B104 An Analysis of High Explosive Compounds Utilizing Gas Chromatography (GC) With Tandem Cold Electron Ionization (EI) Mass Spectrometric Detection and Vacuum Ultraviolet Detection (VUV)

Dennise Montero, BS, Arlington, VA 22203; Ioan Marginean, PhD, The George Washington University, Washington, DC 20007*

Learning Overview: After attending this presentation, attendees will better understand the advantages of using combined Mass Spectrometry (MS) and Vacuum Ultraviolet (VUV) detection following the Gas Chromatography (GC) separation of high explosive compounds.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by introducing an alternative analysis method that enhances the molecular ion of the explosive compound and provides an ultraviolet spectrum to improve confidence in identification.

High explosives are characterized by rapid decomposition and development of high pressures which result in detonation with reaction fronts faster than 1000 m/s. Nitrated organic compounds such as trinitrotoulene (TNT) or unstable peroxide compounds such as triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) are explosives commonly found in bombs. Due to the increasing number of terrorist attacks, explosive identification has become of upmost importance in forensic applications. Most explosive compounds have high thermal instability and require high sensitivity analysis, making their identification a challenging task. Additionally, the variety of explosive groups demands a broad-based analytical technique that is effective with all explosives classes.

Although GC/MS is the most commonly used instrument in forensic analysis, it has certain limitations in the analysis of thermally liable or low volatility compounds (such as high explosives). Traditional GC/MS utilizes classical electron ionization (EI) which may result in excessive fragmentation with little to no molecular ions in the case of labile analytes. Due to absence or very low intensity of the molecular ions in traditional GC/MS with classical EI, explosives are usually identified by their fragmentation pattern. Cold EI often enhances the relative intensity of the molecular ion leading to improved confidence in identification. Survival of molecular ion in the ion source is ensured by intra molecular vibrational cooling of the sample through expansion of supersonic molecular beams prior to their ionization.

In addition to enhanced molecular ion intensities, explosive identification can be further improved through the addition of another analytical dimension such as VUV spectroscopy. Interaction between VUV light and analytes in the gas phase creates unique spectral signatures specific to the chemical structure. The high energy, short wavelength VUV photons probe electronic transitions in the chemical bonds, including ground state to excited state $\sigma \rightarrow \sigma^*$ and $n \rightarrow n^*$. Additionally, the unique spectra allow explosive structural isomers to be clearly differentiated, thus increasing the confidence of identification.

Analysis of high explosives was studied by a cold EI-GC/MS augmented with a VUV detector. Coupling of GC to MS and VUV detectors allows the explosives to be detected by multiple platforms in one run. Various GC parameters (e.g., injection port temperature, ramp rate, and flow rate) were optimized for explosive identification by GC/MS with both classical and cold EI. In most cases, larger relative intensities for molecular ions were observed for explosives analyzed with GC/MS with cold-EI. Certain explosives (for example HMTD) could not be detected in GC/MS with a He flow rate of 1 mL/min. Increasing the He flow rate to 5 mL/min (which is possible in the cold-EI instrument) allows the detection of this analyte. Unique VUV spectra for each explosive were measured and added to the VUV library for future identification. Explosive isomers, such as 2,3-, 2,4-, 2,6-, 3,4, 3,5-dinitrotoulene (DNT), differ only by the position of the two nitro groups on the benzene ring and are difficult to distinguish by GC/MS. However, distinct VUV spectra were obtained, allowing for the isomers to be identified. Overall, the combination of a cold EI-GC/MS with a VUV detector improved the confidence in explosive identification by enhancing molecular ion intensities and providing complementary VUV spectra.

Cold Electron Ionization, Explosives, Vacuum Ultraviolet