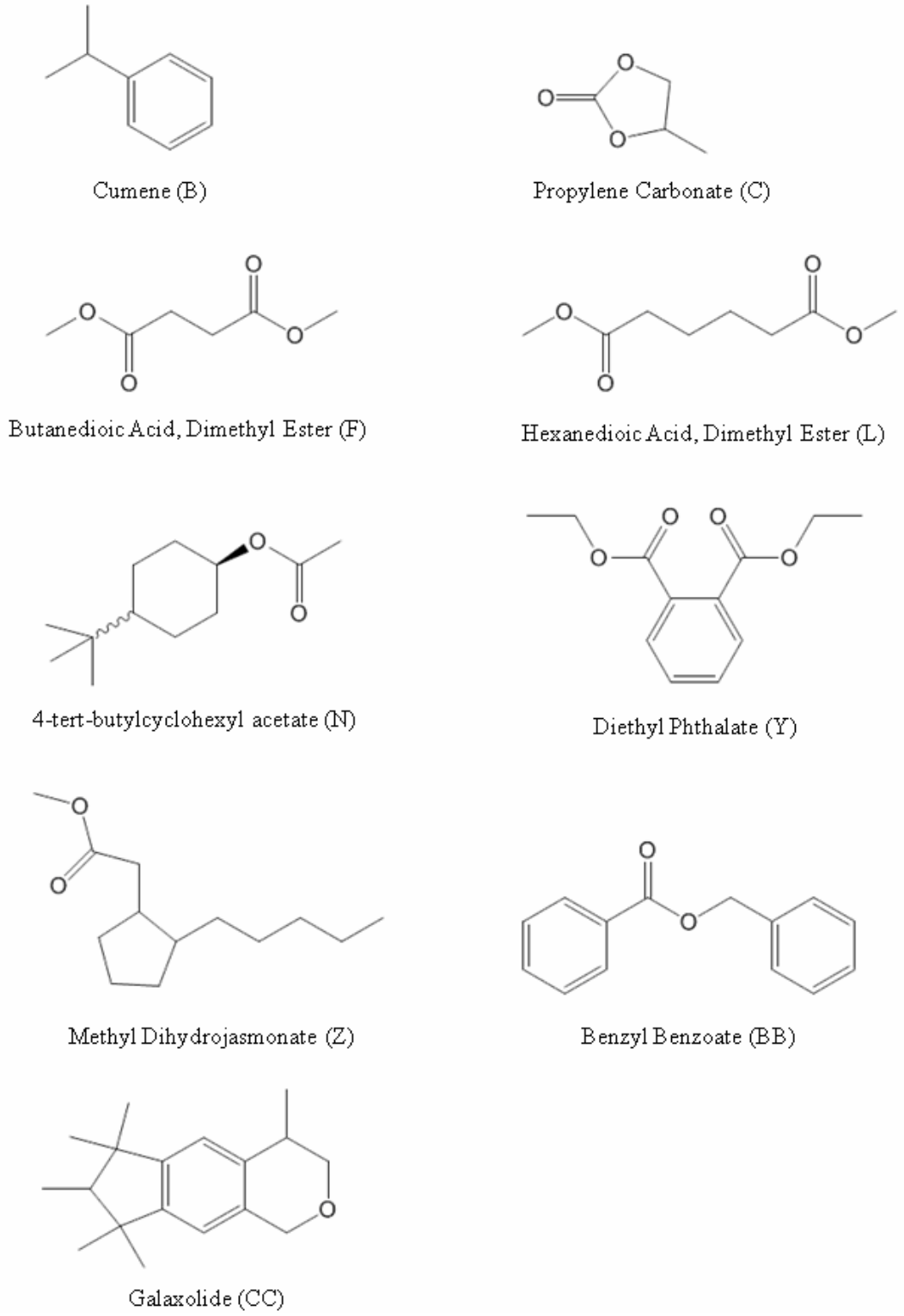


Figure 32: Chemical structures for common organic additives identified in the acetones

Analysis of Pre-Blast TATP Samples

Analyses of the TATP solution and SPME samples gave results which demonstrated that some samples did not contain any carry-over from the acetone source, but the majority of TATP samples contained multiple impurities. Solutions of TATP contained the carry-over analytes but were typically very weak relative to the TATP. The additives could generally be detected at a much higher abundance by SPME sampling the headspace above the TATP (Figure 13). Based on the number of carry over compounds identified in the solution and SPME pre-blast samples (as can be seen in Table 4 and Table 5), SPME sampling was generally the better of the two techniques; however there were a few additives that could only be identified in TATP solution samples. The analytes 3-(4-isopropylphenyl)-2-methylpropionaldehyde (R), lilial (U), and 7-acetyl-6-ethyl-1,1,4,4-tetramethyltetralin (DD) were identified as carry-over from the acetone source in TATP solutions synthesized with acetones #11, #22, and #4 respectively, but could not be identified in pre-blast samples synthesized with those same acetones and sampled by SPME.

Due to the solvent delay for the mass spectrometer, acetone was not identified in the TATP solution samples. A solvent delay was not used for the SPME analysis, and acetone was identified in all 27 TATP samples. Acetone from the synthesis is presumably washed off the crystals when the material is washed with DI water, so the acetone identified in the TATP samples could be from the decomposition of the TATP in the injector port of the GC or it is residual acetone that has become trapped within the TATP crystals. The cyclic dimer, DADP, was identified in the majority of the TATP solution and SPME samples, but was more abundant when the headspace of the TATP was sampled by SPME.

Concentration of Carry-Over in TATP

This experiment was performed to determine the relative concentration of the carry-over analytes present in TATP. The weight of the carry-over compounds relative to the weight of the TATP sample were all determined to be less than 0.1% (Table 7), revealing the very low levels of carry-over components in a given sample of TATP. The benzyl benzoate present in acetone #3 is the major additive in that acetone; however, in a sample of TATP synthesized with that acetone, it was only present at 0.085% (w/w) relative to the total amount of TATP. The benzyl benzoate data also shows that the concentration of these additives varies greatly between acetone sources. The values obtained are only representative and will vary from batch to batch, even among multiple batches synthesized with the same acetone source. The reproducibility of the carry-over levels remaining less than 0.1% decreases the probability of detecting these additives after detonation.

