A73 On the Origin of Volatile Compounds Emitted by Plastic Explosives

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After attending this presentation, attendees will learn about the chemical composition of plastic bonded explosives (pbx) as well as what volatile compounds are emitted by these materials. Data suggesting potential origins for these compounds and the implications for canine detection of PBX will also be discussed.

This presentation will impact the forensic science community by increasing the understanding of how explosive-detecting canines locate explosives and explosive devices.

One of the enduring riddles regarding the performance of explosive- detecting canines is their ability to readily detect samples of plastic- bonded explosives (PBX) whose base explosive is essentially non- volatile. For example, the headspace concentrations of PETN (the base explosive in Detasheet) and RDX (the base explosive in Composition C-

4) are on the order of 10^{-12} and 10^{-13} M, respectively. Therefore, while canines have been shown to be extraordinarily sensitive, it is not unreasonable to hypothesize that perhaps other species that are emitted by PBX are responsible for canine alerts to these materials. Previous studies of the headspace above PBX using Solid Phase Microextraction (SPME) coupled with Gas Chromatography-Mass Spectrometry (GC-MS) have identified taggants such as dimethyldinitrobutane (DMNB), residual solvents such as cyclohexanone, and several other species – all of which are more volatile than the parent explosive.

In particular, 2-ethyl-1-hexanol has been found in the headspace above Composition C-4 and butyl acetate has been found in the headspace above PETN-based flexible sheet explosive. Although the response of explosive-detecting canines to these compounds has been evaluated, response rates varied widely depending upon the amount of the chemicals used. Although not identified as such in the literature, it is hypothesized that these compounds can be formed by hydrolysis of the plasticizers used in PBX. These plasticizers include bis(2-ethylhexyl)adipate (DOA), bis(2-ethylhexyl)sebacate (DOS), and tributylacetylcitrate (citraflex). In addition, plasticizer hydrolysis would be catalyzed due to the natural formation of nitric acid by the base explosive as it degrades.

In this study, several samples of various PBX (Composition C-4, Detasheet, Shape Charge and a "Bubble Gum" Booster) were extracted with pentane, acetone, and water. All solvent extracts were prepared by placing samples of PBX in culture tubes, adding the appropriate solvent, and sonicating. The pentane extracts were analyzed by GC/MS to identify the plasticizer used in the formulation. The acetone extracts were analyzed by LC/MS to identify the base explosive. The water extracts were also analyzed by LC/MS for residual nitrate, which may indicate the formation of nitric acid. Finally, samples of PBX as well as the plasticizers DOA, DOS, and citraflex were analyzed by headspace SPME-GC/MS to identify any volatile compounds. The results of these analyses are summarized in the following table:

Several trends were noted following these analyses. As in previous studies, residual solvents and taggants were identified in the headspace of PBX. In addition, 2-ethyl-1-hexanol appeared in the headspace of all explosives that contained either DOA or DOS (both of which have 2- ethylhexyl side chains). It was also noted that DOS generated significantly higher levels of 2-ethyl-1-hexanol than did DOA. Although 1-butanol appeared in the headspace of all explosives that contained citraflex, it was present at low levels. In contrast, the citraflex plasticizer itself generated significant amounts of butyl acetate, which was not observed in any of the PBX samples. In all cases, the PBX samples did not exhibit any compounds in their headspace that could be associated with the base explosive under the conditions used for SPME-GC/MS. Finally, the levels of residual nitrate found in the PBX samples were significant and this could indicate that nitric acid is being generated and that it also catalyzes the hydrolysis of the PBX plasticizers.

Plastic Explosives, Canine Detection, Headspace Analysis

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