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# Development of a Gas Chromatography with High-Resolution Time-of-Flight Mass Spectrometry Methodology for BDNPA/F

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**ABSTRACT:** Analysis of thermally labile compounds such as bis(2,2-dinitropropyl) acetal/formal (BDNPA/F), an energetic plasticizer, is usually performed via liquid chromatography (LC) as opposed to gas chromatography (GC) due to thermal decomposition in the inlet or the analytical column. While LC is a powerful technique, the analysis of volatile and semivolatile compounds is best suited to GC. Herein, a method was developed for a gas chromatograph coupled to high-resolution mass spectrometer (GC-HRMS), utilizing a programmable temperature vaporizer (PTV) inlet. A subset of the native compounds and several produced by the thermal decomposition of BDNPA/F in the inlet were evaluated by using multiple PTV inlet parameters to determine the optimal ramp rate and final temperature of the inlet



(60 °C/min from 60 to 325 °C). The optimized GC-HRMS method nearly reduced all thermal decomposition, allowing for an excellent separation to be obtained. Furthermore, multiple ionization methods, including electron impact (EI), negative chemical ionization (NCI), and positive chemical ionization (PCI), were used to explore the many chemical differences between the BDNPA/F samples. A preliminary investigation of the benefits of using GC-HRMS to evaluate the chemical differences between unaged and aged BDNPA/F samples for unique insight was evaluated.
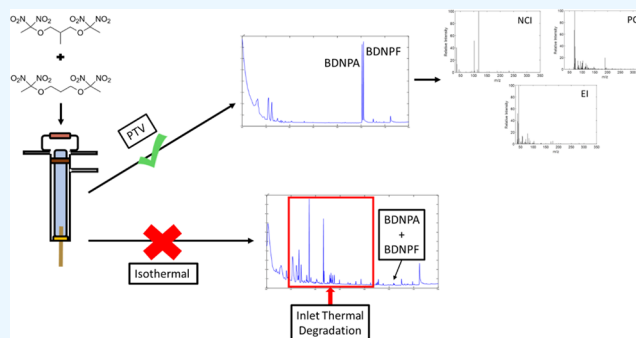
## INTRODUCTION

Analysis of thermally labile compounds such as explosives and energetic materials is often performed using liquid chromatography (LC) as opposed to gas chromatography (GC) to avoid any undesirable thermal decomposition in the inlet or analytical column.[1−6] This is especially true when evaluating decomposition products formed through thermal aging of energetic materials.[5,7,8] However, a drawback of LC is the difficulty in analyzing small molecules with higher volatilities and the lower separation efficiency compared to GC. While LC still appears to be the main choice of technique for the analysis of energetics, the use of GC has been becoming more significant since the introduction of programmed temperature vaporization (PTV) inlets.[9−12] One of the first studies for analyzing energetic materials by GC-MS using a temperature-programmable inlet was performed in 1996 by Yinon who was able to analyze thermally labile energetic samples without compound degradation in the inlet.[13] Moreover, the introduction of PTV inlets has allowed for part per quadrillion (ppq) quantification of PETN[12] and has even allowed the analysis of extremely thermally sensitive explosives such as triacetone triperoxide (TATP).[11]

One of the most widely investigated energetic plasticizers for thermal aging is a 1:1 eutectic liquid mixture of bis(2,2-dinitropropyl) acetal and bis(2,2-dinitropropyl) formal, referred to as BDNPA/F. BDNPA/F is a key component in plastic-

