

# TATP Headspace Study

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**Abstract:** Compositional analysis of crude and recrystallized TATP in solution and the headspace above solid material did not identify acetone presence in any sample. Acetone was detected in trace levels in crude TATP samples heated

to 65 °C for 42 hours. The concentration of which was observed to decrease over time. This is attributed to the removal of the headspace gas.

**Keywords:** TATP · Headspace · GC/MS · LC/MS · DADP

## 1 Introduction

First reported in 1895, triacetone triperoxide (TATP) is a sensitive primary explosive [1]. With an explosive power comparable to TNT combined with its straightforward synthesis from readily available precursors, TATP has received a fair amount of attention by criminals and terrorists [2–4]. Due to the extreme sensitivity to shock, friction, static discharge, and tendency to sublime rapidly, handling and storage of large quantities of TATP is dangerous, precluding its use as a military or commercial explosive [5, 7]. The vapor pressure of TATP is quite high, making it detectable by the olfactory system of humans [6].

The analysis of trace explosives is very important to the forensic community. The focus of the analysis has been on post-blast residue [7–15]. Oxley et al. used IMS coupled to solid-phase microextraction (SPME) and a novel planar solid-phase microextraction (PSPME) technique to determine the viability of the latter for use in fast detection of TATP [16]. Their work was successful at identifying a faster, more sensitive detection method. Missing from the reporting is the identification of the components of the headspace above solid TATP.

The present study presents a first analysis of the headspace above solid TATP. Crude and recrystallized TATP, as well as DADP, were maintained at room temperature and at elevated temperatures (65 °C) to simulate aging in 10 mL headspace vials. Then 10 µL of container headspace are analyzed by GC/MS.

vessel and the ice bath was maintained below 30 °C. After the reactants were combined, the mixture was transferred to the freezer overnight before filtration and rinsing with water and a 0.1% sodium carbonate solution. Following rinsing, the product was air-dried. TATP was recrystallized from methanol to remove impurities in the sample. Reaction yields of 110 grams (70%) are typical.

## Instrumentation

Using a Thermo TSQ FORTIS Triple Stage Quadrupole LC/MS System equipped with an atmospheric pressure chemical ionization (APCI) interface, ions were generated and introduced into the ion transfer tube set 125 °C. All work was performed using positive ion mode. Tune conditions for APCI were: discharge current, 2500–6000 µA; N<sub>2</sub> sheath gas, 8–50 arbitrary units (AU); N<sub>2</sub> auxiliary gas, 5–40 AU; vaporizer temperature 180–350 °C; ion transfer tube, 14 V; tube lens, 35–70 V; and skimmer offset (Exactive), 0 V. The mass resolution was set to 30,000 (LTQ Orbitrap) and 50,000 (Exactive) for all experiments. Solvent delivery was performed using Thermo infusion syringe pumps. Data collection and analysis were performed with Thermo Xcalibur software ver. 2.2, SP 1.48. All data collected within this work is APCI full scan MS unless otherwise noted. Raw chromatographic traces are all from the Thermo Vanquish Flex Binary UHPLC diode array detector. The data was shifted for overlay purposes only.

## 2 Experimental Section

### Preparation of

#### 1,1,4,4,7,7-Hexamethyl-1,4,7-Cyclononatriperoxane (Triacetone Triperoxide or TATP)

Acetone, hydrogen peroxide (50%), and hydrochloric acid were combined in a round bottom flask, partially submerged in an ice/salt bath. The temperature in the reaction

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## Headspace Determination

40 mg samples of crude and recrystallized TATP were sealed in Agilent 10 ml headspace screw-top flat bottom vials with Agilent 20 mm gray butyl headspace vial septa and allowed to equilibrate for 42 hours. Samples were left at room temperature and placed in a lab oven at 65 °C during the equilibration period and returned after each sample was collected. Data collection began on the Monday following the initial equilibration and continued through the week (Days 1–5) with a final sample collected on the second Monday after initial equilibration (Day 6). 10  $\mu$ L samples were injected onto an Agilent 6890 N GC equipped with a RTX-200MS capillary column (7 m $\times$ 0.25 mm $\times$ 0.25 mm film) and an Agilent 5973N MSD. For TATP the GC conditions were as follows:

