



C33 A Baseline Study of Measurement Uncertainty for Peak Ratios of Isoprenoids and PAHs

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After attending this presentation, attendees will understand that when using ratios to identify or differentiate between oils and fuel types it is necessary to take into account the variability or experimental error inherent in the methodology(ies) used. Measured and potential error terms for the use of peak ratios for identification and differentiation of fuels will be illustrated and discussed.

The members of the forensic community attending will be more wary of accepting at face value, ratio comparisons for the purposes of identifying and differentiating between contaminating hydrocarbon fuels. We hope to inform participants that there are questions of variability and experimental error that need to be addressed when interpreting the data.

Several methods for the identification of petroleum products have been proposed and adopted by professional organizations recently [ASTM 5739-00, Nordtest Method NT CHEM 001]. Peer-reviewed journals have published papers describing similar methods for characterizing and differentiating oil sources. These methods generally compare the relative abundances of two or more compounds, which are assumed to be distinctive and characteristic of the samples: hereinafter this approach will be referred to as comparing "peak ratios." Peak ratio methods have some acceptance within the scientific community, and the results of peak ratio analyses have been used successfully in litigation. However, no study has been presented which quantifies the uncertainty of the measurements, and there are no criteria to compare peak ratios within any of these methods. The fundamental questions, "How much variation will be found in the peak ratios for the same material?" and "How much difference must exist between peak ratios to distinguish different materials?" have not been addressed.

This presentation will describe our investigation of the uncertainty of peak ratio measurements for isoprenoids (nor-pristane, pristane, phytane), and for polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues. Isoprenoids, a group of branched alkanes structurally based on isoprene, do not biodegrade readily in the environment and are therefore often used to distinguish middle distillate fuels (diesel, heating oil, fuel oil). AHs are cyclic compounds based on conjoined benzene rings. It is generally assumed that the larger PAHs (four or more rings) are highly resistant to degradation in the environment. PAH patterns which can be compared as a series of ratios have been used to distinguish between samples of different oil sources.

Ratios are usually calculated based on peak heights or areas from a gas chromatogram, generally using a flame ionization detector (GCFID) for the isoprenoids, and a mass spectrometer (GC-MS) for the PAHs. All instrumental analyses are subject to experimental error. Analyzing the same sample or sample extract multiple times on the same instrument will produce a range of results. The range of results, and hence the uncertainty of the peak ratio measurements, increases as other variables are introduced to the analysis, e.g., sample extraction, sample concentration, instrumental method, data analysis methods, etc. This investigation evaluated the uncertainty of peak ratios with respect to concentration, instrumental methods, and data analysis methods for GCFID and GC-MS analyses.

The GC-FID investigation evaluated the measurement uncertainty for the peak ratios of the isoprenoids nor-pristane, pristane, and phytane in a regular automotive diesel fuel (Texaco). The Texaco fuel was used as a reference material in our laboratory for three years. It was analyzed at concentrations ranging from 1000 to 50 µg/g (ppm) on two GC-FID instruments.

The GC-MS investigation evaluated the measurement uncertainty for the peak ratios of the PAHs, parent compounds and alkylated homologues in various crude oils. Multiple Agilent GC/MSD systems were used to perform the analyses in two different laboratories.

Good Laboratory Practice (GLP) requires that results be reported with an "error term" (the result obtained, plus or minus the statistically determined measurement uncertainty for the analytical technique). Error terms readily show the variability inherent in a measurement procedure. When peak ratios are used to differentiate between materials, the reliability of the numbers used to generate the ratio must be assessed. One ratio calculated from the heights of two peaks in a single chromatogram of one sample at a specific location does not address variability: that single ratio cannot reliably be compared to a similarly generated ratio for another sample to distinguish different contaminants.

The Federal Rules of Evidence include, under Rule 702, assessment of whether testimony is based on methodology that is scientifically valid and can be properly applied to the issue at hand. Considerations bearing on this assessment include not only peer review, publication, and existence of standards, but also the known or potential error rate for the methodology used.

While peak ratios can be a very powerful tool for forensic environmental chemistry, in order to be scientifically supportable and defensible an explicit statement of the measurement uncertainty must be included with the result.

PAHs, Ratios, Isoprenoids