Analysis of the Lifetime of the Impurities in TATP

Due to the low levels of the impurities in the TATP, this experiment was conducted to see how long they could be detected in a sample of TATP that was left to air dry in a fume hood. Generally, the more volatile components could not be detected after 6 or 7 hours, while some of the less volatile components were present up to 24 hours. However, if the TATP was in an enclosed container, the lifetimes of these carry-over analytes would be longer because they would not be exposed to the air flow and the probability of detecting them would be greater. Forensically this is important because it addresses the question of whether the acetone source can

be determined by the detection of the acetone additives. If these additives are detected in a sample of TATP, it could lead to the identification of the acetone source.

Analysis of Peroxide Oligomers in TATP

The analysis of the synthetic intermediates of TATP by ESI-MS revealed a series of oligomeric peroxides that were separated by 74 Da as can be seen with ammonium and sodium adducts in Figure 19 and Figure 20. These ions can be attributed to the sequential addition of $[O_2C(CH_3)_2]$ repeat units during the synthesis, and the number of additions corresponds to the value of n assigned to the oligomer, i.e. n = 2, 3,... Both figures show that a range of oligomers can be observed by ESI-MS, and even though the intensity and number of oligomers varies from batch to batch, they are almost always present in TATP samples. TATP was weakly identified when sodium was used as the complexing additive as can be seen in Figure 20; however, when ammonium was used, the TATP adduct was much more abundant (Figure 19).

The oligomers present in Figure 20 are dihydroperoxy terminated, $[H(O_2C(CH_3)_2)_nOOH + Na]^+$, and are present with a sodium adduct at m/z 279, 353, 427, 501, 575, 649, 723, 797, 871, and 945 (n = 3 to 12). The ammonium adducts in Figure 19 have corresponding m/z ratios that are 5 Da less. A second series of oligomers also separated by 74 mass units is observed in both spectra. These lesser abundant oligomers are hydroperoxy/acyl terminated, $[H(O_2C(CH_3)_2)_nOOC(O)CH_3 + Na]^+$, and are present with a sodium adduct at m/z 321, 395, 469, and 543 as shown in Figure 20, with the ammonium adducts having m/z ratios that are 5 Da less as can be seen in Figure 19.

Tandem MS experiments were conducted on some of the higher mass oligomers to determine fragmentation pathways. With ammonium acetate as the additive, the n = 4 oligomer, $[H(O_2C(CH_3)_4OOH + NH_4]^+$ (m/z 348), was isolated and 18% CID energy (0.9 V) applied. The product ions observed were m/z 314, 240, 200, 166, 148, and 126 as shown in Figure 21. The m/z 240 ion corresponds to the ammonium adduct of TATP, $[TATP + NH_4]^+$ and the m/z 166 ion corresponds to $[DADP + NH_4]^+$, while the cylic tetramer is believed to be observed at m/z 314 due to the loss of hydrogen peroxide from the n = 4 oligomer and cyclization. The ion m/z 200 is the n = 2 oligomer which is formed through the loss of two $[O_2C(CH_3)_2]$ units from the n = 4 oligomer, and the n = 1 oligomer is formed through the sequential loss of one more unit. A weak n = 3 oligomer is observed with m/z 274 which results from the loss of a $[O_2C(CH_3)_2]$ unit from the n = 4 oligomer. Through the loss of peroxide and cyclization, TATP is formed from the n = 3 oligomer. A proposed mechanism for the fragmentation of the n = 4 oligomer with ammonium adducts is given in Figure 33.