Inlet: Temp. 50 °C; Splitless Mode; Constant Flow

Oven: Initial Temperature 50 °C; Initial Hold Time 5 min; Ramp 0 °C/min; Final Temperature 50 °C; Final Hold Time 0 min

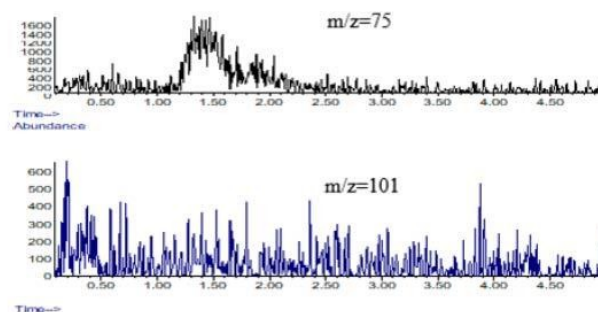
Detector: Agilent 5973N MSD; Source Temperature 230 °C, MS Quad Temperature 150 °C, Pressure 18.4 kPa

Carrier Gas: Helium

## 3 Results and Discussion

### 3.1 Determining Concentration of Acetone in TATP

TATP samples were prepared in UHP methanol. The composition of both crude and recrystallized TATP was analyzed via LC/MS. Figure 1 shows the traces for samples of crude TATP, recrystallized TATP, DADP, and crude TATP with an intentional acetone spike. Acetone was found to elute at ~1.78 minutes in the latter sample. Figure 1 inset highlights the acetone signal in the chromatographs. As can be seen in the traces, acetone is not present at detectable limits in



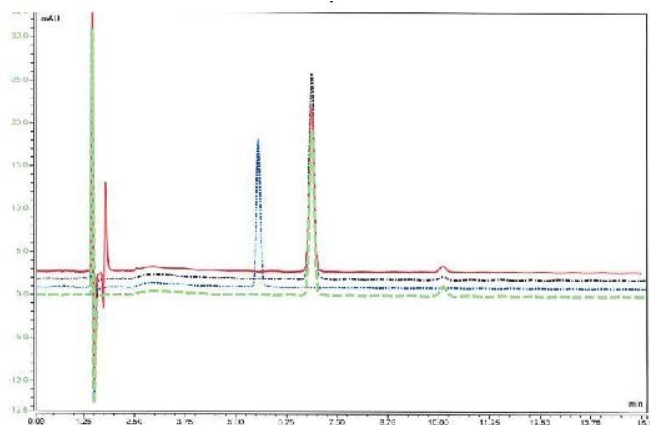
**Figure 2.** XIC traces of  $m/z=75$  (upper) and 101 (lower); crude TATP.

all three peroxide samples. This was verified via LC/MS analysis extracted ion chromatographs (XIC) which showed no signal from acetone. The data in Figure 1 also indicate that DADP is not present at appreciable levels in either TATP sample.

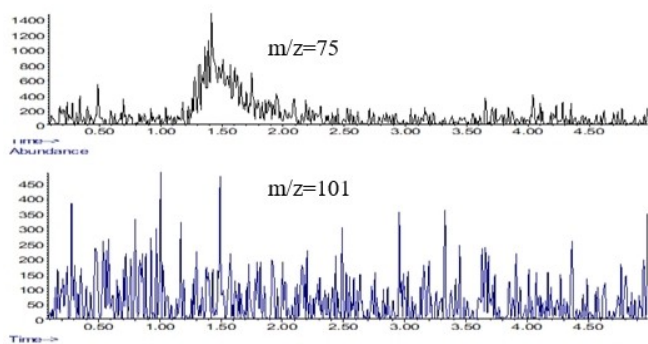
### 3.2 Components of Headspace above TATP

Figure 2–4 shows XIC for  $m/z=75$  and 101 collected from the headspace above crude TATP (Figure 2), recrystallized TATP (Figure 3), and DADP (Figure 4) for reference. The prior is a mass-to-charge ratio indicative of TATP presence while the latter indicates DADP. The signal from the organic peroxides in the headspace was measured near the detection limit of the instrument. XIC was conducted on all samples for TATP, DADP, and acetone.