bonded explosive (PBX) 9501, which is composed of 94.9 wt % of the explosive (1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX)), 2.5 wt % of a polymeric binder (Pearlstick 5703), 0.1 wt % of a radical stabilizer (Irganox 1010), and 2.5 wt % of BDNPA/F. Aging products of BDNPA/F have been investigated using LC coupled to quadrupole time-of-flight mass spectrometry (QTOF), which identified the decomposition pathways of hydrolysis of the acetal/formal functional group and homolysis of the nitro functional group.[5] While LC-QTOF can provide insights into the aging of BDNPA/F as well as the variations in manufacturing processes, it has been hypothesized that these initial aging products can continue to degrade into smaller compounds, which are best analyzed via GC. A minor amount of work has been performed to investigate the decomposition of BDNPA/F using GC albeit in a targeted manner. The headspace of the aged BDNPA/F and PBX 9501 has been monitored for concentrations of $NO_x$, $N_2O$, $CO_2$, CO, $H_2O$, $CH_3CHO$, and
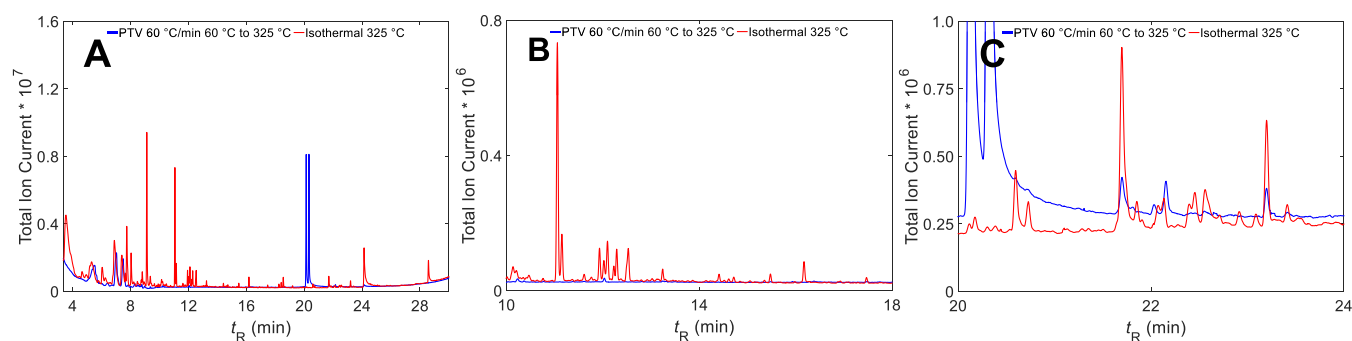
**Figure 1.** (A) TIC chromatogram for the unaged sample of BDNPA/F comparing the optimized to isothermal injection method. (B) Close-up of panel (A) showing the numerous thermal decomposition products from the isothermal method. (C) Zoom-in of panel (A) showing the presence of numerous thermal decomposition products as well as synthesis impurities.

$H_2CO$ using GC-MS.[14] BDNPA/F decomposition has been evaluated in several propellants using gas chromatography-Fourier transform infrared spectroscopy (GC-FTIR), and the authors were able to identify changes to propellant composition and some of the aging products or compound classes (e.g., carboxylic acids).[15] A minimal amount of work has been performed within the High Explosives Science and Technology group at Los Alamos National Laboratory investigating BDNPA/F aging products, targeting BDNPA/F hydrolysis, but previous GC methods have resulted in numerous thermal decomposition products due to decomposition in the GC inlet.

Herein, a GC-MS methodology incorporating a PTV inlet was developed for the analysis of thermal aging products of BDNPA/F. Furthermore, a preliminary investigation of the information gained from high-resolution mass spectrometry, made possible through the reduction of thermal decomposition products from the inlet by using the optimized PTV method, with electron impact (EI), negative chemical ionization (NCI), and positive chemical ionization (PCI), will be demonstrated by comparing a recently manufactured (unaged) sample of BDNPA/F to a naturally aged ~55 year old sample of BDNPA/F.

## ■ EXPERIMENTAL SECTION

**Chemicals and Sample Preparation.** HPLC-grade dichloromethane was obtained from Fisher Scientific (catalog no. D143-4, Fisher Scientific International, Inc., Hampton, NH). Two samples of BDNPA/F were obtained from storage magazines at Los Alamos National Laboratory. A sample of recently manufactured (~6 months old) BDNPA/F by Nalas Engineering (Centerbrook, CT) and a naturally aged sample of BDNPA/F manufactured in ~1966 at the Naval Propellant Plant (Indian Head, Maryland) were obtained using the ter Meer process. This BDNPA/F sample has been sitting in a storage magazine at Los Alamos National Laboratory exposed to ambient temperatures for ~50 years. Samples were prepared at a concentration of 1 mg/mL in dichloromethane.

**Instrumental Conditions.** One microliter of each sample was injected by an L-PAL3-S2-LS (Trajan Scientific and Medical, Austin, TX) splitless into an Agilent 8890 GC (Agilent Technologies, Palo Alto, CA) coupled to a LECO Pegasus HRT + (LECO, St. Joseph, MI) equipped with a 30 m × 0.25 mm i.d. × 0.25 $\mu$m d.f. Rxi-5 ms (Restek, Bellefonte, PA). Prior to injection, dichloromethane was used as a solvent rinse. Ultrahigh purity helium (Grade 5, 99.999%, Airgas, El Paso, TX) was used as the carrier gas at a constant flow rate of 1.4 mL/min. The GC was equipped with a multimode inlet (MMI), which was evaluated under the following conditions: isothermal at 325 °C

as well as temperature ramps of 60, 120, 180, 240, 300, and 360 °C/min to temperatures of 225, 250, 275, 300, and 325 °C all starting at a temperature of 60 °C. After 75 s of runtime, for both the isothermal and MMI, the purge valve was opened with a flow rate of 20 mL/min.

