B150 Pyrolysis Direct Analysis in Real-Time Mass Spectrometry (DART®-MS) Analysis of Ignitable Liquids With Chemometrics

Isabella C. Barnett, BA, Isabella Barnett, Clarksville, TN 37043; Mengliang Zhang, PhD*, Middle Tennessee State University, Murfreesboro, TN 37132*

Learning Overview: The goals of this presentation are to: (1) distinguish among different classes of petroleum-based products, and (2) classify gasoline samples based on their brands by using Direct Analysis in Real-Time Mass Spectrometry (DART®-MS) technique and chemometrics. This research concentrates on analyzing the effects and reliability of the IonRocket system, a pyrolysis device to couple with DART®-MS to assist in analysis of samples on substrates.

Impact on the Forensic Science Community: After attending this presentation, attendees will better understand how DART®-MS and the IonRocket system can be an alternative method for petroleum product identification in forensic arson investigations. This research is a pioneer for gradient heating-controlled pyrolysis DART®-MS, which will hold great potential across a broad range of topics in the analytical chemistry area and within forensic arson investigations.

The evidential link between a suspect and a crime scene could be established based on the identification of fuels or the source of them. Ambient mass spectrometry methods such as direct analysis in real time mass spectrometry (DART®-MS) can be an alternative method for petroleum product identification which enables the direct sample analysis without chromatographic separation steps.[1] DART®-MS method requires limited sample preparation and is applicable to the analysis of both volatile and nonvolatile compounds with excellent analytical sensitivity.[2] The objectives of this research were: (1) to distinguish among different classes of petroleum-based products, and (2) to classify gasoline samples based on their brands by using DART®-MS technique and chemometrics. This research concentrates on analyzing the effects and reliability of the IonRocket system, a pyrolysis device to couple with DART®-MS to assist in analysis of samples on substrates.

The pyrolysis device, IonRocket, was coupled with DART®-MS to assist the analysis. IonRocket system is an ideal unit for the analysis of polymers with which the samples can be heated up to 600°C with accurate temperature gradient control for DART®-MS analysis. The temperature was increased at the rate of 100°C per minute, so data with three dimensions consisting of *m/z*, time (=temperature), and intensity was generated which further enhanced the discriminating power comparing with sole DART®-MS analysis when chemometrics was applied. The pyrolysis DART®-MS system was used for the classification of various petroleum distillates such as gasoline, kerosene, paint remover, lighter fuel, and so on, but also for the differentiation of gasoline from different gas station chains based on the profiles of fuel additives. Other characteristics were analyzed over the course of this research, including time profiles, detection limits, and presence of the ignitable liquids on multiple substrates.

Chemometrics is critical for both data preprocessing and statistical analysis in this case. Statistical and chemometric methods have been widely used to increase the confidence in the association or discrimination and build more definitive links between samples in forensic research.[3-4] In this study, different data preprocessing techniques such as binning, normalization, scaling, and data transformation were tested and both unsupervised and supervised statistic models such as principal component analysis (PCA), partial least square discriminant analysis (PLS-DA), and soft independent modeling of class analogy (SMICA) were established and validated for the differentiation of gasoline with different brands.

This presentation will describe the use of pyrolysis DART®-MS technique and chemometric models for the classification of ignitable liquids and characteristic features to identify each ignitable liquid. The impact of different substrates and weathering will be further discussed.

Reference(s):

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2. R.B. Cody, Observation of molecular ions and analysis of nonpolar compounds with the direct analysis in real time ion source, *Analytical Chemistry* 81(3) (2009) 1101-7.
3. R.W. Smith, R.J. Brehe, J.W. McIlroy, V.L. McGuffin, Mathematically modeling chromatograms of evaporated ignitable liquids for fire debris applications, *Forensic Chemistry* 2 (2016) 37-45.
4. E.E. Waddell, J.L. Frisch-Daiello, M.R. Williams, M.E. Sigman, Hierarchical Cluster Analysis of Ignitable Liquids Based on the Total Ion Spectrum, *Journal of Forensic Sciences* 59(5) (2014) 1198-1204.

DART®-MS, Ignitable Liquids, Chemometrics