



### B127 Optimized Analysis of Triacetone Triperoxide by GC-MS

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After attending this presentation, attendees will have learned about an improved method for the detection of TATP via GC/MS.

This presentation will impact the forensic community and/or humanity by demonstrating the development of an optimized and improved method for the detection of the peroxide explosive TATP by GC/MS using both electron ionization and chemical ionization.

This presentation will focus on the analysis of triacetone triperoxide by gas chromatography-mass spectrometry and optimization of the method to give sub-nanogram detection limits. This presentation will impact society and forensic science by providing new analytical guidelines for the analysis of an explosive which is easily prepared from commercially available materials and is often used by terrorists. The explosive triacetone triperoxide (TATP) has been analyzed by gas chromatography – mass spectrometry (GC-MS) using both electron ionization and chemical ionization to give sub-nanogram detection limits. Ammonia and methane were used as chemical ionization reagent gases. Analysis by positive ion chemical ionization (PCI) with ammonia as the reagent gas gave sub-nanogram levels of detection, while PCI analysis with methane as the reagent gas gave detection limits in the low nanogram range. Analysis by negative ion chemical ionization (NICI) also gave low nanogram detection levels with both methane and ammonia reagent gases. Low detection limits were achieved by optimizing both gas chromatography and mass spectrometry operating parameters. Specifically, lower injector port, GC oven, and MS source temperatures were found to strongly favor trace detection of TATP. Analyses of neat TATP solutions in acetonitrile were carried out on linear quadrupole and quadrupole ion trap instruments. GC-MS analyses of TATP vapor was also performed by sampling the headspace over solid TATP samples at various temperatures. Both SPME and syringe sampling techniques were utilized. Analysis of TATP by PCI GC-MS using ammonia reagent gas is the preferred analytical method, producing lower limits of detection as well as an intense  $m/z$  240 diagnostic adduct ion corresponding to  $[TATP + NH_4]^+$  (base peak for the quadrupole, and greater than 60% of base peak for the ion trap).

Isolation of  $[TATP + NH_4]^+$  in the ion trap mass spectrometer with subsequent collision induced dissociation (CID) produced weak daughter ions in the 60 – 240  $m/z$  range ( $m/z$  168, 132, & 115). No CID product ion mass was observed at  $m/z$  223 ( $[TATP + H]^+$ ), which would correspond to the loss of ammonia from the diagnostic adduct ion at  $m/z$  240 ( $[TATP + NH_4]^+$ ). Density functional theory calculations at the B88LYP/DVZP level gave a TATP-NH<sub>4</sub> binding energy of 25 kcal/mol, which is 11 kcal/mol lower than the peroxide bond energy (36.5 kcal/mol). This result suggests that the  $[TATP + NH_4]^+$  ion may dissociate under CID, rather than fragmenting the TATP moiety. The calculations also showed an energy difference between  $[TATP + NH_4]^+$  and  $[TATP + H]^+ + NH_3$  to be 23 kcal/mol and the structure of the  $[TATP$

+ H]<sup>+</sup> ion had an excessively long C-O bond (2.605 Å). This result suggests CID of the  $[TATP + NH_4]^+$  ion could proceed with a loss of NH<sub>3</sub> and subsequent TATP bond rupture and further fragmentation. CID results are in agreement with the calculations which suggest dissociation of the complex to form NH<sub>4</sub> and TATP at energies lower than peroxide bond dissociation in the mass spectrometer. The results of experiments provide a method for pico-gram detection levels of TATP using commercial instrumentation commonly available in forensic laboratories.

**Mass Spectrometry, Explosives, TATP**