The oven was held at 40 °C for 2.25 min and ramped at 10 °C/min to the final temperature of the MMI. The transfer line temperature was set to the final temperature of the MMI, and the ion source temperature was 250 °C. For the optimization of the MMI, data was collected with election impact ionization at a voltage of 70 eV at a mass range of 35−500 $m/z$. A 200 s solvent delay was used. Three injection replicates were obtained for each method. Using the optimized methodology (discussed in Results and Discussion), electron impact, negative chemical ionization (NCI), and positive chemical ionization (PCI) were collected. Methane was used as the ionization gas at a flow rate of 1.26 mL/min. The ion source for both chemical ionization methods was set to 165 °C. The electron energy for PCI was set to 140 eV and that for NCI was 130 eV. All data was collected at a frequency of 5 Hz. PFTBA was infused into the HRT+ using the "medium flow" option for the final 200 s of the run. Postprocessing of the data was completed in ChromaTOF (version 5.53.70.0.113), which included mass calibration using PFTBA and removal of the mass channels associated with PFTBA for EI (68.9947, 118.9915, 130.9915, 218.9851, 263.9866, and 413.9770), NCI (199.9878, 282.9855, 394.9797, 413.9781, 432.9765, 451.9749, 513.9717, 594.9669, 632.9637), and PCI (99.9931, 130.9915, 218.9851, 263.9866, 413.9770, 501.970, 651.9610). For further postrun data visualization and analysis, the data was exported as .csv files and was imported into MATLAB 2022a (Mathworks, Natick, MA). Chromatograms were baseline-corrected using a rolling minimum function and smoothed using a Savitzky−Golay filter with a third-order polynomial fit.

