A24 Automated Searching of an Ignitable Liquids Library of Summed Ion Spectra by Target Factor Analysis

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The goal of this presentation is to describe the use of summed ion mass spectra combined with target factor analysis (TFA) to identify ignitable liquids and pyrolysis products in fire debris samples.

This presentation will impact the forensic science community by addressing the ability of combining summed ion spectra and target factor analysis as a method for supplementing current techniques of pattern recognition employed in fire debris analysis.

This presentation will describe the use of summed ion mass spectra combined with target factor analysis (TFA) to identify ignitable liquids and pyrolysis products in fire debris samples. Ignitable liquid residues recovered from prepared-in-laboratory fire debris samples were identified by searching a library of ignitable liquid summed ion spectra as TFA test spectra. A second test of this method was applied to determine if pyrolysis products from a particular substrate could be identified by using the summed ion spectra from a library of previously burned substrates as the TFA test spectra. The importance of this method for the fire debris analysts lies in the method's ability to identify an ignitable liquid residue in the presence of significant pyrolysis background.

The summed ion spectrum, created by summing the intensity of each ion across all elution times in a gas chromatography-mass spectrometry (GC-MS) data set retains sufficient information content for the identification of specific components in complex mixtures.[1] The summed ion spectrum is information rich and much faster to calculate than the covariance map of the data set.[2] In traditional fire debris analysis, the chromatographic patterns of total ion, extracted ion, and target compound chromatograms are used to classify an ignitable liquid according to the American Society for Testing and Materials (ASTM) E 1618 standard method. A complementary method of applying principal components analysis (PCA) followed by target factor analysis (TFA) to the summed ion spectra of fire debris samples allows for rapid, automated searching against a library of ignitable liquid summed ion spectra. Receiver operating characteristic (ROC) curves measure how well the model predicts the ASTM-class identification of the ignitable liquid in the fire debris sample based on the correlation between the predicted summed ion spectrum and the test spectrum from the ignitable liquids library.

The summed ion spectra method combined with TFA has been used to correctly identify the particular ASTM classification of ignitable liquids used in the laboratory sample burns for each of the ASTM E 1618 classifications except for the light petroleum distillate classification (the miscellaneous classification was not examined) with a correlation of 0.92 or better. Low correlations between the test and resulting spectra for the light petroleum distillate class were attributed to the high volatility of liquids falling into this classification, resulting in minimal post-burn ignitable liquid residue.

The area under the curve (AUC) from the ROC analysis was above 0.92 for all of the ignitable liquid classifications except for the aromatic liquids and the oxygenated solvents. The AUC indicates the probability that the method will rank a randomly chosen ignitable liquid from the correct classification higher than a randomly chosen ignitable liquid from the incorrect classification. The low AUC for the aromatic liquid and oxygenated solvent classifications indicated difficulty in correctly identifying the broader ASTM classification of ignitable liquid; however, TFA showed a high correlation between the test and resulting spectra for the specific ignitable liquid used in the test burn. The low AUC from the ROC analysis (designating correct identification as the proper ASTM classification) can be explained by the significant variation within the aromatic and oxygenate classifications. Using the aromatic class, sub- classifications of light (C_4-C_9), medium (C_8-C_{13}), and heavy (C_9-C_{20+}) as positive qualifiers for the ROC analysis resulted in an AUC increase from 0.41 to 0.98. The sub-classifications of the aromatic ASTM classification closely parallel subdivisions of the class into single-ring and multi-ring aromatics. Sub-classification cannot be applied to the ASTM oxygenated solvent classification because clustering of the oxygenated solvent classification does not result in groupings of liquids giving similar mass spectral profiles and therefore does not improve the ROC AUC results. These preliminary results indicate that TFA is a promising method for identifying the ignitable liquid present in fire debris, especially in the presence of a significant pyrolysis signature. Statistical analysis of the performance of the method supports this conclusion and points to the summed ion spectrum/TFA as a method of supplementing current techniques of pattern recognition employed in fire debris analysis.

References:

1 Michael E. Sigman, Mary R. Williams, Joseph A. Castelbuono, Joseph G. Colca, and C. Douglas

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Fire Debris, Ignitable Liquid, Summed Ion Spectra Method

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