A Study of How Alternative Buffer Gases can Affect Energetic Material Detection in an Ion Trap Mass Spectrometer

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Abstract

Due to their inherent nature, energetic materials are more reactive than traditional hydrocarbons and are better able to undergo the substitution of one or more groups located in the alpha position to the electron withdrawing nitro- group. The mass spectra of various high explosives were determined using electron ionization and an ion trap containing nitrogen gas. The spectra obtained displayed characteristic fragmentation in accordance with their respective structures. When the nitrogen gas was replaced with labile deuterium gas, the spectrum for certain compounds of interest showed an increase in the M+1 and M+2 peaks indicating whether the compound had been mono- or di-substituted with deuterium.

Objectives/Introduction

1. **Synthesize and characterize energetic materials by traditional GC/MS methods**
2. **Utilize labile proton exchange with deuterium in an ion trap to enhance detection**
3. **Implement these improved detection schemes for unambiguous detection of energetic materials**

Energetic materials pose a number of problems for traditional analytical instrumentation.[1] Gas chromatography in particular poses a challenge because of the elevated temperatures needed for efficient separation.[2] Modifying instrumental parameters allows for efficient separation though a GC with minimal decomposition, but there is still a challenge to detect these species in a mass spectrometer.[1-3] One approach is to substitute deuterium in place of nitrogen as the buffer gas in an ion trap. In this manner it may be possible to exchange the labile protons on a structure with deuterium. This will improve the ability of the analyst to provide unambiguous identification of energetic materials and their constituent fragments.

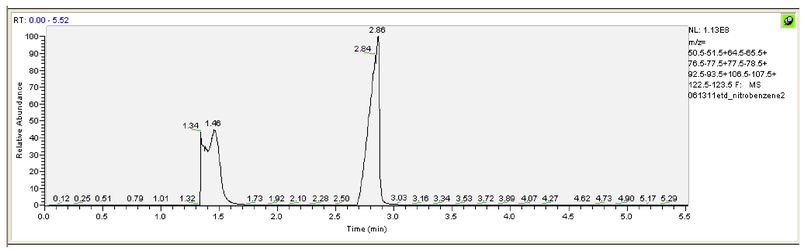


Figure 1: Selected Ion Chromatogram demonstrating the separation achieved between benzene and nitrobenzene

