



Engineering Sciences Section – 2003

C11 Age-Dating Diesel Fuel: Facts and Fallacies

Denise A. Shepperd, BS*, Trillium, Inc., 2014 Carol Drive, Wilmington, DE; and Todd R. Crawford, BA, Center for Toxicology and Environmental Health, LLC, 615 West Markham Street, Little Rock, AR

The goal of this presentation is to inform participants of some of the pitfalls of Age-Dating petroleum products.

Petroleum distillates, such as diesel fuel, heating oil, and fuel oil #2, have been in widespread use for nearly 100 years, with minimal changes to their manufacturing process and chemical composition during that time. They are also common environmental contaminants. The degradation of these products in the environment has been widely studied and is generally well understood to be comprised of three major pathways: biodegradation, evaporation, and dissolution. Biodegradation and evaporation are easily recognized in the traces of fresh and weathered products analyzed by gas chromatography with flame-ionization detection (GC-FID). Consequently, it is tempting to assume that the date of release or "age" of a petroleum distillate may be determined simply by comparing the chromatograms of the samples with known standards.

GC-FID is a chemical analysis process that separates the components in a mixture based on physical properties, primarily boiling point, polarity, and molecular weight, and detects them using their tendency to create ions in a flame. Thus, mixtures with similar chemical composition will have similar GC-FID traces. Hydrocarbons are commonly grouped in chemical classes of aliphatics (alkanes and isoalkanes), naphthenes (cycloalkanes), aromatics (BTEX), polycyclic aromatic hydrocarbons (PAHs), and olefins (alkenes). The hydrocarbons seen in the GC-FID traces of diesel fuels generally form a pattern of tall, regularly spaced peaks interspersed with shorter, irregularly spaced peaks, all surmounting an unresolved "hump." The tall, regularly spaced peaks are n-alkanes and the shorter, irregular peaks are generally isoalkanes, some of which belong to a particular chemical class called "isoprenoids" (branched alkanes based on the structure of isoprene.) The majority of the material in a middle distillate fuel will elute between n-C₁₀ and n-C₂₅ on the GC-FID chromatogram.

The process of evaporation is so common that it is sometimes oversimplified, particularly when applied to mixtures, such as diesel fuel. The GC-FID chromatogram of a diesel fuel that has evaporated at ambient temperature and pressure is quite distinctive, showing a loss of most of the hydrocarbons lighter than n-C₁₂. However, useful reference standards of evaporated diesel fuel are more difficult to generate because a diesel fuel distributed over a large surface area, such as a surface spill on sandy soil, will evaporate very differently from the same fuel confined in a column of product such as might be found in a monitoring well. A rate of evaporation of bulk material determined at standard temperature and pressure cannot be reliably applied, either directly or indirectly, to the evaporation rate of identical material distributed in the environment.

Biodegradation of diesel fuel by microbial populations has been described by many researchers. It generally follows a pattern based on the chemical structure: e.g., n-alkanes will be lost more rapidly than isoalkanes, which will in turn be lost more rapidly than PAHs. However, the actual rate of biodegradation of any of these chemical classes varies with the type(s) of microbial population(s) present, the temperature, moisture, pH, oxygen, and nutrient content of the environment, the geometry of the spill, etc. Thus, while the amount of biodegradation may be described (e.g., highly biodegraded, slightly biodegraded) for a petroleum product by looking at the relative levels of n-alkanes versus isoalkanes in fresh and weathered materials, it is not possible to determine the age of the material, as the rate of loss of these components over time has certainly not been constant. In addition, some hydrocarbons are known to occur naturally and some are created during the biodegradation process, further confounding the determination of age based on the apparent losses of the peaks in the GC-FID chromatogram.

Despite the many factors confounding the empirical determination of degradation rates for diesel fuel in the environment, it is still possible to measure and estimate the TPH concentrations and the individual component concentrations for environmental samples. It is possible to determine relative amounts of degradation from these data. The measured amounts of degradation may be related to the samples' situation in the environment, and from that information a relative age may be assigned. For example, two samples that appear to have undergone identical types and amounts of degradation but which were collected at different distances from the source may be inferred to have different ages; and similarly, two samples that were collected at the same distance but which show different amounts of degradation may be different from each other in age, assuming all other factors to remain constant.

The accuracy of these relative determinations is a function of the number and distribution of the samples collected and analyzed. It is also important to note that these determinations can only be relative: sample 'A' is older than sample 'B'. Unless a set of samples can be related to a particular date, either by knowledge of a specific release or site activity, it is not possible to age date the contaminant.

The environmental processes that degrade middle distillates, such as diesel fuel, can be recognized from GC-FID analyses, and rates of degradation can be experimentally determined. However, there are no empirical formulas to describe the rate of degradation of diesel fuel in the environment. The confounding interactions of evaporation, biodegradation, and biotransformation make it impossible to 'age-date' petroleum distillates. It is possible to estimate or measure the amounts of material lost from the original material in the



Engineering Sciences Section – 2003

environment, and relative amounts of degradation may be calculated for field samples, which may be used to infer relative aging of the material. However, such estimates are subject to great uncertainty unless the sampling and analysis meets specific data quality objectives.

Petroleum Products, GC-FID, Diesel Fuel