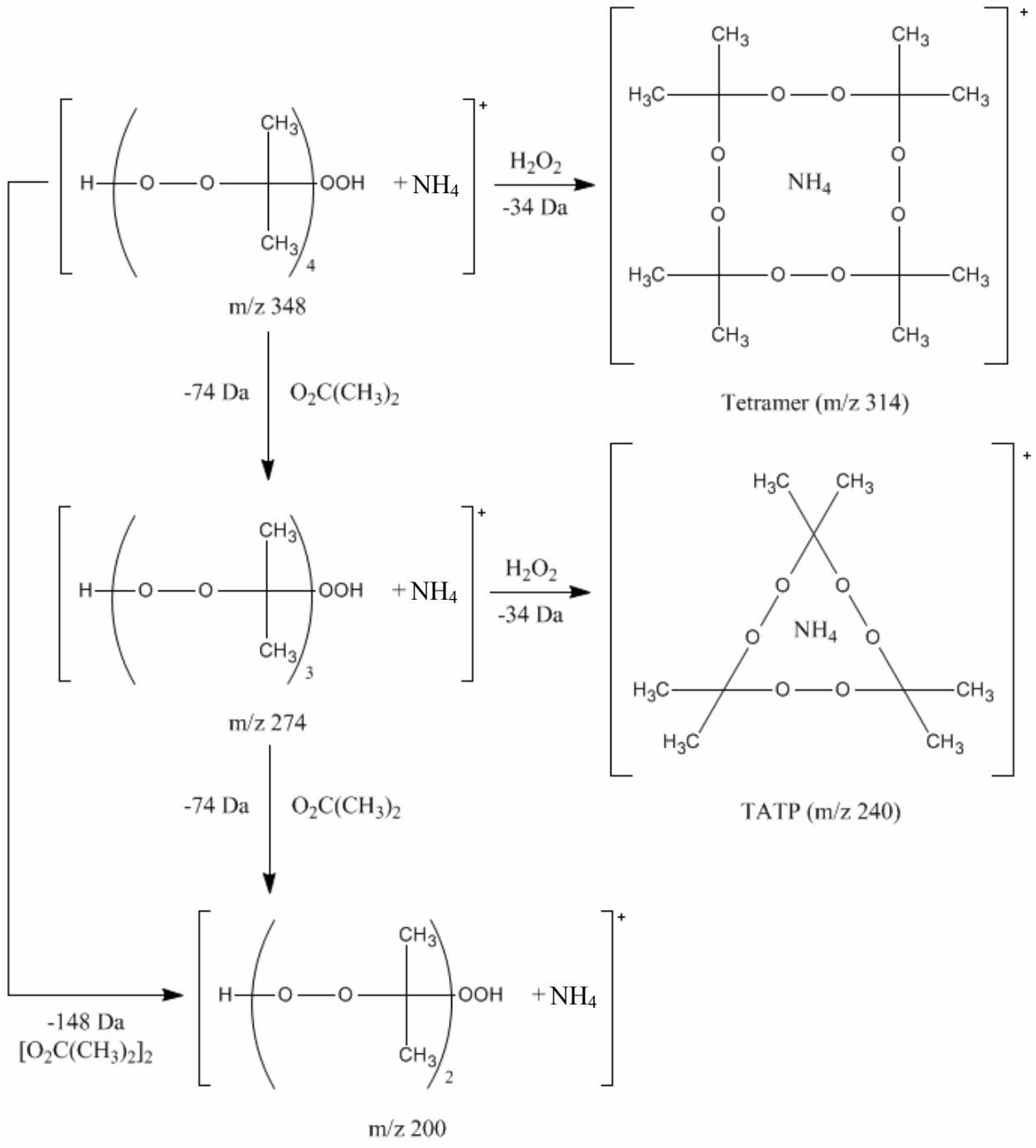


Figure 33: Proposed mechanism for the fragmentation of n = 4 (m/z 348) with NH_4^+ adducts

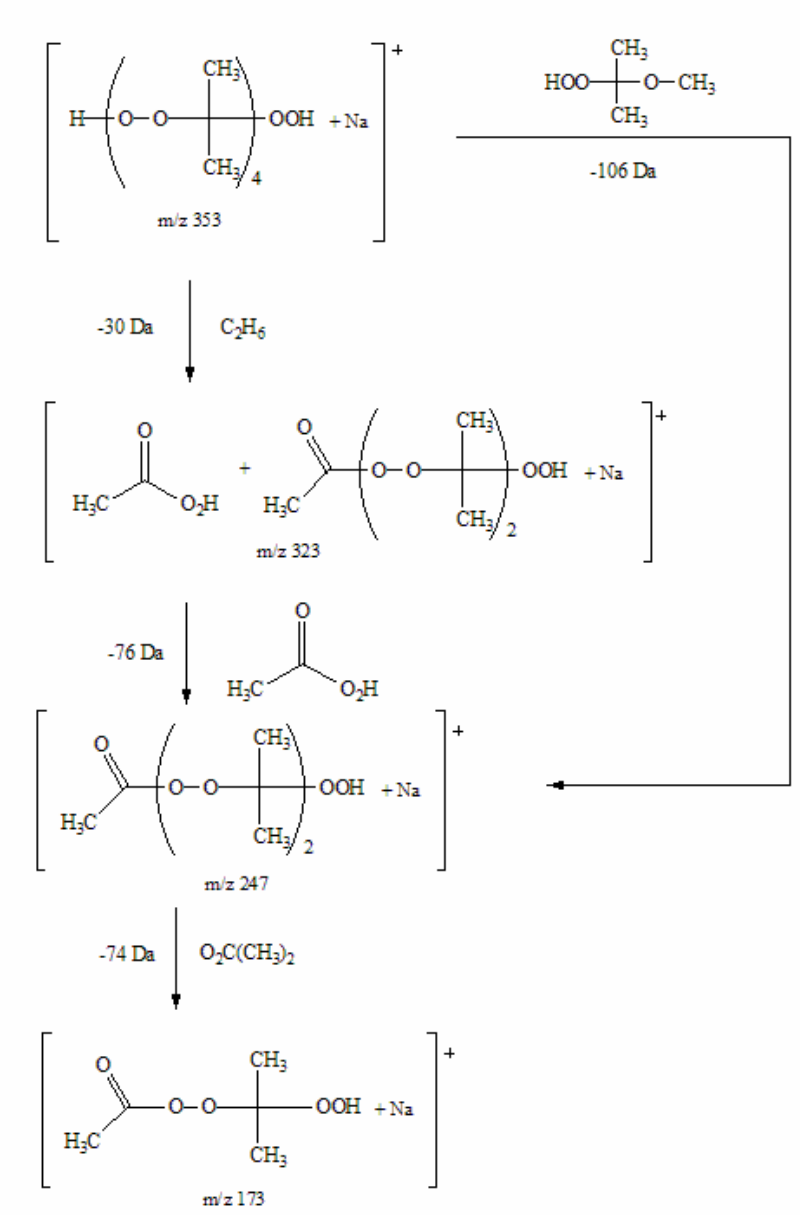


Figure 34: Proposed mechanism for the fragmentation of n = 4 (m/z 348) with Na^+ adducts

The fragmentation pattern of the n = 4 oligomer with sodium adducts differs from the fragmentation pattern with the ammonium adduct. The n = 4 oligomer complexed with a sodium ion breaks down into smaller hydroperoxy/acyl terminated oligomers with m/z 247 and 173

(Figure 22). Unlike the fragmentation of this oligomer with an ammonium adduct, cyclized products are not observed from the break down of the n = 4 oligomer with sodium adducts. The proposed mechanism for the fragmentation of the n = 4 oligomer with sodium adducts is shown above in Figure 34.

Similar tandem MS experiments were performed using positive GC-(CI)MS and DIP-(CI)MS on the peroxide oligomers with ammonia as the ionization gas. GC-MS analysis is sensitive to the detection of TATP but the oligoperoxides are not as readily identified by GC-MS as they are by ESI-MS. The results from the GC-(CI)MS^2 analysis of the n = 3 oligomer showed that n = 3, $[H(O_2C(CH_3)_3OOH + NH_4]^+$ (m/z 274), loses hydrogen peroxide and cyclizes to give the TATP ion m/z 240. The n = 3 oligomer also loses two $[O_2C(CH_3)_2]$ units to give a weak product ion of m/z 126 which is n =1, $[H(O_2C(CH_3)_2OOH + NH_4]^+$. The DIP analysis of the n = 3 oligomer resulted in a strong TATP ammonium adduct ion at m/z 240 because of the loss of hydrogen peroxide from the n = 3 ammonium adduct oligomer and cyclization, as was observed in the GC-(CI)MS analysis.

