B121 The Prevalence of Promethazine Dimerization in Forensic Samples of "Purple Drank"

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After attending this presentation, attendees will understand how exposure to Ultraviolet (UV) light can cause the formation of a promethazine dimer.

This presentation will impact the forensic science community by providing an explanation for the presence of additional chromatographic peaks with promethazine-like mass spectra in seized samples containing promethazine.

In certain parts of the country, codeine cough syrups are consumed as a recreational drug known as "purple drank." One of the other main components in this cough syrup is an antihistamine and antiemetic drug called promethazine. When "purple drank" beverages are collected and analyzed by forensic laboratories, they often find two or more chromatographic peaks with indistinguishable promethazine-like Electron Ionization (EI) mass spectra. One of these peaks has a Gas Chromatography (GC) retention time equal to standard promethazine, whereas a second GC peak can elute more than a minute later, with an indistinguishable mass spectrum. This study was conducted to help identify the cause and identity of the second mystery peak.

Samples of promethazine were dissolved in chloroform at 50ppm and analyzed via Gas Chromatography/Mass Spectrometry (GC/MS) to determine the origin of the second peak. Initial experiments replicated the Standard Operating Procedure (SOP) of an American National Standards Institute-American Society of Quality (ANSI-ASQ) National Accreditation Board/Forensic Quality Services (ANAB/FQS) -accredited crime laboratory for the extraction and GC/MS analysis of aqueous samples suspected to contain promethazine and codeine. Standard promethazine was dissolved in water to simulate the cough syrup, and aliquots were made basic using sodium hydroxide or a saturated sodium carbonate solution and extracted into chloroform. Neither of these caused the appearance of the second peak. The samples were also made acidic using hydrochloric acid and extracted into chloroform, but these results did not show any additional peaks besides the normal promethazine peak.

The core/base structure of promethazine is phenothiazine, and it has been found to form radicals when exposed to UV light. For this reason, the possibility of UV-induced chemistry of this phenothiazine derivative was explored. Samples of promethazine were dissolved in chloroform and were left under long-wave or short-wave UV light for different times. Upon examination using the GC/MS, the long-wave UV exposure for two or four hours showed no additional peaks, but the sample exposed to short-wave UV for four hours showed a new small GC peak more than a minute later than the promethazine peak, which was also readily abundant. Additional studies were then conducted to determine the cause of the "new" peak. One aliquot of dissolved promethazine was placed on a windowsill for two days, one was placed under short-wave UV light for seven hours, one was placed on a desktop (away from an outside window) for two days, and one was placed in the dark for two days. The samples in the dark and on the desk showed no sign of the second peak. The sample left on the windowsill and the sample left under short-wave UV light for seven hours showed that more than 50% of the promethazine had either oxidized or converted to the dimer form. Additional Nuclear Magnetic Resonance (NMR) studies were also conducted to confirm the dimerization product.

In conclusion, this study provides evidence that upon exposure to UV light, promethazine will form degradation products, which include a dimerized form of the drug. This additional peak could presumably be avoided by storing casework in amber vials or otherwise limiting the exposure to UV radiation.

Drug Chemistry, Gas Chromatography, Promethazine

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