## ■ RESULTS AND DISCUSSION

An excellent separation of the recently manufactured (unaged) BDNPA/F was achieved using GC-HRMS. In order to highlight the differences between the use of a PTV inlet operated isothermally at 325 °C and the optimal PTV conditions (60 °C/min from 60 to 325 °C), Figure 1A has been prepared. The intensities of BDNPA ($t_r$ 20.13 min) and BDNPF ($t_r$ 20.33 min) are significantly higher when a PTV inlet is implemented, and there is a lack of numerous thermal decomposition products observed at the lower retention times. Figure 1B shows a zoom-in of retention times of 10.00−18.00 min to highlight the presence of several compounds found at moderate $t_r$ that are
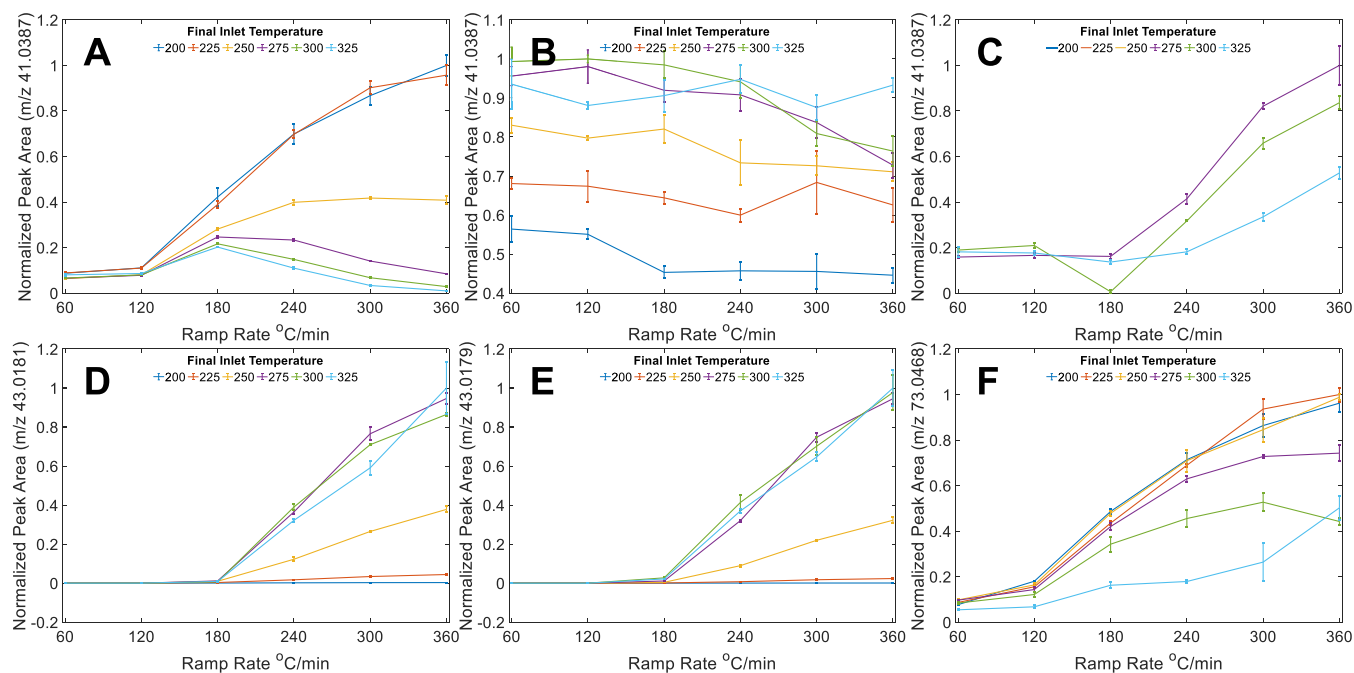
**Figure 2.** Optimization of the PTV parameters comparing the peak areas of 3 native and 3 non-native compounds. (A) BDNPA ($t_r$ 20.13 min). (B) Unknown synthesis impurity with a $t_r$ of 6.33 min. (C) Unknown synthesis impurity with a $t_r$ of 24.16 min. (D) Unknown thermal decomposition product with a $t_r$ of 4.85 min. (E) Unknown thermal decomposition product with a $t_r$ of 9.16 min. (F) Unknown thermal decomposition product with a $t_r$ of 15.35 min.
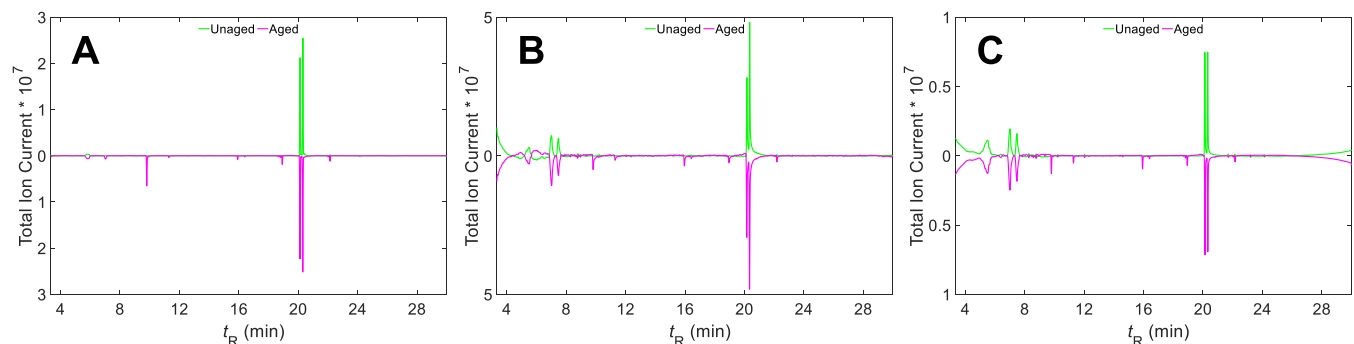


**Figure 3.** Comparison of the unaged and aged BDNPA/F TIC chromatograms for (A) negative chemical ionization (NCI), (B) positive chemical ionization (PCI), and (C) electron impact ionization (EI).

present when the inlet is operated isothermally, resulting in thermal decomposition of BDNPA/F. To further illustrate the differences between the PTV operated isothermally versus optimally, Figure 1C has been prepared. Figure 1C shows a zoom-in of retention times of 20.00−24.00 min to highlight not only the numerous compounds caused by the thermal decomposition of the BDNPA/F in the inlet but also the presence of numerous compounds in the unaged sample. These compounds are assumed to be synthesis impurities and are found at extremely low concentrations relative to BDNPA and BDNPF, which compose ∼1−5% of the sample.[16] The addition of the thermal decomposition products obviously provides a challenging endeavor to separate.