Analysis of TATP Synthesized with Different Acids

Samples of TATP were synthesized with H_2SO_4, HCl, HNO_3, and H_3PO_4 to determine if it is possible to identify the type of acid used in the synthesis of TATP. All samples were analyzed by GC-MS to monitor changes in the headspace of the samples, by APCI-MS to determine the oligomeric composition, and by IMS to see if there were any differences in the plasmagrams among TATP synthesized with the various acids.

Samples analyzed by GC-MS were sampled by SPME at room temperature and while gently heating at 50°C to determine if heat had an effect on the abundances of acetone, DADP, TATP, or oligomeric peroxides present in the headspace of the material and if those differences could lead to the determination of which acid was used in the synthesis.

The sulfuric acid catalyzed TATP sample at room temperature contained little acetone, some DADP, and TATP as shown in Figure 23. Upon heating, both acetone and DADP increased in abundance along with one of the oligoperoxides shown in Figure 24. TATP was synthesized with dilute sulfuric acid as well, and the analysis of the headspace at room temperature and upon heating gave similar results as the ones obtained for the sample prepared with concentrated sulfuric acid. The room temperature sample of TATP prepared with HCl contained very little acetone and DADP and upon heating, the abundance of DADP and acetone did not change substantially, but there was a slight increase in the abundance of the oligomer (Figure 24). Similarly, the room temperature sample of TATP synthesized with nitric acid contained trace amounts of acetone and DADP. Upon heating, only the oligomeric peroxide increased noticeably in abundance, while the increase in abundance of acetone and DADP was minimal (Figure 25). TATP synthesized with phosphoric acid produced similar results to those obtained from the analysis of the samples of TATP synthesized with sulfuric acid. When the TATP sample synthesized with phosphoric acid was heated, the abundances of acetone, DADP, and the oligoperoxide increased relative to the TATP but not as great as the increase in the TATP prepared with sulfuric acid (Figure 25). Table 12 shows that some discrimination among the acids is possible by observing the changes in abundance of acetone, DADP, and the n = 2 oligomer in the heated TATP samples.

Table 12: Changes in the headspace of heated TATP samples synthesized with different acids

Acid	Acetone	DADP	n = 2 oligomer
H_2SO_4	+	+	+
HCl	-	-	+
HNO_3	-	-	+
H_3PO_4	+	+	+

+: substantial increase in abundance
+: increase in abundance
-: no substantial change

TATP samples were also synthesized with commercial acid sources such as drain cleaners that contained either sulfuric or hydrochloric acid. The GC-MS analysis of these TATP samples by room temperature and heated SPME sampling produced similar results to their lab grade acid counterparts. It should be noted that additives present in those acid sources failed to carry over through the synthesis and were not detected in the TATP. Discrimination among the TATP samples synthesized with different acids by use of GC-MS analysis alone is not entirely possible since some of the acids exhibit the same type of behavior upon heating.

The TATP samples were analyzed to determine if the oligomer composition of the TATP could lead to the discrimination among the acids. Multiple batches were synthesized using the same acids to try and achieve reproducible results, but the variation of oligomers from batch to batch was too large, and there was no reproducible pattern to the composition of oligomers in TATP samples synthesized with each acid as can be seen in Figure 26. Variation in oligomeric composition even among TATP synthesized with the same acid source prevents determining the type of acid used in the TATP synthesis only based on the distribution of oligomers in the product.

Crystals of TATP synthesized with sulfuric, hydrochloric, nitric, and phosphoric acid were directly desorbed into the IMS, operating in both the positive and negative modes. The plasmagrams were compared to see if any differences in them could lead to the discrimination between the acids. The plasmagrams from each of the TATP samples were all similar when the IMS was operated in the positive mode; however, some discrimination could be made when operating the instrument in the negative mode.

The plasmagram of the TATP synthesized with sulfuric acid contained two extra peaks with longer drift times than TATP and the calibrant that were not present in the other three samples and were consistent among multiple batches of TATP synthesized in the laboratory (Figure 27). TATP prepared with nitric acid triggered the alarm for the presence of a nitrate ion and the plasmagram contained a very intense nitrate peak which is consistent with the acid used during the synthesis. Some of the other samples contained weaker nitrate peaks because nitrate is commonly observed in very small quantities as a background ion by IMS, but none of which were as intense as the nitrate peak from the nitric acid sample. There were no identifying characteristics in the plasmagrams of TATP synthesized with HCl or H_3PO_4. The flow chart in Figure 35 shows the possible discrimination among acids based on analysis by GC-MS and IMS.