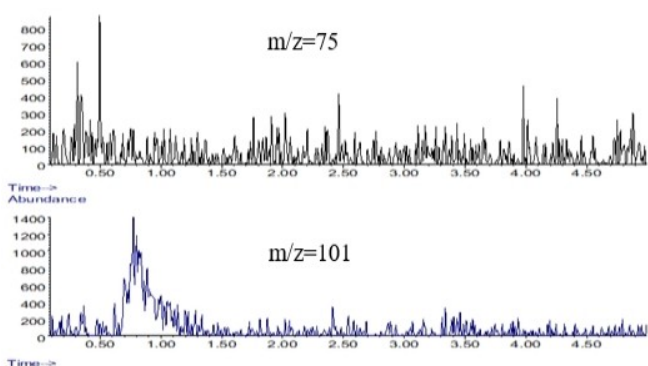
One  $\mu$ L of acetone was added to the same headspace vial configuration as used with the organic peroxides. Ten  $\mu$ L of headspace over the liquid was collected and injected into the GC/MS for analysis. Figure 5 is the chromatograph for acetone-only headspace. Free acetone has a measured



**Figure 1.** LC traces of crude TATP (—), DADP (—), Recrystallized TATP (—), and crude TATP with intentional acetone spike (—).



**Figure 3.** XIC traces of  $m/z=75$  (upper) and 101 (lower); recrystallized TATP.



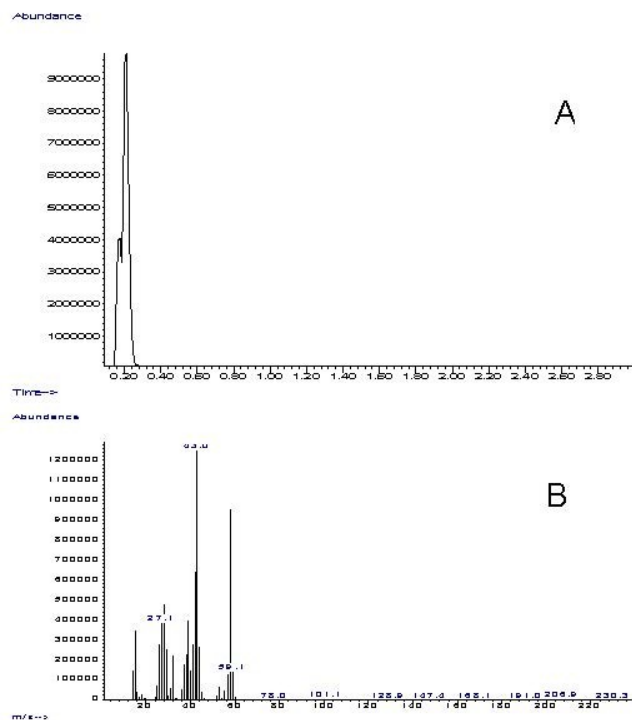
**Figure 4.** XIC traces of  $m/z=75$  (upper) and 101 (lower); DADP.

retention time of 12 seconds with these detection parameters. As shown in the mass spectrum, Figure 9B,  $m/z=15$  (methyl), 43 (methyl carbonyl), and 58 (molecular ion) and the ratios indicative of acetone presence. There is a high level of overlap between the acetone peak and the peak due to air in the headspace vials. The additional peaks seen in the acetone mass spectrum can be attributed to the overlap with air.

