# B82 Identification of Organic Components in Intact and Burned Black Powder Substitutes Using GC-MS

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After attending this presentation, attendees will learn the history of black powder substitutes and the challenges in identifying the alternative fuels present, particularly ascorbic acid. A newly developed method that addresses this issue will be presented and its applicability to intact and burned powder samples will be discussed.

This presentation will demonstrate that black powder substitutes are likely to grow in popularity and therefore they will be more commonly encountered in improvised explosive devices. This presentation will share a new method for analyzing these explosive samples as they have been difficult or impossible to fully characterize in the past.

Black powder substitutes such as Pyrodex or Golden Powder were originally designed to have improved properties relative to black powder. For example, these propellants generate similar muzzle velocities at lower peak pressures, demonstrate lower sensitivity to friction and shock, and generate fewer or no corrosive combustion by-products. The latter is accomplished through reducing or eliminating sulfur content and replacing it with other organic fuels such as sodium benzoate, dicyandiamide (DCDA), ascorbic acid, or fruit sugars. The first product of this type was Pyrodex, which was patented in 1978 by Pawlak and Levenson. This propellant contains $KNO_3$ and $KClO_4$ as oxidizers and charcoal, sulfur, sodium benzoate, and DCDA as fuels. Since that time, a number of commercial products have been developed that contain ascorbic acid as an alternative to sulfur. The original patent for Golden Powder (containing $KNO_3$ and ascorbic acid) was granted in 1985. The Golden Powder formulation was later modified and produced as Black Mag Powder (containing $KNO_3$, $KClO_4$, and ascorbic acid) by the Arco Powder Company from early 1996 through January 1997. This product has been subsequently re-released as “Black Mag ‘3”. Legend Products manufactured Black Canyon Powder (containing $KNO_3$ and ascorbic acid) in 1996 and 1997. Clean Shot Powder (containing $KNO_3$, $KClO_4$, and ascorbic acid) was introduced in 1999 and is manufactured by Clean Shot Technologies. Most recently, GOEX briefly produced Clear Shot Powder (containing $KNO_3$ and cooked sugars, rather than ascorbic acid) in 2001.

Among organic additives, ascorbic acid demonstrates the most significant chemical instability, particularly when in the presence of moisture or metal ions. In this mechanism, ascorbic acid (aa) reversibly degrades to dehydroascorbic acid, then irreversibly to diketogulonic acid. Further degradation yields a vast array of compounds, including dihydroxybutanedioic acid, 2,3,4-trihydroxybutanoic acid, glycoaldehyde and glyceraldehyde. As a result, ascorbic acid can be gradually lost from powders, making its identification difficult or even impossible by traditional methods such as X-ray diffraction analysis or infrared spectroscopy. As a result, various instrumental methods have been developed to determine these species in clinical and food samples. In particular, the use of trimethylsilyl (TMS) derivatization agents has been successful in the separation and analysis of AA and its degradation products by gas chromatography-mass spectrometry (GC-MS). In addition, ascorbic acid and benzoate have been successfully identified in intact Clean Shot Powder and Pyrodex, respectively, using electrospray ionization mass spectrometry.

In this study, the TMS derivatization method was used to identify organic fuels and their degradation products by GC-MS. Black powder substitutes were extracted with *bis*(trimethylsilyl)acetamide (BSA) in acetonitrile, which converts carboxylic acid and/or alcohol functional groups into trimethylsilyl esters and ethers, respectively. Subsequent analysis by GC-MS allowed for the identification of trace amounts of ascorbic acid, benzoate, DCDA, sulfur (if present), and degradation products such as hydroxylated carboxylic acids, furanones, and lactones. Unburned samples of black powder substitutes such as Clean Shot, Pyrodex, Triple Seven, Clear Shot, Black Canyon, Black Mag ‘3, and Golden Powder were successfully analyzed with sample amounts ranging from 2 – 20 mg. Ascorbic acid and/or its degradation products were detected in Clean Shot, Black Canyon, Black Mag ‘3, and Golden Powder. Of these samples, Black Canyon showed the greatest amount of ascorbic acid degradation. In contrast, a lack of ascorbic acid but detectable amounts of simple fruit sugars allowed Clear Shot to be differentiated from the other products. The presence of benzoate, sulfur, and DCDA in Pyrodex and Triple Seven was also evident using this method. Lastly, burned samples of pure ascorbic acid and various black powder substitutes were analyzed for residual organic fuels and their breakdown products.

**Explosives, GC/MS, Ascorbic Acid**

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