



### A7 Development of a Method for the Trace Analysis of Hexamethylenetriperoxide Diamine (HMTD) Using Liquid Chromatography/Atmospheric Pressure Chemical Ionization-Mass Spectrometry

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After attending this presentation, attendees will have a greater understanding for the prevalence of Hexamethylenetriperoxide Diamine (HMTD) in Improvised Explosive Devices (IEDs) and how to qualitatively detect trace/residue amounts of this peroxide explosive.

This presentation will impact the forensic science community by providing insight into the use of Liquid Chromatography/Atmospheric Pressure Chemical Ionization-Mass Spectrometry (LC/APCI/MS) to analyze evidence related to IEDs suspected of containing HMTD.

Terrorist groups are increasingly using peroxide explosives in IEDs. HMTD and Triacetone Triperoxide (TATP) are the most commonly used peroxide explosives and have similar explosive power to commercial and military high explosives. These compounds can be used as a main charge or an initiating explosive because they are extremely unstable, very sensitive to heat, friction, shock, and impact. Additionally, HMTD can be made from easily obtained retail materials, which results in it being a frequently identified component of IEDs. Consequently, with the increasing use of HMTD in terrorist explosive devices, it is imperative to be able to identify trace amounts of HMTD on items of evidence.

A qualitative method has been developed using LC/MS with an APCI ionization source in the full scan positive mode. Items suspected of containing trace amounts of HMTD are first extracted with deionized water for five minutes before filtering with 0.2µm syringe filters. Extracts are then injected into a separations module with a C18 column (150 x 2.1mm, 5µm particle size) and a solvent gradient of water: methanol, both containing 1.25mM ammonium nitrate. Lastly, an ion trap mass spectrometer is used for HMTD detection and identification.

Using the above method, HMTD elutes at approximately five minutes during an overall run time of 20 minutes. The observed mass spectrum contains m/z 207 and 224 that correspond to [HMTD-1]<sup>+</sup> and [HMTD+NH<sub>4</sub>]<sup>+</sup>, respectively, in addition to 145, 177, and 209. Interference studies were performed by extracting different substrates to determine if anything present in commonly used materials will interfere with the assay. Results have shown that the following materials do not interfere with HMTD: cotton swabs, cotton balls, plastic scoops, wooden tongue depressors, rocky soil, and sandy soil. In addition, chemicals commonly used in HMTD synthesis were tested for interferences, and the following did not interfere with HMTD: hydrogen peroxide, reagent grade hexamine, reagent grade citric acid, sports tablet hexamine, and Gefen Sour Salt citric acid. TATP and HMTD were analyzed simultaneously, and results indicate that TATP is not an interference for the method.

An ion suppression/enhancement test was performed using a series of ten cotton swabs by fortifying the negative matrix extracts with HMTD before analysis, and the signal from the matrix samples was compared to the HMTD signal from a reference material at this same concentration. Also, matrix samples were processed and fortified with an HMTD standard and were analyzed every six hours following preparation for 72 hours to verify the processed sample stability. Lastly, the matrix limit of detection was determined by analyzing triplicates of matrix-matched reference materials fortified with HMTD reference material at 5, 10, and 15ppm levels.

This detection method yields sufficient peak resolution for the tested substrates and can qualitatively detect and identify HMTD at or above 10ppm.

**Peroxide Explosives, HMTD, LC/MS**