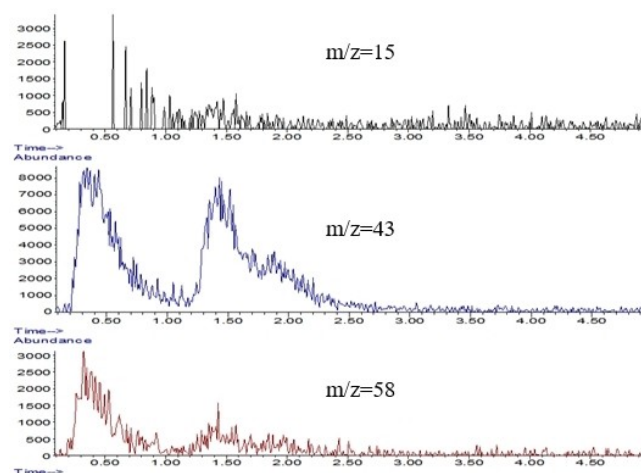
Traces for acetone, with XICs at 15 (methyl group), 43 (methyl carbonyl), and 58 (molecular ion), can be found in Figure 4. Masses 43 and 58 are also seen in the spectra for TATP and DADP. The presence of all three masses, 15, 43, and 58, is the best indication of acetone presence. Based on these results, the data represented in Figures 2 and 4 and 6–8 indicates only the targeted synthetic product can be seen in the headspace above the sample. Only DADP was seen over the DADP sample and only TATP has seen over both TATP samples.

### 3.3 Effects on Headspace Content from Storing TATP at Elevated Temperatures

Exposing the samples to 65 °C for an initial period of 72 hours with continuous heating throughout the data col-



**Figure 5.** Acetone chromatograph (A) and mass spectrum (B).



**Figure 6.** Acetone  $m/z$  XIC for crude TATP (A).

lection (five days), had an appreciable effect on the concentration of organic peroxide in the headspace. The crude TATP sample contained the most significant difference in headspace composition. As shown in Figure 9A, the chromatograph contains four overlapping peaks. XIC for acetone  $m/z$ , Figure 9B, finds signal attributable to acetone within the signal of the earliest peak. The abundance of the signal is close to the detection limits of the instrument. Notice the presence of 15, 43, and 58  $m/z$  in later peaks. These

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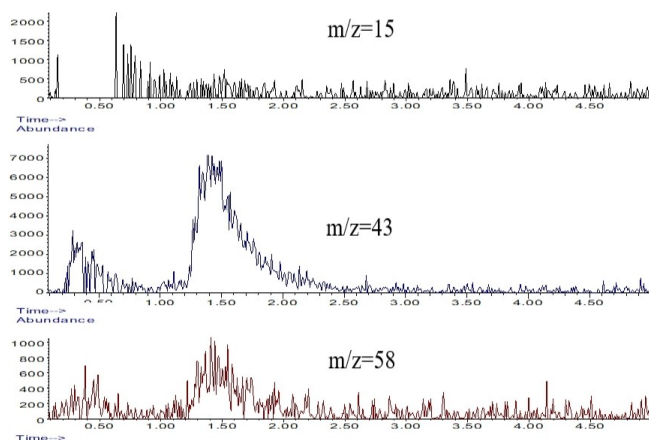


Figure 7. Acetone  $m/z$  XIC for recrystallized TATP.

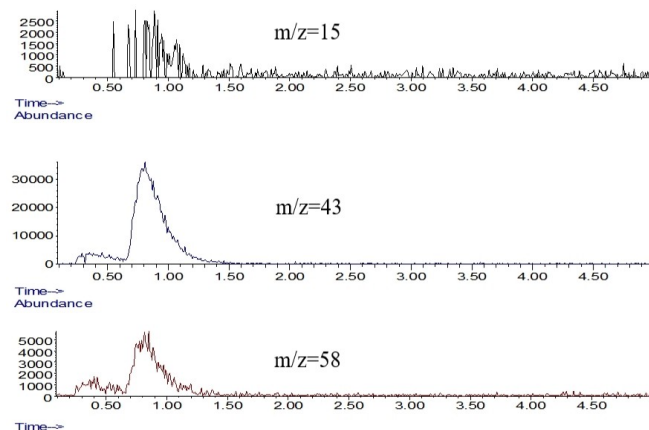


Figure 8. Acetone  $m/z$  XIC for DADP (C).

masses are also present in the mass spectra for TATP and DADP. It is noted that  $m/z$  75 and 101 are not present in the  $\sim 0.5$  minutes peak.