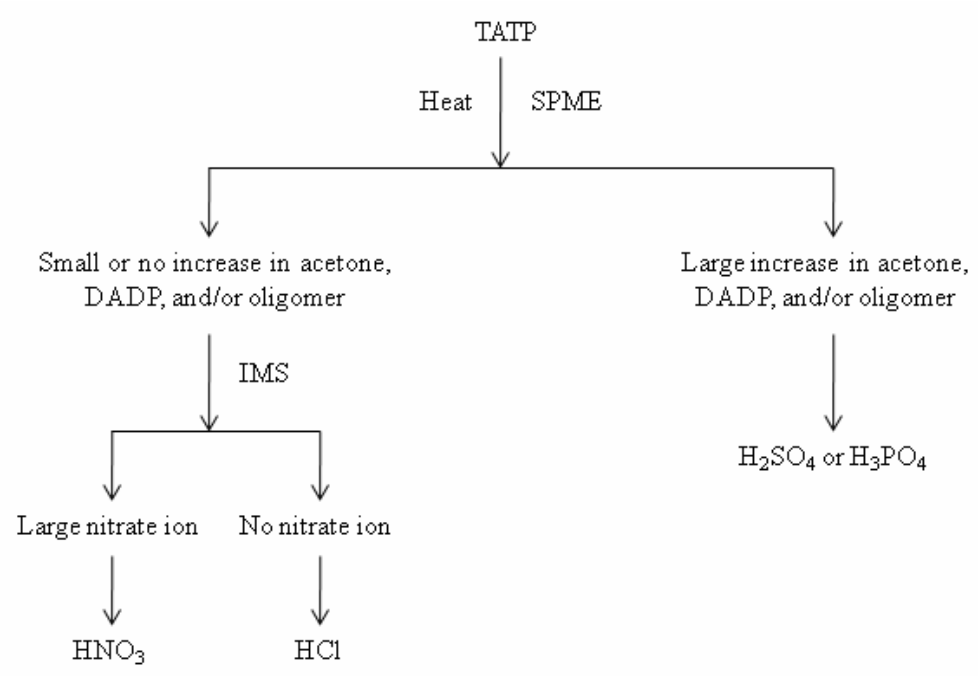


Figure 35: Flow chart showing the tentative identification of the acid catalyst

Laboratory Post-blast TATP Analysis

Organic carryover products were detected in a limited number of post-blast samples in laboratory-scale tests. Even though two different methods were utilized to sample the post-blast material, neither led to significant detection of carry-over products. Multiple samples were detonated that had been synthesized with acetones known to contain additives, and most failed to produce any detectable carry-over. TATP synthesized with acetone #3 was the only sample in which a single impurity, benzyl benzoate (BB), was detected post-blast. The abundant amount of benzyl benzoate in pre-blast samples of TATP synthesized with acetone #3 and the long lifetime of benzyl benzoate in TATP likely contribute to the post-blast detection of the carry-

over. Nonetheless, the analysis after the laboratory detonation of milligram samples of TATP did allow detection of the carry-over, benzyl benzoate, in trace amounts.

Large Scale Pre- and Post-blast TATP Analysis

Pre-blast Analysis

The results from the laboratory analysis were compared with results obtained prior to and after detonation of TATP synthesized on a much larger scale. On the large scale, additives from the acetone source were also found to carry through the synthesis and were detected in the pre-blast TATP. The oligomeric peroxides were identified in all of the pre-blast samples, but varied in intensity and composition as was the case in the laboratory analysis of pre-blast TATP. Analysis of the post-blast debris revealed the detection of a single carry-over additive, benzyl benzoate, which is consistent with the results obtained in the laboratory using the fallhammer device. IMS analysis of cotton swabs used to wipe down the post-blast debris failed to detect TATP in some of the samples that were detonated, however, TATP could be detected by GC-MS analysis of the headspace above every post-blast debris sample that was sealed in K-pak bags. The melting points for each of the samples were almost identical (84-92°C), except for control sample #1 (58-85°C), which had a melting point that was depressed significantly to the rest of the samples. The abundance of oligomers present in control sample #1 which was synthesized with laboratory acetone was greater than any of the other samples, as determined by APCI-MS analysis of methanol solutions of the pre-blast material, and possibly accounts for the lower melting point of the sample.

Analysis of the pre-blast material for the presence of carry-over impurities from the acetone source produced results similar to those obtained from the laboratory analysis of milligram samples of TATP; however, there were some notable differences. Most of the additives identified by solution samples were also identified via SPME sampling of the headspace above the material (Table 9 and Table 10), which was not true for the laboratory-scale samples. Based on the results of TATP prepared on a laboratory-scale (milligram quantities), SPME sampling was the better technique because it allowed for the detection of more carry-over analytes. The results of the large-scale analysis, however, show that both methods detected the majority of the same compounds, so one sampling technique does not seem to be better than the other on the larger scale. The TATP samples synthesized on the larger scale were dried to a lesser extent to increase handling safety. The reduced drying could result in higher additive concentration.

Similar to the laboratory results, certain compounds were only identified via one sampling method or the other. The compounds that were only identified by analysis of solution TATP samples were 3-(4-isopropylphenyl)-2-methylpropionaldehyde (R), 5-heptyldihydro-2(3H)-furanone (W), and 2-(phenylmethylene)-octanal (AA). Nonanoic acid, methyl ester (K), hexanedioic acid, dimethyl ester (L) and butanoic acid, phenylmethyl ester (O) were only identified by SPME sampling the headspace above the pre-blast material.

As in the analysis of the laboratory-scale synthesis of TATP, the oligoperoxides were identified in the pre-blast material of the large scale TATP samples. The two control samples contained the most abundant amount of oligomers (Figure 29 (upper) shows the oligomers present in control sample #1), while TATP synthesized with acetones #21 and #22 contained

virtually no oligomers. Samples that were synthesized with acetones #3 and #27 contained oligomers, but they were not as abundant as those in the two control samples (oligomers in TATP synthesized with acetone #3 are shown in Figure 29 (lower)). A weak m/z 230 ion was observed in TATP synthesized with acetone #3 and reasonably corresponds to the molecular ion of the benzyl benzoate additive (BB) of m/z 212 with an ammonium adduct ion (identified in Figure 29). The additives within the acetones may have an effect on the amount of oligomers present. The two TATP samples that contain the highest quantity of additives contained minimal amounts of oligomers, while the two control samples did not contain any additives, but did contain multiple oligomeric peroxides. The two control samples contain very weak TATP ions, while the two samples synthesized with acetones #3 and #27 contain the most abundant TATP ions. The two control samples, and TATP synthesized with acetones #3 and #27 also contain a second set of oligomers that are dihydroperoxy/acyl terminated, but are much less intense than the dihydroperoxy terminated oligomers. The additives present in the acetone source may hinder the formation of the oligoperoxides which could explain why the oligomers were weak in two of the samples.

Post-blast Analysis

The TATP samples synthesized on a larger scale were detonated using a Number 8 blasting cap or an exploding wire detonator. Most of the detonations produced a plume of white smoke, with the larger samples producing the largest plumes and no fireball. However, TATP synthesized with acetone #22 created a large fireball upon detonation even though the sample

was a little less than 2 grams. Analysis of the pre-blast material showed significant quantities of limonene in the sample (Figure 28) which may have attributed to the fireball since limonene is combustible. Figure 36 compares the detonation of the 2 gram sample of TATP that created a fireball and the 88 gram sample of TATP.

Figure 36: Pictures showing the comparison of the detonations of 2 grams of TATP (upper) and 88 g of TATP (lower)

After detonation, the debris was sampled to determine if TATP and the carry-over analytes could be detected post-blast on the larger scale. The results of sampling the headspace of the K-pak bag containing the aluminum plates produced results that coincided with the results

achieved in the analysis of post-blast TATP in the laboratory. TATP was identified in all five of the post-blast samples, and benzyl benzoate (BB) was the only carry-over analyte that could be detected on the larger scale, as it was with samples detonated by the fallhammer. With the small scale analysis, benzyl benzoate was only identified in one post-blast TATP sample that had been synthesized with acetone #3. On the larger scale, however, benzyl benzoate was identified in the headspace of the bags containing debris from TATP synthesized with acetones #3, #21, and #27 (Figure 30 shows the identification of benzyl benzoate in post-blast debris from TATP synthesized with acetone #3). As with the laboratory experiments, the low concentration of the impurities relative to the TATP limits their detection in post-blast debris.

