B42 Chemometric Analysis of Gasoline Samples Utilizing Direct Analysis in Real-Time Mass Spectrometry (DART®-MS)

Ashley Davis, MS, Boston University School of Medicine, 72 E Concord Street, Boston, MA 02118; Matthew Pavlovich, PhD, Northeastern University, 360 Huntington Avenue, 140 The Fenway, Boston, MA 02115; Joseph H. LaPointe, BSc, IonSense, Inc., 999 Broadway, Ste 404, Saugus, MA 01906; Brian Musselman, PhD, IonSense, Inc., 999 Broadway, Ste 404, Saugus, MA 10906; and Adam B. Hall, PhD, Northeastern University, 360 Huntington Avenue, 140 The Fenway, 421TF, Boston, MA 02115*

After attending this presentation, attendees will better understand current and past efforts to provide brand differentiation of gasoline, a common ignitable liquid utilized by arsonists worldwide. In this research, DART®-MS was employed as an analytical approach for the analysis of gasoline in an effort to generate chemical attribute signatures for a wide variety of gasoline brands at various states of weathering.

This presentation will impact the forensic science community by providing information pertaining to current research applicable to the fire debris analysis community. This data shows that even in highly evaporated samples (75% and >90%), unique ions can be used to differentiate common gasoline brands from one another in a fraction of the total analysis time in comparison to current analytical approaches.

Gasoline is an easily obtainable ignitable liquid that arsonists commonly use to initiate or expedite the spread of an intentionally set fire. Current methods for the extraction and concentration of ignitable liquids from fire debris utilize passive headspace concentration with activated carbon strips. Typical extractions are conducted between 60°C-80°C for 12-16 hours based on American Society for Testing and Materials (ASTM) guidelines followed by Gas Chromatography/Mass Spectrometry (GC/MS) analysis. Normally, hundreds of low molecular weight hydrocarbons are detected resulting in chromatograms showing distinctive patterns characteristic of various ignitable liquid classes. While traditional GC/MS methods are sensitive and generate data, which can be classified as gasoline based on the ASTM classification scheme, they do not allow for differentiation of brands of gasoline (especially weathered samples) or detect higher mass ions that may permit the determination of unique chemical attribute signatures. Gasoline samples were obtained from various vendors including Shell®, Sunoco®, Irving®, Gulf®, and Cumberland Farms®. An evaporation series was created for each of the brands and analyzed utilizing QuickStrip™ cards by DART®-MS and also by GC/MS methods. The goals and objectives of this research were to optimize the DART®-MS parameters for gasoline analysis, evaluate the potential for DART®-MS to distinguish gasolines by brand, develop chemometric models to appropriately classify gasoline samples, and finally lay the groundwork for future studies that could further develop a more efficient and discriminating DART®-MS gasoline analysis method for forensic casework.

Preliminary studies using DART®-MS to analyze weathered gasoline samples using desorption ionization produced characteristic spectra for various brands of gasoline. Significantly, unique ions were detected in the higher mass range of the spectrum (>m/z 500). Using an ion trap mass analyzer and a scan range of 50amu-1,000amu, mass spectra rich in various ions were detected. Many of these ions are likely gasoline additives and are non-hydrocarbon in their nature. The data shows that DART®-MS detected higher mass ions not observed in the GC/MS data and also showed differential spectra for the varying gasoline brands. Principle Component Analysis (PCA) plots of the data created through these methods have shown that gasoline brands tend to cluster separately from one another, despite the extent of weathering as represented by the evaporation percentage. Using these unique ions and advanced chemometric analysis, statistical analysis software was used to build models that can discriminate analyzed samples in a fraction of the time in comparison to a traditional GC/MS approach. Although variables including the season of purchase, storage time, dilution, and age of the gasoline were observed to contribute to the resulting mass spectral data, once the mass spectra are further evaluated, they could offer even more discriminating power between samples in addition to brand identification. Techniques such as DART®-MS in combination with chemometric approaches could enable forensic laboratories to confidently identify questioned gasoline samples by brand in the future.

Fire Debris, Chemometrics, (DART®-MS)

*Presenting Author