The presence of acetone in the oven headspace sample is predictable at the elevated temperature and if residual acid is contained in the crude TATP sample. Should this be the case, one would predict no acetone in the recrystallized heated samples. The chromatographs in Figure 10 prove this to be the case. In these samples, no acetone was detected throughout the study.

The TATP chromatographs for crude maintained at elevated temperatures contain four distinct peaks. The first is comprised of air and acetone. The others are attributed to TATP (peak at  $\sim 1.4$  minutes), DADP (peak/shoulder at  $\sim 1.8$  minutes), and acetone peroxide (peak at  $\sim 1$  minute). The TATP and DADP peaks were validated with XIC of  $m/z$  75 and 101. The identification of the one-minute peak to the monomer was extrapolated from the similarities and differences between its mass spectrum and that of TATP and DADP. Seen in Figure 11 are the mass spectra for the one-

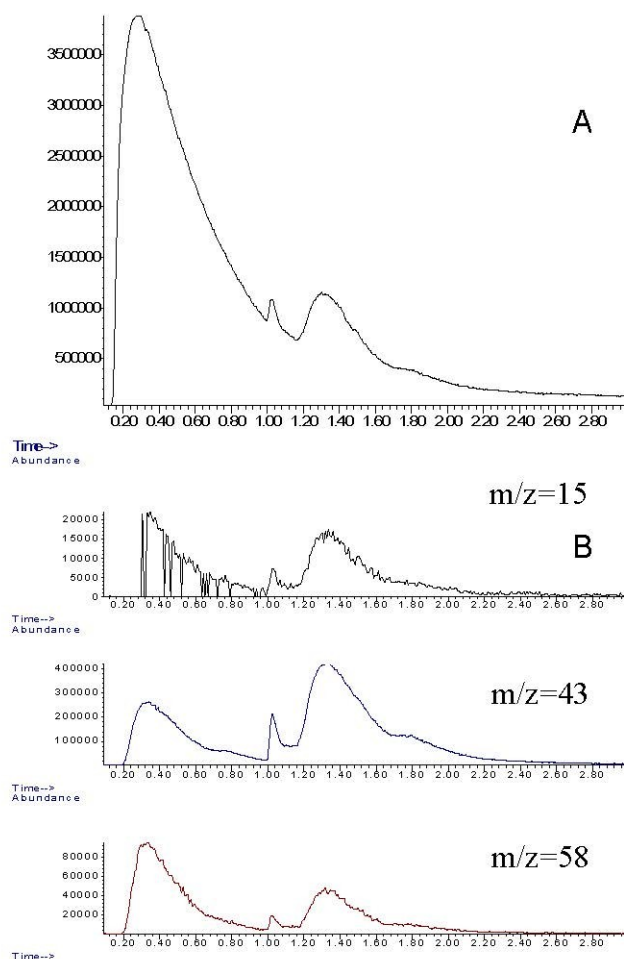
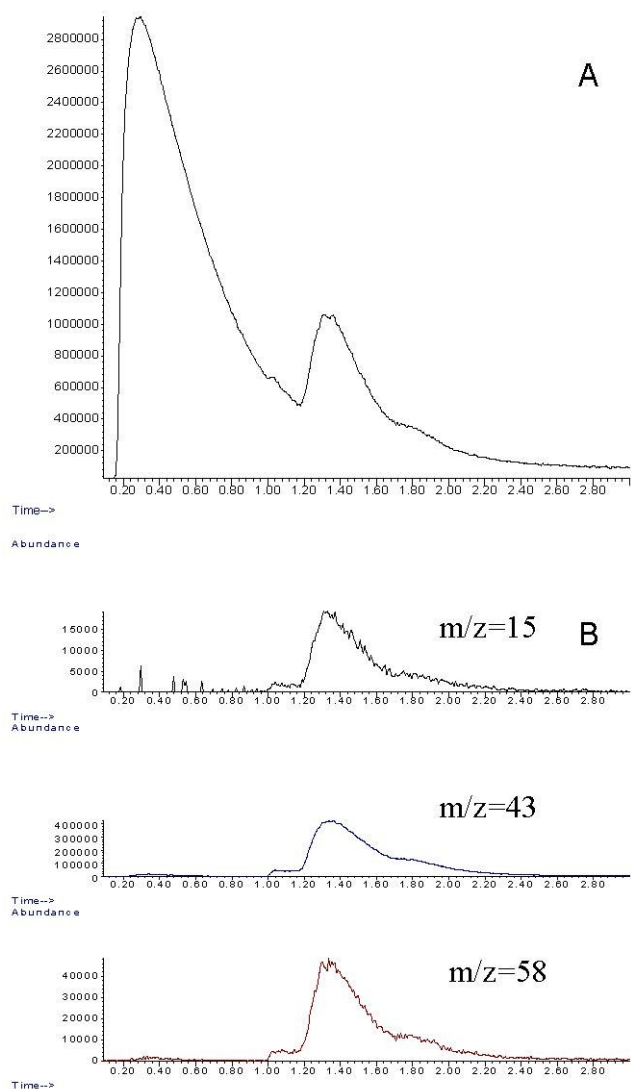


