



### B91 The Refinement and Application of a Kinetic Model to Predict the Evaporation of Gasoline for Fire Debris Analysis

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**Learning Overview:** The goal of this presentation is to demonstrate refinement of a kinetic model to predict the evaporation of gasoline for use in forensic fire debris analysis.

**Impact on the Forensic Science Community:** This presentation will impact the forensic science community by describing the theoretical basis, refinement, and application of the model, which is subsequently used to predict chromatograms corresponding to gasoline evaporated to different levels.

One of the major challenges encountered in identifying gasoline in fire debris is the evaporation that occurs due to the high volatility of the liquid. In the heat of fire, the more volatile compounds undergo evaporation, changing the chemical composition of the liquid. The evaporation process can make comparisons of chromatograms of fire debris samples to ignitable liquids in a reference library more challenging. To address this challenge, reference libraries often contain chromatograms of experimentally evaporated ignitable liquids. However, as experimental evaporations can be time consuming, not every liquid in the library will be evaporated, and many liquids may only be evaporated to a few different levels.

The work presented here describes the refinement of a previously developed kinetic model to predict evaporation rate constants of compounds in ignitable liquids as a function of retention index ( $I^T$ ). In this case, retention indices are used as a surrogate for boiling point or vapor pressure, such that the chemical identity of the compounds in the liquid need not be known. The predicted rate constants are used to determine the total fraction remaining ( $F_{Total}$ ) of the liquid, which is related to the evaporation level. The fraction remaining is then plotted as a function of  $I^T$  to predict chromatograms corresponding to a range of evaporation levels. The model was originally developed and validated with petroleum distillates and, for these liquids, strong correlation was observed between experimental and predicted chromatograms corresponding to evaporation levels of 30%–90% evaporated. However, for gasoline, only moderate correlation was observed between experimental and predicted chromatograms, particularly at higher evaporation levels.

In this work, the model was refined to enhance the predictive accuracy, specifically for gasoline. The original model was developed across the  $I^T$  range 800–2,200; however, gasoline contains very volatile compounds that elute at  $I^T < 800$ . The first step in refining the model was to identify these volatile compounds and to experimentally determine corresponding evaporation rate constants. Unevaporated gasoline samples were analyzed by Gas Chromatography/Mass Spectrometry (GC/MS), and volatile compounds eluting before toluene ( $I^T=750$ ) were identified. A total of 14 compounds with  $I^T < 750$  were identified, including methyl butane ( $I^T=478$ ), hexane ( $I^T=600$ ), benzene ( $I^T=640$ ), heptane ( $I^T=700$ ), and methylcyclohexane ( $I^T=710$ ).

For safety reasons, two-component mixtures of the 14 volatile compounds were then prepared and experimentally evaporated to determine evaporation rate constants. Each mixture was evaporated in replicate in a temperature- and humidity-controlled chamber for up to 16 hours. Samples were removed at various time points during the evaporation process and analyzed by GC/MS using standard procedures. The chromatographic abundance of each compound was normalized and plotted versus time to generate first-order decay curves, from which the experimental rate constant was determined. For example, the experimentally determined evaporation rate constants for heptane, toluene, and octane were  $0.298\text{hr}^{-1}$ ,  $0.168\text{hr}^{-1}$ , and  $0.118\text{hr}^{-1}$ , respectively, which compare well with the rate constants predicted using the original model ( $0.307\text{hr}^{-1}$ ,  $0.189\text{hr}^{-1}$ , and  $0.105\text{hr}^{-1}$ , respectively). The experimentally determined rate constants were then plotted as a function of  $I^T$ , and linear regression was performed to refine the model across the  $I^T$  range 500–800.

#### Fire Debris, Kinetic Model, GC/MS