B46 Mathematically Modeling Chromatograms of Evaporated Ignitable Liquids for Fire Debris Applications

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After attending this presentation, attendees will be familiar with a mathematical model that can be used to generate chromatograms of ignitable liquids evaporated to different levels. The mathematically generated chromatograms can be used to populate reference databases that are used to aid in the identification of ignitable liquids in fire debris samples.

This presentation will impact the forensic science community by providing a method to generate the chromatogram of an ignitable liquid at any level of evaporation, thereby overcoming the variable and time-consuming nature of evaporating ignitable liquids experimentally.

Fire debris samples are typically extracted and analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) to identify any ignitable liquid present. Identification is based on comparison of chromatograms to a database of ignitable liquid reference standards with mass spectral interpretation to identify specific compounds. To account for chemical changes in the liquid that occur during the fire, reference standards experimentally evaporated to different levels are often included in these databases; however, there are numerous variables to consider in performing an evaporation, all of which affect the rate of evaporation. Further, evaporating liquids experimentally can be time consuming, particularly for less volatile liquids (e.g., heavy petroleum distillates) and, as a result, the database may be limited in the number of liquids or levels of evaporation that are included.

In this research, a previously developed mathematical model was further investigated for applications in fire debris analysis. Briefly, the model, which is based on first-order kinetics, is used to predict evaporation rate constants for each compound in the ignitable liquid as a function of retention index. For a given evaporation level, the rate constants are used to predict the fraction of each compound remaining. The fraction remaining is plotted versus retention index to generate a fraction remaining curve for a given evaporation level. This curve is multiplied by the chromatogram of the unevaporated liquid to generate the chromatogram corresponding to that evaporation level.

To test the application of the mathematical model, three petroleum distillates (spanning the light to heavy subclasses) and gasoline were analyzed in the unevaporated state by GC/MS using a 100% dimethylpolysiloxane stationary phase, which was necessary to allow calculation of retention indices. The model was applied to the chromatogram of each unevaporated liquid to generate chromatograms corresponding to evaporation levels of 25%, 50%, 75%, and 90% by mass. Each liquid was also evaporated experimentally to the same levels and analyzed by GC/MS in a similar manner. The chromatograms of the evaporated liquids generated using the model and those derived experimentally were compared using Pearson Product-Moment Correlation (PPMC) coefficients. These coefficients offer a pairwise comparison to assess similarity between the chromatograms, with coefficients greater than 0.8 indicating strong correlation.

For the petroleum distillates, PPMC coefficients indicated strong correlation between the mathematically generated chromatogram and the corresponding experimentally derived chromatogram; however, there was a slight decrease in PPMC coefficient as evaporation level increased. For example, PPMC coefficients between the experimental and mathematically generated kerosene chromatograms ranged from 0.9942±0.0005 at 26% evaporated by volume to 0.954±0.002 at 90% evaporated by volume.

For gasoline at the 25% evaporation level, PPMC coefficients indicated a strong correlation between the mathematically generated and experimentally derived chromatograms (0.9620±0.0014). The PPMC coefficients again decreased as evaporation level increased; however, in this case, the strength of the correlation also decreased, with a PPMC coefficient of 0.535±0.015 at the 90% evaporation level, which indicates only moderate correlation. The lower correlation occurred in part due to the mass of highly volatile compounds present in gasoline. These compounds eluted before and during the solvent front, meaning that they were not detected using the current GC/MS method. After taking these compounds into account, the correlation between the mathematically generated and experimentally derived chromatograms increased to 0.986±0.002 at the 90% evaporation level, indicating strong correlation. This presentation will describe the application of the model and indicate ways in which this model could be applied in fire debris analysis.

Mathematical Modeling, Evaporation, Fire Debris Analysis