Figure 9. Chromatograph of crude TATP after heating; A: Total Ion Count, B: XIC for acetone.

minute peak (A), 1.4-minute peak (B), and 1.8-minute peak (C). As expected, the spectrum in 11 A has a high abundance of nitrogen due to the heavy overlap with the air peak. The monomer would also contain a peak for  $m/z$  of 75 corresponding to the molecular ion peak for the monomer. A noticeable difference is seen in the abundance of 43 and 59. In the TATP spectrum (B) the ratio of 43:59 abundance is 5.8. Where in Figure 11A it is 6.4. To note:  $m/z=43$  is not seen in air control samples.

The recrystallized samples have a similar chromatograph to that of the crude TATP samples. Two major differences were observed. The first difference, no acetone was detected, Figure 10A, and the peak around one minute is exceptionally less abundant in the recrystallized samples than in the crude samples. This can be attributed to the lack of acid-catalyzed decomposition of the monomer species.

Throughout this study, the abundance for all peaks decreased. This indicates that all materials were in the gas phase after the initial 42-hour equilibration period. A decrease was also observed for the acetone signal. This would

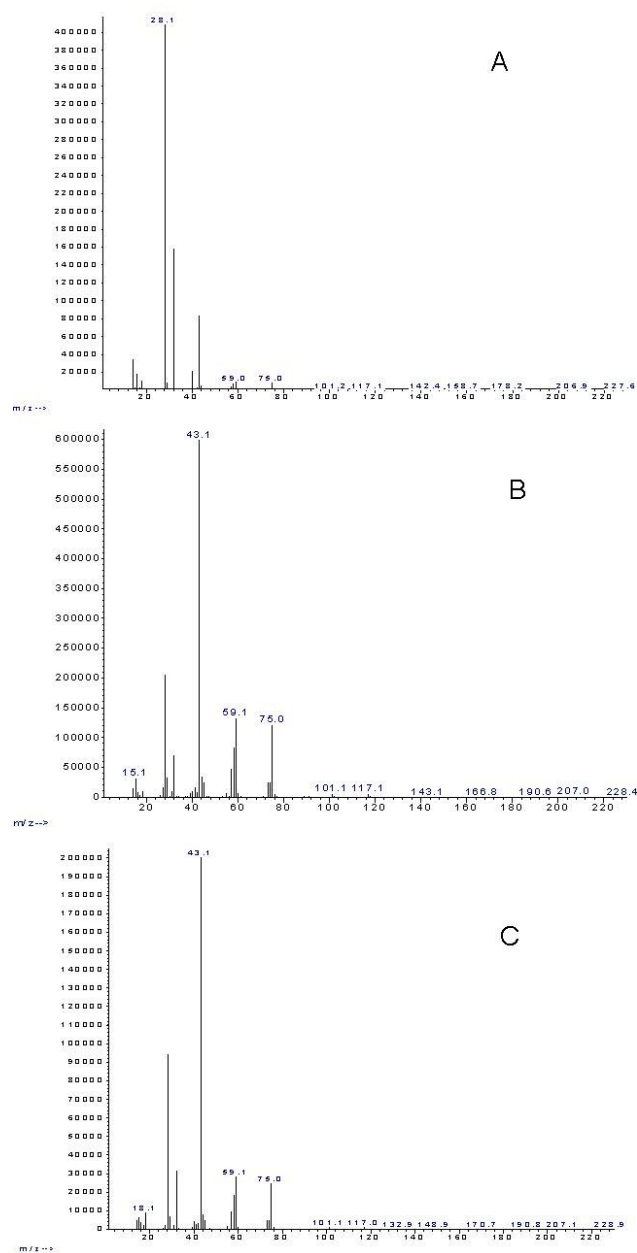


**Figure 10.** Chromatograms for recrystallized TATP; A) TIC, B) XIC for  $m/z = 15$ , 43, and 58.

be expected if the reaction that caused the creation of acetone to have also been completed within the initial equilibration period. The continual decrease is most probably due to the minimal removal of headspace gases throughout the study.

