B57 Mathematical Modeling of Evaporated Petroleum Distillate Standards

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After attending this presentation, attendees will be familiar with a mathematical model that can be used to generate chromatograms corresponding to different evaporation levels of petroleum distillate standards. These chromatograms can be included in reference collections that are currently used in the analysis of fire debris to determine the presence of an ignitable liquid in a submitted sample.

This presentation will impact the forensic science community by mathematically modeling chromatograms for different evaporation levels of petroleum distillate standards based on the original, unevaporated standard, with no additional experimental measurement necessary.

Fire debris samples are typically analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) and the resulting chromatograms are compared to a reference collection of ignitable liquid standards to identify any liquid in the debris samples. Reference collections include chromatograms of ignitable liquids representative of the chemical classes defined by American Society for Testing and Materials (ASTM) International, as well as chromatograms of the liquid standards evaporated to different levels; however, evaporating liquids to a range of different volumes or masses can be time consuming and it may not be practical to generate evaporated counterparts for every liquid in the reference collection.

In this research, a mathematical model was used to generate chromatograms corresponding to different evaporation levels for a range of petroleum distillate reference standards. The utility of the model was investigated by comparing chromatograms of experimentally obtained evaporated petroleum distillate reference standards to chromatograms derived theoretically using the model.

For the experimentally obtained data, several petroleum distillate reference standards, including torch fuel, lamp oil, and kerosene, were evaporated to various levels under nitrogen, and the volume and mass remaining at each evaporation level was recorded. All unevaporated and evaporated liquids were subsequently analyzed by GC/MS and retention indices were calculated for all compounds in each chromatogram.

The mathematical model was then applied to the chromatographic data for the unevaporated petroleum distillate standards. The model predicts evaporation rate constants for compounds in each standard as a function of retention index. The determined rate constants were used to predict the fraction of individual compounds remaining, which ranges from one to zero, where one indicates no evaporation and zero indicates complete evaporation. The distribution of compounds determined using the model was then plotted versus retention index to generate chromatograms corresponding to the different evaporation levels.

Chromatograms derived theoretically using the model were compared to the experimentally derived chromatograms using Pearson Product-Moment Correlation (PPMC) coefficients, which offer a side-by-side comparison of all variables in the two chromatograms. Coefficients range from ±1 to 0, with coefficients greater than ±0.8 indicating strong correlation. For these data, PPMC coefficients indicated strong correlation ($r>0.95$) between the theoretically derived chromatogram and the corresponding chromatogram obtained experimentally for each evaporation level.

This presentation will demonstrate the utility of the mathematical model to generate chromatograms representative of evaporated petroleum distillate standards based only on the unevaporated standard. Modification of the model to improve correlation between the theoretically derived and experimentally obtained chromatograms will be discussed, as well as further applications of the model.

Fire Debris Analysis, Evaporation, Mathematical Model