B194 Forensic Applications of Chemometrics: Statistical Comparison of Differential and Ion Mobility Spectrometry for Gas Chromatographic Detection and Three-Way Classification of Ignitable Liquids From Fire Debris

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After attending this presentation, attendees will have learned about the benefits of gas chromatography and multi-channel detection by ion and differential mobility spectrometry, intelligent instrumentation that automatically classifies samples based on the complete set of data furnished by the analytical measurement, and how to statistically compare method performance using analysis of variance.

This presentation will impact the forensic community and/or humanity by demonstrating that:

1. Ion mobility spectrometers are routinely used by law enforcement and security agencies, but the coupling of these instruments to gas chromatographs is somewhat rare, yet this coupling greatly increases the amount of information furnished for complex samples.
2. Three-way classification is very important to the forensic community because it provides a powerful method for comparing complex samples that exploits all the information furnished from the measurement. Typically, two-way classification is used which discards significant chemical information.
3. Differential mobility is a new and burgeoning method for ion measurement that complements ion mobility spectrometry.
4. The audience will learn to use analysis of variance for statistically comparing two complex instrumental methods. Although this method is old and simple, its use is often neglected and as a consequence many scientific studies are inconclusive.

Forensic analysis of paper was one of the earliest papers to incorporate the term chemometrics and report the use of pattern recognition of chemical profiles.[1] The approach of using chemical profiling as forensic evidence has been expanding, with DNA typing being the most quintessential and prevalent example. The role of chemometrics in the forensic sciences is evolving which is driven by lowered cost of chemical sensors, rising demand for security, and the increased costs of criminal justice. The classification of petroleum-based ignitable liquids is of forensic importance in arson investigation. Arson causes great losses in lives and money. In 2003, the U.S. Fire Administration estimated that there were 37,500 intentionally set structure fires, which resulted in 305 civilian deaths and $692 million in property loss.[2]

A fuzzy rule building expert system (FuRES)[3] was used for three- way classification of different types of accelerants from fire debris according to their gas chromatography-ion mobility spectrometry and gas chromatography-differential mobility spectrometry (GC-DMS) maps. The two detectors differ in the modes of ion formation and selection. The IMS uses a radioactive ^{63}Ni source to form both positive and negative ions. The DMS uses a 10.6 eV source to furnish ions. Both sensitivity and selectivity of the two detectors will be compared.

Different types of ignitable liquids, such as gasoline, kerosene, turpentine, and paint thinner, were analyzed. Nylon and polyester carpet samples were used for the fire debris. Polydimethylsiloxane solid-phase microextraction (SPME) was used for the sample collection of the headspace above the fire debris. Pattern recognition of the three-way data allowed the identification of the ignitable liquids from headspace samples of the fire debris. Bootstrap analysis of the FuRES discriminants coupled with Latin-partition[4] allowed peaks specific to the accelerants to be extracted, characterized with respect to retention time and compensation voltage, and statistically ranked with respect to significance.

References:

1 D. L. Duwer and B. R. Kowalski, Forensic Data Analysis by Pattern Recognition. Categorization of White Bond Papers by Elemental Composition. *Analytical Chemistry*, 1975, *47*, 526-530.

2 USFA Arson Fire Statistics. http://www.usfa.fema.gov/ statistics/arson/ (Accessed May 25, 2006).

3 Harrington, P. B. Fuzzy Multivariate Rule-Building Expert Systems-Minimal Neural Networks. *Journal of Chemometrics* 1991, *5*, 467-486.

4 Wan, C. H.; Harrington, P. B. Screening GC-MS Data for Carbamate Pesticides with Temperature-Constrained Cascade Correlation Neural Networks. *Analytica Chimica Acta* 2000, *408*, 1-12.

Chemometrics, Ignitable Fluids, Gas Chromatography-Ion Mobility Spectrometry

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