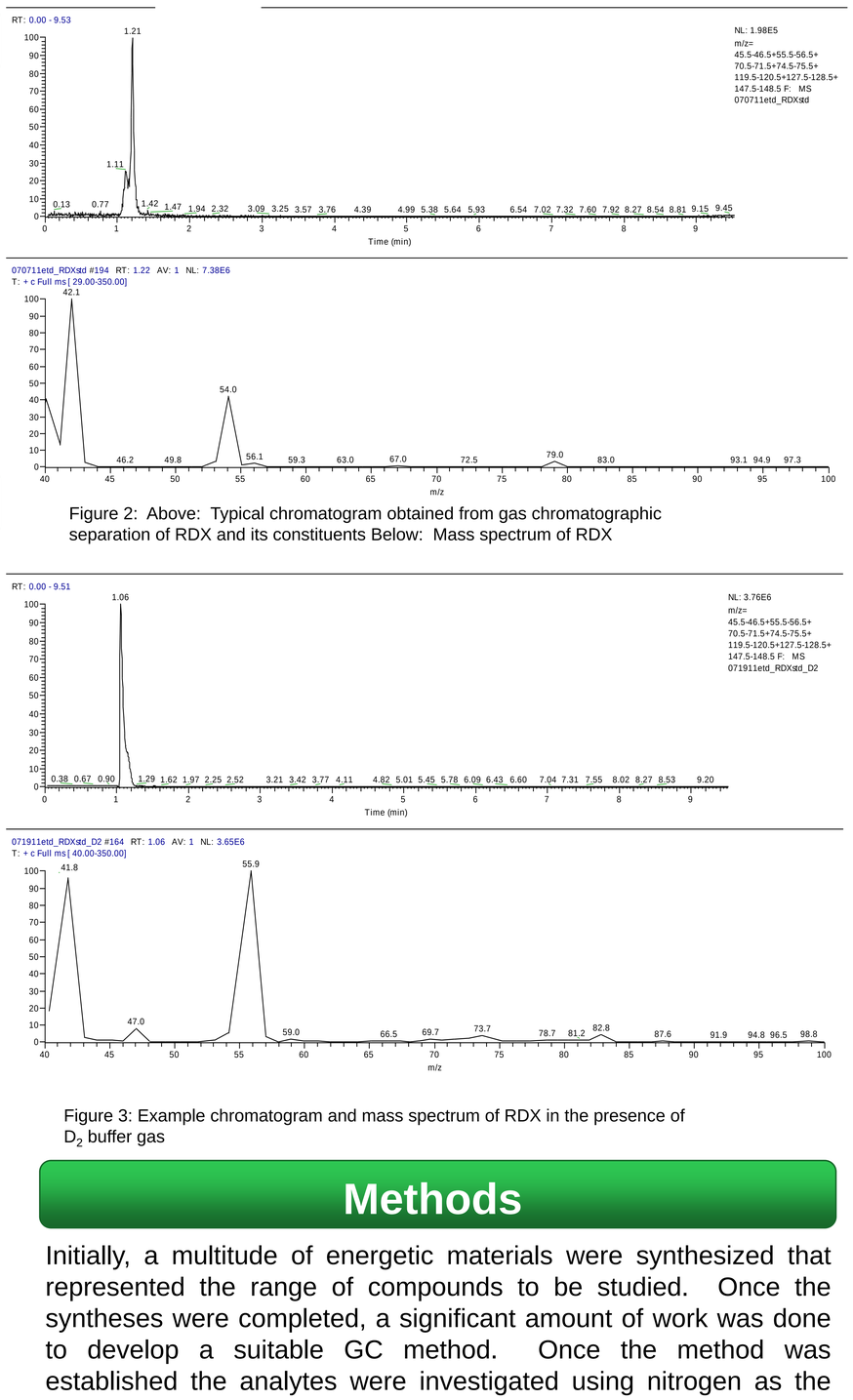
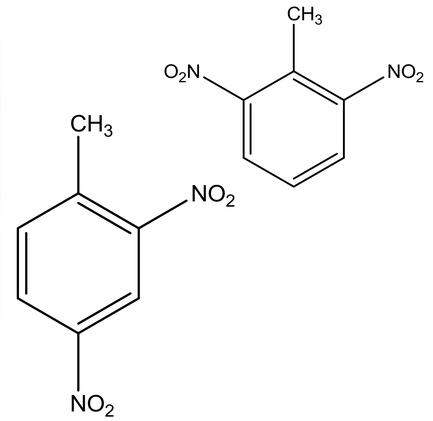


Figure 2: Above: Typical chromatogram obtained from gas chromatographic separation of RDX and its constituents Below: Mass spectrum of RDX

Figure 3: Example chromatogram and mass spectrum of RDX in the presence of D_2 buffer gas

Methods

Initially, a multitude of energetic materials were synthesized that represented the range of compounds to be studied. Once the syntheses were completed, a significant amount of work was done to develop a suitable GC method. Once the method was established the analytes were investigated using nitrogen as the buffer gas in the ion trap. Figure 2 above shows a representative spectrum obtained under these conditions. The lack of a parent ion



Above: As synthesized dinitrotoluene along with the corresponding molecular structures

Methods (cont'd)

is typical for this class of compounds based on their tendency to fragment easily. In an attempt to deconvolute the spectra, deuterium was substituted for nitrogen to facilitate labile proton exchange. In this case, helium remained the carrier gas, but deuterium replaced nitrogen as the buffer gas within the trap.

Conclusions

Due to the small potential well on the miniature ion traps and the ability to undergo many neutral collisions, it is an ideal environment to couple chemistry with ion fragmentation to reduce false positives in the spectrum. As hydrocarbons and even some energetic materials do not undergo these substitutions, one can rapidly test (1-2 minutes) for a specific group of high explosives by identifying the M+1 and M+2 peaks. The ideal high explosives are stable enough to undergo electron ionization and substitution without completely decomposing, yet not so stable that they do not substitute at all.

References

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