B133 The Refinement of a Mathematical Model to Predict Evaporation of Gasoline

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After attending this presentation, attendees will be familiar with the application of a mathematical model that can be used to generate chromatograms of evaporated ignitable liquids. More specifically, this presentation will discuss the refinement of the model to generate chromatograms corresponding to evaporated gasoline in a more accurate manner.

This presentation will impact the forensic science community by providing a method by which chromatograms corresponding to evaporated gasoline can be generated mathematically, thus eliminating the need for experimental evaporation. The modeled chromatograms can be used as a reference collection that can aid in the identification of gasoline present at any evaporation level in fire debris samples.

During an intentional fire, ignitable liquids used as accelerants undergo evaporation, among other processes. To aid in identification, chromatograms of the ignitable liquid residue are compared to a database containing chromatograms of ignitable liquid reference standards. Databases typically contain chromatograms corresponding to the unevaporated liquid, as well as the liquid evaporated to different levels to account for chemical changes as a result of evaporation; however, experimentally evaporating a liquid to different levels can be a time-intensive process with many variables to take into account, for example, agitating or heating the reference liquid.

A mathematical model was developed that predicts the evaporation rate constant of compounds as a function of retention index (I^T). The model was developed using diesel, a heavy petroleum distillate that contains compounds that elute over the I^T range 800–2,200. The predicted evaporation rate constants are used to determine the fraction remaining of each compound which can then be used to generate the modeled chromatogram.

In the initial assessment of model performance, Pearson Product-Moment Correlation (PPMC) coefficients were used to compare modeled chromatograms to those obtained from the corresponding, experimentally evaporated liquid. For the petroleum distillates tested, PPMC coefficients greater than 0.9 indicated strong correlation between the modeled and experimentally derived chromatograms; however, performance was diminished when the model was applied to gasoline, with a mean PPMC coefficient of 0.806±0.004 indicating only a moderate correlation for comparison of the modeled chromatogram and the corresponding chromatogram for a 50% experimentally evaporated gasoline.

This presentation will focus on refinement of the model to improve performance in generating chromatograms corresponding to evaporated gasoline. As a more volatile liquid, gasoline contains compounds that elute in the I^T range 400–1,500; a majority of these compounds were not included in the original model. Thus, the model was refined to broaden the I^T range and, hence, include these more volatile compounds.

To accomplish this, gasoline was experimentally evaporated from 10%–90% (by mass) in 10% increments. Each evaporated gasoline was analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) initially using a 100% polydimethylsiloxane column (100m x 0.25mm i.d. x 0.50µm d.f.). The longer column and thicker stationary phase film were necessary to identify the highly volatile compounds present in gasoline. Using the more conventional 30-m column, these compounds eluted with the solvent front and were not observed.

The performance of the model improved with the more representative chemical profile for gasoline in the experimentally evaporated samples. For example, for comparison of predicted and gasoline experimentally evaporated to 50% by mass, the PPMC coefficient increased from 0.8 to greater than 0.97, which indicated strong, rather than moderate, correlation. To investigate the potential for further improvement, the model was refined to span the wider I^T range 400–2,200. To refine the model, the abundance of the early eluting compounds (e.g., butane, pentane, hexane, and branched isomers of these alkanes) was plotted as a function of evaporation time. The resulting decay curves were fit to the first-order kinetic rate equation to determine evaporation rate constants, which were then plotted as a function of I^T. These data were combined with corresponding data from the original model and linear regression was applied to redefine the model.

This presentation will describe refinement of the model in more detail and will further discuss the improvements in model performance to predict chromatograms corresponding to gasoline evaporated to any level.

Mathematical Model, Gasoline, Evaporation

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