In order to determine the optimum PTV conditions, the concentration (peak area) of 6 analytes, 3 native to the sample and 3 caused by thermal aging, was evaluated using 25 different PTV conditions. Figure 2A−C shows the peak areas for native compounds at retention times of 20.13 min (BDNPA), 6.33 min, and 24.16 min, while Figure 2D−F shows the peak areas for three thermal aging products at retention times of 4.85, 9.16, and

15.035 min, respectively. The peak areas for all 6 compounds (native and non-native) are strongly influenced by the ramp rate with a minor influence from the final temperature of the PTV. BDNPA (Figure 2A) exhibits an interesting trend where the peak area increases as the ramp rate increases to 180 °C/min for each final inlet temperature but begins to divert based on the final inlet temperature. While the higher ramp rate allows for a more efficient and higher transfer of BDNPA to the capillary column, too high of a final temperature will cause the BDNPA to start to decompose. Figure 2B shows the peak area for the compound eluting at 6.33 min, which is a synthesis impurity from the production of BDNPA/F. The peak area for this compound is relatively uniform across the various ramp rates and appears to be more influenced by the final inlet temperature of the PTV with 275, 300, and 325 °C yielding equivalent results. Figure 2C shows the peak area for the compounds eluting at 24.16 min, which is also a synthesis impurity from the production of BDNPA/F. This compound was observed only at higher final inlet temperatures with a higher ramp rate yielding a higher peak area. This is due to the fact that the compound
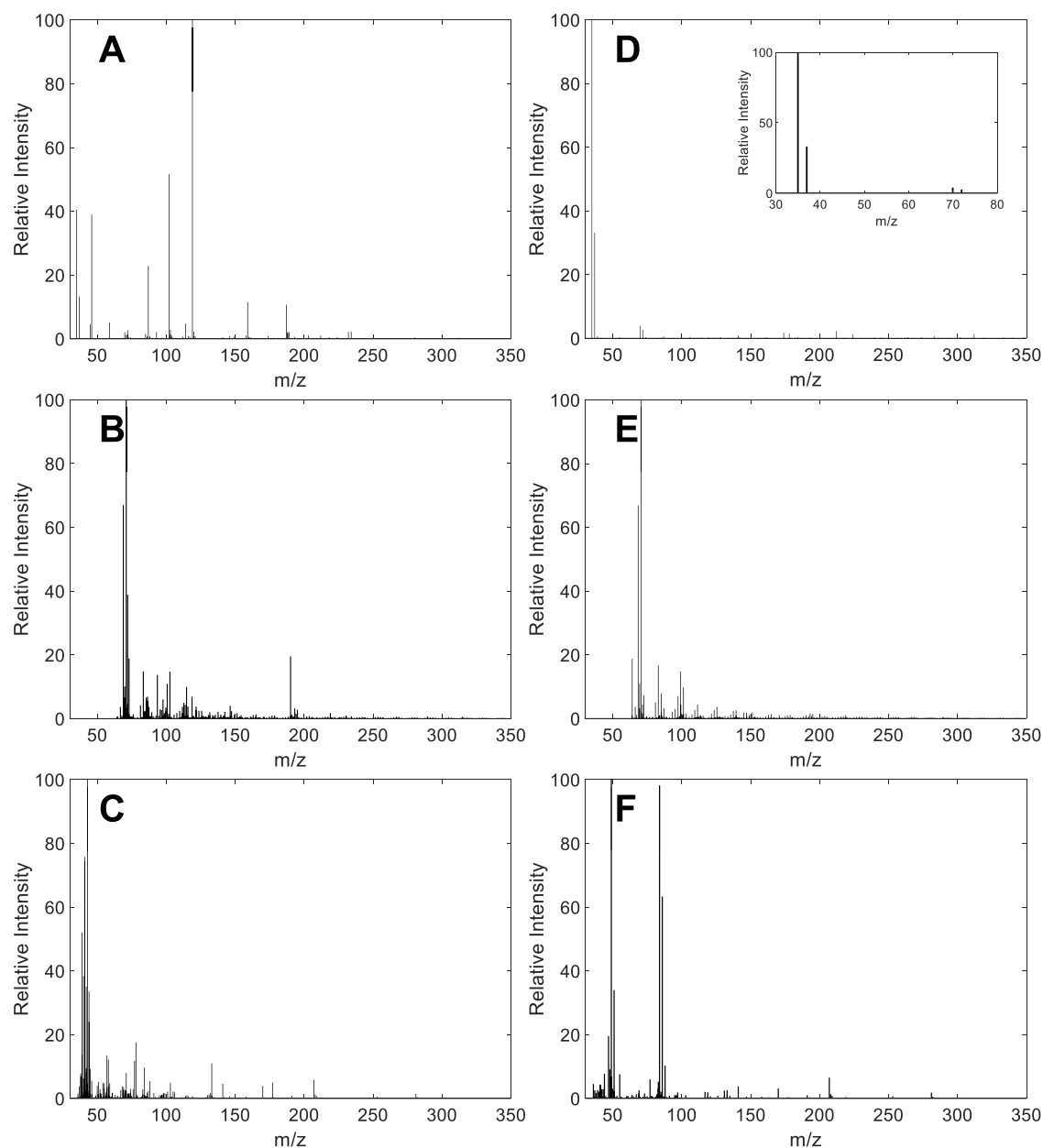
**Figure 4.** Comparison of BDNPA spectra using NCI (A), PCI (B), and EI (C) ionization. Comparison of unknown synthesis impurity spectra using NCI (D), PCI (E), and EI (F) ionization.