## 4 Conclusion

The headspace above crude and recrystallized TATP was investigated to determine the composition and the effect of heating on headspace composition. As a control, the headspace above DADP was also investigated. The only compound measurable in the headspace was found to be the parent organic peroxide. The heating of the samples caused



**Figure 11.** Mass spectra from crude TATP heated to 65°C for 42 hours from chromatograph peak at A) ~1 minute, B) ~1.4 minutes, and C) ~1.8 minutes.

thermal decomposition in the case of recrystallized TATP. Evidence of thermal and acid-catalyzed decomposition was observed in crude TATP. Trace levels of acetone were detected in the crude heated TATP headspace. Analysis of both TATP variants via LC/MS did not identify the presence of acetone. The results of this study strongly suggest the proposal that diacetone alcohol and acetone are intractable components of TATP's "vapor signature" is incorrect.



## Symbols and Abbreviations

APCI	Atmospheric Pressure Chemical Ionization
ARA	Applied Research Associates, Inc.
AU	Arbitrary Units
DADP	1,1,4,4-Tetramethyl-1,4-cyclohexadiperoxane; Diacetone Diperoxide
DHS	Department of Homeland Security
GC	Gas Chromatography
GC/MS	Gas Chromatography-Mass Spectrometry
HME	Homemade explosives
LC	Liquid Chromatography
LC/MS	Liquid Chromatography-Mass Spectrometry
MS	Mass Spectrometer
MSD	Mass Spectrometry Detector
m/z	Mass-to-Charge Ratio
nm	Nanometer
ppm	Parts Per Million
RT	Room Temperature
TATP	1,1,4,4,7,7-Hexamethyl-1,4,7-cyclononatriperoxide; Triacetone Triperoxide
TIC	Total Ion Count
UHPLC	Ultra-High Pressure (Performance) Liquid Chromatography
μL	MicroLiter
UV-Vis	Ultra-Violet Visible
VOC	Volatile Organic Compound
WVL	Wavelength
XIC	Extracted Ion Chromatograph

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## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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