IMS analysis of cotton swabs used to wipe down the aluminum plates after detonation failed to trigger the programmed TATP alarm in some of the samples. The TATP peaks in the plasmagrams for TATP synthesized with lab-grade acetone and TATP synthesized with acetone #3 were the most intense (Figure 31), while the TATP peak from the synthesis with acetone #27 was slightly weaker, and the peak in the TATP sample synthesized with acetone #21 was weak but still triggered the alarm. TATP prepared with acetone #22 did not trigger the alarm for TATP when the aluminum plate was wiped down with a cotton swab, but when another cotton swab was used to wipe down the steel plate under the aluminum sheet, TATP was detected by the IMS. This may be due to the large fireball that was created upon detonation of the material which could have consumed any of the TATP residue on the aluminum plate.

CHAPTER 5: CONCLUSIONS AND FUTURE RESEARCH

Conclusions

TATP can be synthesized using a wide variety of commercially available starting materials. The purity of these materials calls into question whether additives present in the precursors can carry through the TATP synthesis and be detected in the final product. The acetones analyzed in this research ranged from relatively pure such as those used as paint thinners and solvents to nail polish removers which contain multiple additives.

Upon analysis of TATP synthesized with the various acetone sources, additives that were identified in the source could be detected in the final product. The purity level of the acetones seemed to have an effect on whether the additives could be detected in the TATP. Additives that were identified in acetones that are used as solvents and paint thinners generally failed to carry over through the synthesis, while additives present in nail polish removers were readily identified in the TATP. Generally, these additives were better detected by SPME sampling the headspace above the material rather than creating solution samples from the TATP.

The concentration of the impurities in the TATP samples was determined to be very low relative to the weight of the TATP. For all batches of TATP synthesized in this experiment, the concentration of the impurities was determined to be less than 0.1% (w/w) relative to the concentration of TATP. Benzyl benzoate (BB), a common additive in many of the acetone sources, had the highest weight percent at 0.085% (w/w) of all the impurities in the TATP when it was synthesized with acetone #3. The analysis of acetone #3 showed that benzyl benzoate was very abundant in the source, but was still only detected at trace levels in the TATP sample.

Because of the low concentrations, studies were conducted to determine the approximate length of time the impurities could be detected in a sample of TATP that was left to air dry. The length of time impurities could be detected varied from a few hours up to 24 hours. Forensically this is important because it addresses the question of whether the acetone source can be determined by the identification of the acetone additives in the TATP and how long after the synthesis they can be detected. If these additives are detected in a sample of TATP, it could lead to the identification of the acetone source.

Samples of TATP synthesized with laboratory grade acetone and analyzed by GC-MS seem to be relatively pure TATP; however, ESI-MS or APCI-MS analysis of these same samples reveals the presence of multiple oligoperoxides. The peroxide oligomers can be identified through the use of ammonium and sodium complexes, and they vary in length and composition among TATP samples. By isolating one of the oligomers in an ion trap and fragmenting it with an applied CID voltage, the product ions formed can be used to aid in the determination of selected reaction monitoring methods for the detection of the peroxide oligomers. The choice of complexing additive has an effect on the CID product ions. With ammonium as the adduct, the product ions can break down and cyclize to form the cyclic tetramer, TATP, and DADP, but oligomers complexed with sodium ions break down to form smaller hydroperoxy/acyl terminated oligoperoxides.

The discrimination among TATP samples synthesized with different acids can tentatively be accomplished through the combined use of different instrumental analyses. By comparing the changes in the composition of the headspace of the TATP between a room temperature sample and a sample that has been gently heated, a considerable increase in abundance of acetone,

DADP, and/or the oligoperoxides suggests that either sulfuric or phosphoric acid was used in the synthesis. The headspace of samples synthesized with hydrochloric or nitric acid exhibit very little change in composition upon heating. Analyzing the TATP crystals by IMS provides further classification of sulfuric and nitric acid samples. In the plasmagram of samples synthesized with sulfuric acid in the laboratory, there were two additional peaks that were reproducible among samples prepared with sulfuric acid that were not present in the plasmagram of TATP synthesized with the other acids. On the larger scale, however, those two peaks were not present in TATP prepared with sulfuric acid. TATP samples synthesized with nitric acid gave results in which an intense nitrate ion peak was observed in the plasmagram. The nitrate ion peak was also identified in the plasmagrams of TATP synthesized with the other acids, but none of which were remarkably as intense as the ones in the TATP sample prepared with nitric acid.

The analysis of laboratory-scale post-blast samples for the presence of carry-over products resulted in the detection of a single additive, benzyl benzoate, identified in TATP synthesized with acetone #3. The lifetime of benzyl benzoate along with its abundance in pre-blast samples likely has an effect on why it can be detected after detonation. The trace levels of the carry-over analytes in pre-blast material make it difficult to detect them in post-blast debris.

TATP synthesized on a larger scale produced results similar to those of the laboratory analyses. Multiple impurities were identified in the pre-blast material, including the majority of the analytes identified as carry-over in the small-scale TATP samples. A notable difference between the small-scale and large-scale analyses for carry-over products is that the impurities in the laboratory samples were generally better detected by SPME sampling the headspace above the TATP, while on the larger scale, most of the carry-over products were identified by both

solution and SPME sampling. The large-scale TATP samples were not dried as thoroughly as the laboratory-scale samples to increase safety when handling the material, so that may have contributed to the detection of more carry-over analytes. The oligomeric peroxides were present in each sample of TATP synthesized on the large-scale; however, the variability of the composition of the oligomers between batches is too great to discriminate TATP samples that have been synthesized with different acids.

