



### A104 Effects of Matrix Interferences on the Identification of Mixed Ignitable Liquids in Fire Debris Using Chemometric Procedures

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After attending this presentation, attendees will have an understanding of an objective method for the association of mixtures of ignitable liquids to the corresponding neat liquids despite the presence of matrix interferences, using principal components analysis (PCA) and Pearson product moment correlation (PPMC) coefficients.

This presentation will impact the forensic science community by providing a more objective method for the identification of an ignitable liquid residue in fire debris, even in the presence of mixed ignitable liquids and matrix interferences.

In fire debris analysis, ignitable liquid residues (ILRs) are extracted from the collected fire debris and analyzed by gas chromatography-mass spectrometry (GC-MS). Chromatograms are compared visually to a reference collection of ignitable liquids analyzed on the same instrument to confirm the presence, or absence, of an ignitable liquid. However, visual examination is highly subjective and increases in difficulty due to weathering of the ignitable liquid, the presence of mixed ignitable liquids, and the formation of pyrolysis and thermal degradation products, as well as matrix interferences from the debris. Thus, in order to reduce the subjectivity of visual comparisons of chromatograms, an objective method must be developed for identification of ILRs in fire debris.

The purpose of this research is to investigate association of ignitable liquid mixtures to the corresponding neat liquids, even in the presence of

matrix interferences. In the first study, the potential of principal components analysis (PCA) and Pearson product moment correlation (PPMC) coefficients to associate the mixed liquids to the corresponding neat liquids with discrimination from other liquids was investigated. In the second study, the effect of matrix interferences on the association and discrimination was assessed.

Six ignitable liquids, one from each of six classes defined by the American Society for Testing and Materials (ASTM), were chosen for this initial study. Each ignitable liquid was spiked onto a Kimwipe™ and extracted using passive headspace extraction with activated carbon strips. Extracts were then analyzed in triplicate by GC-MS under standard conditions. Two of the liquids, gasoline and kerosene, were then evaporated to two different levels (50% and 90%), and a set of mixed ignitable liquids was prepared using all combinations of the evaporated gasoline and kerosene (1:1 v/v), as well as the neat gasoline and kerosene. The mixed liquids were extracted and analyzed as described previously. Total ion chromatograms (TIC) and extracted ion profiles (EIP) of the aromatic ( $m/z$  91+105+119+133) and alkane ( $m/z$  57+71+85+99) components were generated for each liquid and three data sets were compiled: one containing TICs of the neat and evaporated liquids, one containing the aromatic EIPs of the neat and evaporated liquids, and the last containing the alkane EIPs of the neat and evaporated liquids. Each data set was subjected to retention time alignment using a commercially available algorithm to account for slight variation in retention time between analyses. Each data set was then peak area normalized to account for variation in injection volume and instrument sensitivity between analyses.

Principal components analysis was used to identify the natural clusters among the neat ignitable liquids and the mixed ignitable liquids based on the TICs as well as the EIPs. In the PCA scores plot, replicates of the neat liquids and replicates of the mixed liquids were closely clustered, while liquids of different classes were distinct. The mixed liquids were more closely associated with the corresponding neat liquids than the other liquids in the sample set. Loadings plots were generated to identify the chemical components that were most variable among the liquids. PPMC coefficients were calculated to further confirm the association and discrimination afforded by PCA.

To assess the effect of matrix interferences on association, each mixed liquid was spiked onto a carpet matrix, which was then burned and extinguished through covering with a petri dish. The ILR and matrix interferences were extracted and analyzed in the same manner, generating TICs and EIPs as described previously. Then, PCA was used to assess the association of the mixed ignitable liquids to the neat ignitable liquids in the presence of matrix interferences based on the TIC and each EIP. PPMC coefficients were also calculated and were used to aid in associations that were not clearly determined from the scores plots alone.

#### **Ignitable Liquids, Chemometrics, Matrix Interferences**