elutes at a relatively high temperature and thus requires a higher final temperature to transfer the analyte onto the analytical column. Figure 2D,E shows two thermal aging products that show nearly identical trends. At higher ramp rates and higher final inlet temperatures, these compounds are quite intense, but at a ramp rate of 60 °C/min regardless of the final inlet temperature, both compounds have extremely low concentrations and are near or at the limit of detection. Figure 2F is another thermal decomposition product that shows an inverse trend compared to those of the other thermal decomposition products (Figure 2D,E). This compound appears to be more intense at lower final inlet temperatures with higher ramp rates. A possible explanation for this observed trend is this compound continues to break down at higher inlet temperatures, further creating other thermal decomposition products. Based on the observed trends for these 6 compounds, the ideal PTV conditions were determined to be a ramp rate of 60 °C/min

and a final temperature of 325 °C as this yielded the lowest number and intensity of thermal decomposition products while still providing adequate intensity for the native compounds and extending the overall temperature range for the analysis.

In order to initially investigate the advantages of incorporating chemical ionization for identifying unknowns using this methodology, as well as preliminarily evaluate the differences between unaged and aged BDNPA/F, negative chemical ionization (NCI) and positive chemical ionization (PCI) were performed. Figure 3A−C shows the NCI, PCI, and EI TIC chromatograms comparing unaged and aged BDNPA/F. Both BDNPA and BDNPF significantly ionize better in NCI, which is expected as protonation of the $NO_2$ and -O- functional groups (e.g., PCI) is unfavored due to their low $pK_a$ values. Because of this, there are not a significant number of differences between the EI and PCI methods, other than intensity, when only looking at the chromatography of the samples. It is also important to

note that regardless of which ionization method is used, there is a reduced number of decomposition products caused by the inlet present in the chromatogram This allows for easier comparison between the aged and unaged samples that previously would not be possible when using GC.

Comparing the unaged and aged samples, it is apparent that there are significant chemical differences that can be explored using the three ionization methods. For example, as shown in Figure 3A, the peak at ∼6 min was identified as containing a chlorinated functional group using NCI (Figure 4E). This compound was found only in the aged sample and would not have been easily identifiable if only EI was used. To visualize the differences between the spectra of different compounds using the three ionization methods, Figure 4A−F has been prepared. Figure 4A−C shows the EI, NCI, and PCI spectra for BDNPA, while Figure 4D−F shows the EI, NCI, and PCI spectra for an unknown compound that elutes earlier in the chromatogram. While the chromatograms for PCI and EI are not significantly different, other than in intensity, the mass spectra for all three ionization methods do show chemical differences, which can help with compound identification. Future work will focus on evaluating all of the chemical differences between the aged and unaged samples of BDNPA/F using the methodology developed in this study.

## CONCLUSIONS

A gas chromatography−mass spectrometry methodology for the analysis of BDNPA/F, a thermally labile compound, has been developed. Incorporating a PTV inlet as part of the instrumentation allowed for the analysis of BDNPA/F, synthesis impurities, and aging products while nearly eliminating any thermal decomposition caused by the inlet. Furthermore, different modes of ionization (NCI, PCI, and EI) led to the detection of different compounds present in the unaged and aged samples. The results presented in this work suggest that the use of a PTV inlet for the reduction of thermal decomposition products created using an isothermal inlet, along with mass spectral analysis using different ionization methods, gives rise to the potential that thermally labile energetic materials can be analyzed with GC methods in addition to current LC methodologies.

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### Notes

The authors declare no competing financial interest.

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