B136 The Determination of Weathering Levels of Gasoline Using Various Methods of Analysis

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Learning Overview: After attending this presentation, attendees will understand the value and limitation on the use of quantitative and/or qualitative analysis of weathered gasoline samples using various methods and their use in determining the extent of weathering in a gasoline sample.

Impact on the Forensic Science Community: This presentation will influence the forensic science community by looking at the possibilities of adding a metric to analyzing weathered gasoline samples in addition to observing the patterns that weathered gasoline samples display.

When suspicious fires are started with ignitable liquids, the evidence is partially or wholly consumed. The process by which the liquid evaporates is akin to weathering where the most volatile components of a mixture diminish in quantity by continuous exposure to the atmosphere. Weathering is temperature-dependent and results in a sequential loss of volatiles as a function of the component's vapor pressure at a given temperature.

Fire debris analysts are trained to recognize weathered ignitable liquid residues and consider it when classifying a detected substance. The fire debris community relies upon the ASTM E1618 standard that requires reference liquids and reference chromatograms in a case file. A ratiometric approach is proposed to estimate weathering of the most common ignitable liquid, gasoline. The integration ratios of target compound peaks by gas chromatography with mass-selective detection (GC/MS) could be a starting point.

Five gasoline samples were examined, all summer blends from the Houston area, that were weathered at 20ºC under a continuous stream of nitrogen to extents ranging from 10% to 90% by increments of 10%. The samples were then analyzed by GC/MS. Five sets of data were collected for each of five brands. Integration results for 11 target compounds (2,2,4-trimethylpentane, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, 1,2,4-trimethylbenzene, 1,2,4,5-tetramethylbenzene, naphthalene, 2-methylnaphthalene and 1-methylnaphthalene) were tabulated. Intra-sample integration ratios were then calculated for each compound. These ratios were then compared with the observed inter-compound ratios between unweathered exemplars. Finally, the latter ratios were averaged over the five brands.

In all gasoline samples that were weathered to ≥ 80% the two moieties with the highest room temperature vapor pressures, 2,2,4-trimethylpentane and toluene, were undetected. In other samples, ethylbenzene was undetected at 90% weathering. Another noticeable feature is that all ratios remain relatively unaffected when weathering is less than 50%. For all gasoline samples, the two compounds with disparate vapor pressures (o-xylene and 1-methylnaphthalene) were detected throughout. The inter-compound ratios of 2-methylnaphthalene to o-xylene ranged 1 to 9 and followed a complex polynomial function (n=6). A drawback in this technique is the variance in the formulations of the gasoline. O-xylene to 1-methylnaphthalene ratios range from about 5:1 to 20:1 making estimates unreliable. The most consistent ratios are those between o-xylene and 1,2,4-trimethyl benzene (0.43-0.47). However, given the similarity in vapor pressures the variation as a function of weathering is less dramatic.

A second approach was investigated where integrated results for the ten most abundant compounds were converted to pseudo-mole fractions and then used to calculate their combined contribution to the vapor pressure using Raoult's Law. Again, small changes are observed up to 50% weathering.

Fire Debris, Arson, Weathered Gasoline

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