C41 Dialkyl Disulfides: Another Diagnostic Tool for Petroleum Products in the Environment?

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After attending this presentation, attendees will learn about an unusual petroleum product fingerprint that may prove useful in determining the source or identification of released materials.

This presentation will impact the forensic community and/or humanity by presenting data to illustrate an unusual fingerprint in a petroleum product found in the environment; this information may offer additional forensic clues as to the source or identification of the product released.

Fingerprinting techniques are commonly used in environmental forensics to identify classes of petroleum products and/or to link contamination to a particular source. Gas chromatography with flame ionization detection (GC/FID), a very sensitive measurement technique for alkanes and acyclic isoprenoids (e.g., pristane and phytane), allows evaluation of characteristic peak patterns to establish the type of petroleum product (gasoline, kerosene, diesel fuel, motor oil, etc.) present. Gas chromatography with electron capture detection (GC/ECD) is not sensitive to hydrocarbons but readily detects halogenated and unsaturated materials, among others, and is often used in tandem with GC/FID to evaluate the presence of additives such as the alkyl lead compounds (e.g., tetraethyl lead).

Typical GC/FID and GC/ECD fingerprints of a modern Jet A fuel are presented in Figure 1. The hydrocarbon pattern exhibited in the FID fingerprint is characteristic, and the ECD fingerprint gives little additional information.

A recent GC/FID fingerprint analysis of ground water samples taken from a petroleum storage facility showed the presence of several different petroleum products, including Jet A fuel. GC/ECD fingerprints were also generated, and, as expected, most gave little additional information. In three samples, however, the GC/ECD chromatogram showed a peak pattern very similar to the GC/FID fingerprint but eluting approximately 8 minutes later (Figure 2).

What was this? Too early in the chromatogram to be polychlorinated biphenyls, the ECD results were quite puzzling. To generate more information, the extract was subjected to gas chromatography/mass spectrometry (GC/MS) analysis to allow a closer look at these peaks, and, hopefully, to facilitate identification of the compounds they represent. The answer: a series of dialkyl disulfides, ranging from C_{11} to C_{18}.

ASTM specifications regarding sulfur content of Jet A fuel have not changed since 1959, when *Standard Specification for Aviation Turbine Fuels* (ASTM D 1655) was first issued. So, the presence or absence of dialkyl disulfides does not appear to be a candidate for forensic age-dating based on a particular point in time when the total sulfur content of Jet A had to be reduced to meet specifications.

However, high concentrations of organic sulfur compounds (mercaptans) are undesirable in petroleum refining for many reasons, including corrosivity, color changes, and unpleasant odors. Removing mercaptans from petroleum streams is a process known as sweetening. When the total sulfur content of the petroleum product is already within final product requirements, most gasoline, jet fuel, kerosene, and diesel fractions can be successfully sweetened using a caustic solution to oxidize the odorous and corrosive mercaptans to disulfides, which have much more acceptable characteristics. Thus, the total sulfur content remains unchanged but the undesirable characteristics are eliminated.

Perhaps, then, the presence of dialkyl disulfides can serve as an indicator of the characteristics of the crude oil from which the petroleum product was distilled. While this type of information may or may not be particularly helpful in every site investigation, it is clear that careful, comprehensive evaluation of all available forensic data can provide clues - potentially important clues - for answering the “who, what, where, when, how, and whys” surrounding a contaminated site.

References:

1. F.J. Suarez, *Pluses and Minuses of Caustic Treating*, reprinted from *Hydrocarbon Processing*, October 1996, www.merichem.com/ process/Technical Articles/Causticplus.htm.
2. Test Plan for Reclaimed Substances: Streams Containing Naphthenic Acids, Phenolics, Disulfides, Acids, or Caustics, The American Petroleum Institute, Petroleum HPV Testing Group, Consortium Registration #1100997, December 15, 2003.
3. ASTM D 1655, Standard Specification for Aviation Turbine Fuels, 1959 through 2000.

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Figure 1 - Jet A Fuel Standard. Top - FID fingerprint; Bottom - ECD fingerprint.

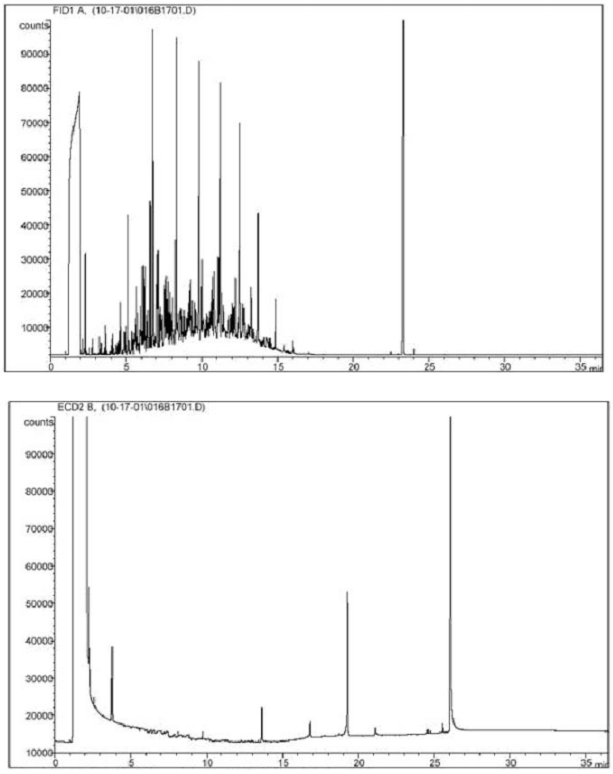
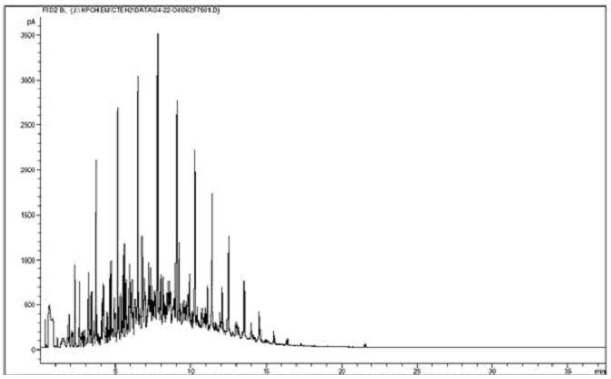


Figure 2 - Site Sample. Top - FID fingerprint. Bottom - ECD fingerprint.



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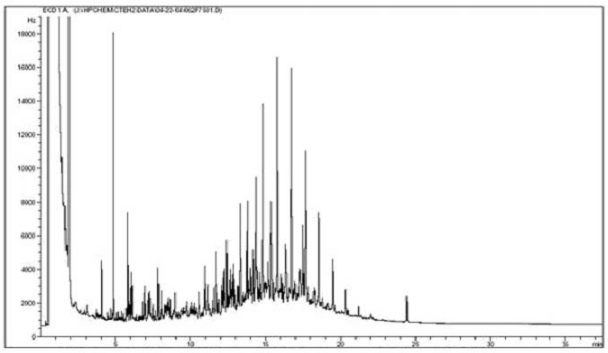

Dialkyl Disulfides, Jet A Fuel, Fingerprinting

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