The post-blast analysis of the large-scale samples revealed that, although weak, benzyl benzoate was still the only carry-over impurity that could be detected post-blast as was observed in the laboratory analyses. SPME sampling the headspace of the K-pak bags containing the post-blast debris proved to be a better technique than sampling the headspace above a cotton swab used to wipe down the aluminum sheet after detonation. IMS analysis of the second set of cotton swabs used to wipe down the aluminum sheet after detonation triggered the alarm for TATP in four of the five samples. The sample that did not trigger the alarm was also the sample that created the large fireball upon detonation, so any TATP residue was likely consumed in the fire; however, when the steel plate under the aluminum sheet was swabbed and analyzed by IMS, TATP was detected.

Future Research

The increase use of TATP in recent years shows the need for a better understanding of the properties and behavior of TATP. The research presented here focuses on the analysis of the synthetic precursors and the effects they have on the final product. Both the acetone and acid precursors were studied in detail, but more research is needed on the peroxide used to synthesize

the material. The effects of varying the concentration of lab grade hydrogen peroxide on TATP were briefly looked into, as was the analysis of TATP synthesized with a few different commercially available peroxide sources, but a more extensive study should be conducted. The behavior of TATP during the large scale detonations should be researched further since those are the samples that would typically be encountered forensically. Further research could also be conducted to investigate why a fireball was produced during the large-scale tests during this research to see if it was a factor of the additives in the acetone or if it was just an anomaly. Detection of TATP and the carry-over impurities after a length of time in post-blast debris is forensically important. This research focused on analyzing the post-blast debris from the laboratory and large-scale tests as soon after detonation as possible; however, the length of time the additives and TATP can be detected after detonation could be investigated as well to give a general idea of how long they are present in a sample of post-blast debris.

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REFERENCES

1. Meidl, J.H., Explosives and Hazardous Materials, ed. H.N. Gruber. 1970, Beverly Hills: Glencoe Press.

2. Yinon, J. and S. Zitrin, Modern Methods and Applications in Analysis of Explosives. 1993, West Sussex: Wiley.

3. Beveridge, A., Forensic Investigation of Explosions. Taylor and Francis Forensic Science Series, ed. J. Roberson. 1998, London: Taylor and Francis.

4. Akhavan, J., The Chemistry of Explosives. 2nd ed. 2004, Cambridge: The Royal Society of Chemistry.

5. Urbanski, T., Chemistry and Technology of Explosives. Vol. 4. 1984, Oxford: Pergamon Press.

6. Trace Chemical Sensing of Explosives, ed. R.L. Woodfin. 2007, Hoboken, NJ: Wiley-Interscience.

7. Aspects of Explosive Detection. 1st ed, ed. M. Marshall and J. Oxley. 2009, Amsterdam;Boston: Elsevier.

8. Wolffenstein, R., Uber die Einwirkung von Wasserstoff Superoxyd auf Aceton und Mesityloxyd. Chemische Berichte, 1895. 28: p. 2265-2269.

9. Meyer, R., J. Kohler, and A. Homburg, Explosives. 6th ed. 2007, Weinheim;Cambridge: Wiley-VCH.

10. Bellamy, A., Triacetone Triperoxide: Its Chemical Destruction. Journal of Forensic Sciences, 1999. 44(3): p. 603-608.

11. Dubnikova, F., et al., Decomposition of Triacetone Triperoxide is an Entropic Explosion. Journal of the American Chemical Society, 2005. 127(4): p. 1146-1159.

12. Oxley, J., et al., Determination of the vapor density of triacetone triperoxide using a gas chromatography headspace technique. Propellants, Explosives, Pyrotechnics, 2005. 30(2): p. 127-130.

13. Schulte-Ladbeck, R., P. Kolla, and U. Karst, Trace Analysis of Peroxide-Based Explosives. Analytical Chemistry, 2003. 75(4): p. 731-735.

14. Cotte-Rodriguez, I., H. Chen, and R. Cooks, Rapid trace detection of triacetone triperoxide (TATP) by complexation reactions during desorption electrospray ionization. Chemical Communications, 2006(9): p. 935-955.

15. Shen, C., et al., Triacetone Triperoxide detection using low reduced-field proton transfer reaction mass spectrometer. International Journal of Mass Spectrometry, 2009. 285(1-2): p. 100-103.

16. Sigman, M., et al., Analysis of Triacetone Triperoxide by gas chromatography/mass spectrometry and gas chromatography/tandem mass spectrometry by electron and

chemical ionization. Rapid Communications in Mass Spectrometry, 2006. 20(19): p. 2851-2857.

17. Fedoroff, B., O. Sheffield, and S. Kaye, in Encyclopedia of explosives and related items. 1960-1983, Picatinny Arsenal: Dover, NJ.

18. Rieche, A., Die Oxydation des Diisopropylathers. Chemische Berichte, 1942. 75: p. 1016.

19. Milas, N.A. and A. Golubovic, Studies in Organic Peroxides. XXVI. Organic Peroxides Derived from Acetone and Hydrogen Peroxide. Journal of the American Chemical Society, 1959. 81(24): p. 6461-6462.

20. Sauer, M. and J. Edwards, The Reactions of Acetone and Hydrogen Peroxide. I. The Primary Adduct. The Journal of Physical Chemistry, 1971. 75(19): p. 3004-3009.

21. Sauer, M. and J. Edwards, The Reactions of Acetone and Hydrogen Peroxide. II. Higher Adducts. The Journal of Physical Chemistry, 1972. 76(9): p. 1283-1288.

22. Oxley, J., J. Smith, and H. Chen, Decomposition of a Multi-Peroxidic Compound: Triacetone Triperoxide (TATP). Propellants, Explosives, Pyrotechnics, 2002. 27(4): p. 209-216.

23. Armitt, D., P. Zimmermann, and S. Ellis-Steinborner, Gas chromatography/mass spectrometry analysis of triacetone triperoxide (TATP) degradation products. Rapid Communications in Mass Spectrometry, 2008. 22: p. 950-958.

24. Haberman, C., At least 14 dead as suicide bomber strikes Jerusalem, in The New York Times. 2001: New York.

25. Belluck, P. and K. Chang, A Nation Challenged: The Investigation; Shoes were a 'homemade bomb' FBI Agent Says, in The New York Times. 2001: New York.

