C3 Finding the Genie in a Bottle

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The goal of this presentation is to describe how to use forensic science investigation/evaluation approaches on environmental release work where soil was impacted by past dumping practices.

This presentation will impact the forensic science community, by adding to the arsenal of petroleum hydrocarbon release site investigation techniques, using typically available or easily obtainable chemical analysis data to investigate the release. This technique has direct impact on who is the liable party for the release.

In 1994 during the removal of an underground heating oil tank behind a gasoline service station, a light non-aqueous phase liquid (LNAPL) described as a black viscous oil, was discovered floating on top of the groundwater. The service station at this location has been in operation since the 1930's. The underground heating oil tank, used to supply fuel for heating the station building, did not appear to be leaking when it was removed. Other potential sources of the LNAPL were the gasoline, diesel fuel, and kerosene stored in underground storage tanks (USTs) and dispensed at the service station. The service station building, USTs, and dispensers are located in the southeast corner of the property. About 100 yards of empty land separates the service station building from a tidal creek along the western boundary. The property is prone to flooding during extremely high tides. The groundwater is only about three feet below the ground surface. In the past, fill material was added to the east and north sides of the service station to raise the elevation of the property. Additional LNAPL was found in twenty-two test pits located within this fill material.

Samples of the LNAPL were submitted for gas chromatographic analysis using a flame ionization detector (GC/FID). The GC/FID chromatogram of the LNAPL collected from a pit in the southwestern corner of the property is shown in Figure 1. The chromatogram is a lubrication-type oil (i.e., mineral oil) with the center of the unresolved complex mixture (UCM) in the C_{22} to C_{23} n-alkane retention window. The n-alkanes C_{17} and C_{18} are present in the chromatogram along with the isoprenoids pristane and phytane. LNAPL samples from the eastern portion of the site do not have the C_{17} and C_{18} n-alkanes indicating that more aerobic biodegradation has taken place. Finding the lubrication-type oil next to the service station would lead one to suspect that this oil was used crankcase oil from oil changes that were performed at the station; however, zinc, lead, chromium, and copper were either not detected or were present at only a few parts per million in the oil. Zinc compounds are added to motor oil for antiwear and anticorrosion properties. Lead, chromium, and copper are wear metals from the engine that contaminates used crankcase oils. The concentrations of these metals in the LNAPL were too low to be considered used crankcase oil.

Other indicators that the LNAPL was not used crankcase oil was the polynuclear aromatic hydrocarbons (PAHs) content. There are two sources of PAHs in used crankcase oil, petrogenic and pyrogenic. Petrogenic PAHs are from the crude oil used to refine the oil while pyrogenic PAHs are formed from combustion. For pyrogenic PAHs, the unsubstituted parent PAH predominates over the alkylated PAHs of the parent and the abundance of the alkylated PAHs decreases with the increasing level of alkylation. For petrogenic PAHs, the alkylated PAHs predominate over the parent PAH. In used crankcase oil, there will be an increase in pyrogenic PAHs as the result of combustion blow-by in the engine.[1] In the LNAPL samples, the alkylated PAHs predominated over the parent PAH indicating that the source of the PAHs was petrogenic and not from combustion.

The LNAPL found at the site was co-located with fill material containing trash, glass bottles, glass shards, and documents from a nearby glass bottle manufacturer. One of the documents found dated back to 1940. Other material identified in the fill that was associated glass bottle manufacturing including bottle molds, bottle slugs, mold swabs, bottle brushes, and oil cans used to squirt oil into the molds. The trademark molded into the bottom of the intact bottles belonged to the same glass bottle manufacturer identified in the documents found in the fill. Research into glass bottle manufacturing practices revealed that the molds used to form the glass bottles are coated with a releasing agent called a mold dope before the molten glass is added. A mold dope is an oil containing a small percentage of other materials such as sulfur, graphite, rubber, and even old shoe heels.[2] The oil used in commercial mold dopes is mineral oil.[3] The GC/FID chromatogram of one commercial mold dope contains mineral oil similar to the LNAPL including the n-alkanes, pristane and phytane. The mold dope entered the waste stream of the glass manufacturer from drippings collected in pans and on absorbents, in sweepings, from used mold swabs, rags, and discarded mold oil containers. Workers from the glass manufacturer transported these wastes along with general trash, used bricks from the ovens, and unusable glass in dump trucks where it was used as fill in the marsh next to the service station.

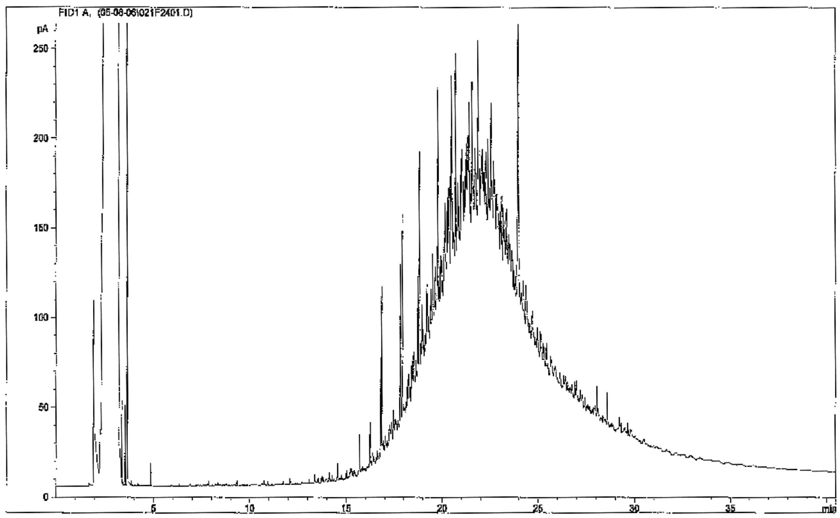

Figure 1

References:

1. Wang, Z., and J. H. Christensen, *Chapter 17: Crude Oil and Refined Product Fingerprinting Applications*, In: R. D. Morrison and B. L. Murphy, eds., *Environmental Forensics Contaminant Specific Guide*, Elsevier, London, 2006.
2. Tooley, F. V., ed., *The Handbook of Glass Manufacture*, Volume 1, Books for Industry and The Glass Industry Magazine, New York, 1974.
3. Kampf, R. P., Lubricants for Shears, Lehrs, and Everything in Between, Glass, 2006, 83(6), 14.

Environmental Forensics, Lubricating Oil, LNAPL

