B89 Association and Discrimination of Diesel Fuels Using Chemometric Procedures for Forensic Arson Investigations

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The goal of this presentation is to demonstrate the practical use of statistical and chemometric procedures to associate and discriminate diesel samples based on chemical composition. The presentation will further demonstrate the potential of linking a burned diesel sample to its unburned equivalent as a practical application for forensic arson investigations.

This presentation will impact the forensic community by providing an alternative, more objective procedure for the association and discrimination of accelerants in forensic arson investigations.

The identification of a petroleum-based product in fire debris is indicative of an intentional fire and hence, is significant evidence in arson investigations. Currently, gas chromatography-mass spectrometry (GC-MS) is the conventional analytical technique used for the identification of accelerants through chromatographic pattern matching. Visual analysis of chromatograms can easily distinguish different classes of accelerants *e.g.* gasoline from kerosene. However, in order to link an accelerant extracted from fire debris to one found in the possession of a suspect, discrimination of accelerants of similar type is necessary—a difficult process through visual assessment of chromatograms alone. In this work, chemometric procedures were used to statistically associate and discriminate burned and unburned diesel fuels from different sources, to eliminate subjectivity associated with visual chromatographic assessment.

Thirty diesel samples were collected from the mid-Michigan area and analyzed by GC-MS. Pearson Product Moment Correlation (PPMC) coefficients were calculated to allow pairwise comparisons of diesels based on similarity in chromatograms. Principal component analysis (PCA) was used to identify clusters of similar diesels using total ion chromatograms (TIC). Extracted ion chromatograms (EIC) corresponding to characteristic compound classes in the diesel samples were also generated and subjected to PPMC and PCA in order to compare the discrimination ability offered with that of the TIC.

The Pearson correlation coefficients served to reduce the differences in a pair of chromatograms to a single value to which other pairs of chromatogram could be compared. On the whole, the coefficients were considered high by conventional statistical standards. These higher correlations were expected, due to the similar chemical nature of diesel fuels. Although correlations generated for the TICs began to show discriminatory capabilities, the power of the PPMC procedure was demonstrated in the EIC correlations. The mass-to- charge (m/z) 57 ion, which corresponds to linear alkane fragments, did not appear to provide any more discrimination than the TIC. However, other more characteristic ions, such as m/z 91, which corresponds to alkylbenzene fragments, demonstrated a wider spread in the correlation values, and hence greater potential for discrimination. The discrimination potential of other characteristic ions will also be discussed.

Analysis by PCA was performed in order to show natural clusters of the diesel samples and to determine the factors contributing the most to the variance among the diesel sample set. The clusters formed in the PCA scores plots served as another method for associating samples that are similar based on chemical composition. The loadings plots generated from the PCA highlight the chemical markers that cause the clustering to occur. In the same manner as the PPMC calculations, specific EICs showed more discriminating potential than the TICs after PCA. Therefore, the combination of sample comparison and feature selection from PCA for the association and discrimination of diesel samples is demonstrated.

To explore the idea of association and discrimination of burned and unburned diesels, a subset of the diesels was spiked onto different matrices commonly found in the home, such as wood, carpet, and vinyl. Spiked samples were burned under controlled conditions and the residue was extracted and analyzed by GC-MS. In addition, extractions of an unburned matrix, a burned matrix not spiked with diesel, a matrix spiked with diesel but unburned, and lastly a burned diesel not spiked onto a matrix were also gathered and analyzed in an attempt to further investigate the factors that significantly alter diesel during burning. The data generated from the burnings was compiled into the same set as the data generated from the neat diesels so that PPMC and PCA could be applied to the entire data set. The potential for association of the burned diesel to the corresponding unburned diesel using these procedures will be discussed.

Diesel, Chemometrics, Arson

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