26. Natta, D.V. and E. Sciolino, Bombings in London: Terror Threat; Subway suspect is shot to death by London police, in The New York Times. 2005: New York.

27. London bombers used every day materials-US police. 2005, Reuters News: New York/London.

28. Cole, C., Police bomb expert shares details of OU bombing, in The Norman Transcript. 2006.

29. Moran, K. and E. Hanson, Experts set off blast at complex/Texas City officials look to survivor of initial explosion for clues, in The Houston Chronicle. 2006: Houston.

30. Rashbaum, W.K., Terror Suspect is Charged with Plot to Use Bombs, in The New York Times. 2009.

31. Sigman, M., et al., Analysis of oligomeric peroxides in synthetic triacetone triperoxide samples by tandem mass spectrometry. Rapid Communications in Mass Spectrometry, 2009. 23(3): p. 349-356.

32. Baeyer, A. and V. Villiger, Einwirkung des Caro'schen Reagens auf Ketone. Chemische Berichte, 1899. 32(3): p. 3625-3633.

33. Baeyer, A. and V. Villiger, Ueber die Einwirkung des Caro'schen Reagens auf Ketone. Chemische Berichte, 1900. 33(1): p. 858-864.

34. Criegee, R. and K. Metz, A third crystallized acetone peroxide. Chemische Berichte, 1956. 89: p. 1714-1718.

35. Criegee, R., W. Schnorrenber, and J. Becke, Constitution of ketone peroxides. Annalen der Chemie, Justus Liebigs, 1949. 565: p. 7-21.

36. Rieche, A., Alkyl Peroxyde und Ozonide. 1931, Erlangen, Berlin.

37. Swern, D. and L.S. Silbert, Studies in the Structure of Organic Peroxides. Analytical Chemistry, 1963. 35(7): p. 880-885.

38. Hiatt, R., ed. Hydroperoxides. Organic Peroxides, ed. D. Swern. Vol. 2. 1971, John Wiley: New York. 1-152.

39. Sigman, M., et al., Analysis of Triacetone Triperoxide (TATP) and TATP synthetic intermediates by electrospray ionization mass spectrometry. Rapid Communications in Mass Spectrometry, 2008. 22(2): p. 84-90.

40. Muller, D., et al., Improved method for the detection of TATP after explosion. Journal of Forensic Sciences, 2004. 49(5): p. 935-938.

41. Zitrin, S., S. Kraus, and B. Glattstein. in Proc 1st Int Symp on the Analysis and Detection of Explosives. 1983. FBI Academy, Quantico, VA, USA.

42. Zitrin, S., S. Kraus, and B. Glattstein. Proceedings of the International Symposium on the Analysis and Detection of Explosives. in International Symposium on the Analysis and Detection of Explosives. 1984: US Government Printing Office.

43. Buttigieg, G., et al., Characterization of the explosive triacetone triperoxide and detection by ion mobility spectrometry. Forensic Science International, 2003. 135: p. 53-59.

44. Cotte-Rodriguez, I., et al., In Situ Trace Detection of Peroxide Explosives by Desorption Electrospray Ionization and Desorption Atmospheric Pressure Chemical Ionization. Analytical Chemistry, 2008. 80: p. 1512-1519.

45. Arai, H. and J. Nakmura, 4th IAFS Tokyo 1996 Fires and Explosions. 1996.

46. Fialkov, A.B. and A. Amirav, Cluster chemical ionization for improved confidence level in sample identification by gas chromatography/mass spectrometry. Rapid Communications in Mass Spectrometry, 2003. 17(12): p. 1326-1338.

47. White, G., An Explosive Drug Case. Journal of Forensic Sciences, 1992. 37(2): p. 652-656.

48. Crowson, A. and M. Beardah, Development of an LC/MS method for the trace analysis of hexamethylenetriperoxidediamine (HMTD). Analyst, 2001. 126(10): p. 1689-1693.

49. Widmer, L., et al., Development of an LC/MS method for the trace analysis of triacetone triperoxide (TATP). Analyst, 2002. 127: p. 1627-1632.

50. Xu, X., et al., Trace analysis of peroxide explosives by high performance liquid chromatography—atmospheric pressure chemical ionization—tandem mass spectrometry (HPLC-API-MS/MS) for forensic applications. Journal of Forensic Sciences, 2004. 49(6): p. 1230-1236.

51. Scott, R.P., Introduction to Analytical Gas Chromatography. 2nd ed. 1998, New York: Marcel, Dekker, Inc.

52. Skoog, D.A., E.J. Holler, and S.R. Crouch, Principles of Instrumental Analysis. 6th ed. 2007: Thomson Brooks/Cole.

53. Vestal, M.L., Methods of Ion Generation. Chemical Reviews, 2001. 101(2): p. 361-376.

54. Herbert, C.G. and R.A. Johnstone, Mass Spectrometry Basics. 2003, Boca Raton: CRC Press.

55. McMaster, M.C., HPLC: A Practical User's Guide. 2007, Hoboken, NJ: John Wiley.

56. Abian, J., The coupling of gas and liquid chromatography with mass spectrometry. Journal of Mass Spectrometry, 1999. 34: p. 157-168.

57. Kostianinen, R. and T. Kauppila, Effect of eluent on the ionization process in liquid chromatography-mass spectrometry. Journal of Chromatography A, 2009. 1216: p. 685-699.

58. Eiceman, G. and Z. Karpas, Ion Mobility Spectrometry. 2nd ed. 2005, New York: CRC Press: Taylor and Francis Group.

59. Arthur, C. and J. Pawlisyn, Solid phase microextractioni with thermal desorption fused silica optical fibers. Anal Chem, 1990. 62: p. 2145-2148.

60. Zhang, Z. and J. Pawliszyn, Headspace solid-phase microextraction. Analytical Chemistry, 1993. 65(14): p. 1843-1852.

61. Almirall, J., J. Bruna, and K. Furton, The recovery of accelerants in aqueous samples from fire debris using solid-phase microextraction. Science & Justice, 1996. 36: p. 283-287.

62. Milas, N. and A. Golubovic, Organic Peroxides. XXIV. Preparation, Separation, and Identification of Peroxides Derived from Diethyl Ketone and Hydrogen Peroxide. Journal of the American Chemical Society, 1959. 81: p. 3361-3364.