



# ENVIRONMENTAL TOOL BOX



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## How to Sample An Oil Sheen for Forensic Analysis

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A classic problem in collecting an oil sheen from a stream, lake, ocean or puddle of water is the difficulty in obtaining a sufficient volume of the sample without cross contamination. The classical use of bottle is not applicable for sheen due to the insufficient amount of sheen that may be collected floating on water.

The best available technique for collection of sheen samples uses open mesh fabric such as precision woven synthetic monofilament fabrics. The woven open mesh fabric is a highly specialized monofilament fabric, characterized by precisely defined and controlled, consistent and repeatable material properties such as pore size, thickness, cleanliness, tensile strength, dimensional stability, etc. As compared to non-precision woven open mesh fabrics, precision fabrics present several advantages including a tightly controlled thread diameter and consistent surface properties without irregularities, thickness tolerance within microns, and guaranteed repeatability. DPRA has analyzed the fabric (ethylene-tetra-fluoroethylene or ETFE) and has detected no compounds which can potentially interfere with petroleum hydrocarbon testing.

In practice, the material is placed on the surface of the water

where the sheen is observed and the petroleum hydrocarbons are preferentially sorbed into the fabric. The fabric material is then placed into a specially prepared plastic bag which is certified to be free of potential cross contaminants. The bag and chain of custody is then forwarded to an appropriate forensics laboratory for analysis.

The photograph shows Nina Vitalia using the ETFE sheet attached to a fishing rod and reel which is used to cast the material onto an oil sheen in a lake in Finland where the Finish National Bureau of Investigation has used this technique for collection of oil sheen samples in criminal forensic cases.



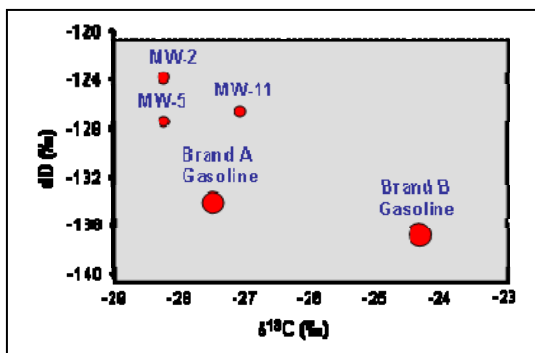
The ETFE fabric is manufactured by the Filtration Division of Sefar, Inc. For information on sampling techniques, please contact [trisha.van.stright@dpra.com](mailto:trisha.van.stright@dpra.com).

## Zymax Forensics Joins DPRA

In late 2005, DPRA acquired ZymaX Forensics laboratory located in San Luis Obispo, California. ZymaX is considered to be the premier environmental forensics laboratory in North America. The ZymaX acquisition provides DPRA the ability to provide its litigation clients with sophisticated petroleum hydrocarbon fingerprinting and stable isotopic analyses as well as the interpretation of this information.

The primary service provided by ZymaX Forensics is the ability to perform sophisticated analysis of samples to identify:

- types of fuel released into the environment;
- distinguish between similar products from different sources;
- estimate the age of the product;
- estimate the mixing ratios of different products (for allocation purposes);
- assign probable responsibility for contamination.



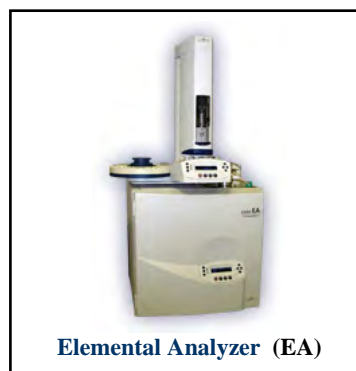
A graph of the stable isotopes of carbon and hydrogen demonstrate how gasoline detected in three monitoring wells (MW2, MW5 and MW11) is more closely associated with Brand A gasoline than Brand B gasoline.

Techniques employed and often developed by ZymaX include a wide range of forensic analyses, including isotopic analysis. The specific isotopic analyses performed by ZymaX Forensics include:

- **For Gas Samples:**
  - Carbon Isotope Analysis,  $^{13}\text{C}/^{12}\text{C}$ ;
  - Deuterium;
  - $^{13}\text{C}/^{12}\text{C}$  of  $\text{CO}_2$ ;
  - Carbon 14 Analysis; C-14, and
  - Sulfur, Nitrogen and Oxygen Analysis

- **For Water Samples:**
  - D/H and  $^{18}\text{O}/^{16}\text{O}$ ;
  - $^{34}\text{S}/^{32}\text{S}$  of Dissolved Sulfate or  $\text{H}_2\text{S}$ ;
  - $^{34}\text{S}/^{32}\text{S}$  of Dissolved Sulfate or  $\text{H}_2\text{S}$  with %S;
  - $^{13}\text{C}/^{12}\text{C}$  of Dissolved  $\text{CO}_2$  (precipitation method);
  - $^{13}\text{C}/^{12}\text{C}$  of Solid Carbonate/Bicarbonate;
  - $^{15}\text{N}/^{14}\text{N}$  of Dissolved Nitrate and/or Ammonia;
  - Cl-37 for Chloride or solvent
- **For Soil and Mineral Samples:**
  - $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{34}\text{S}$ , D/H;
  - C-14 of Carbonate or organic

State-of-the-art equipment used for isotope analysis includes the IsoPrime Continuous Flow Mass Spectrometer which provides Zymax with the ability to analyze large volumes of samples for hydrogen, oxygen, carbon, nitrogen and sulfur isotopic ratios.



With its environmental forensics experience, personnel, and instrumentation, ZymaX Forensics yields high quality results while assuring top efficiency. For information on ZymaX Forensics, visit <http://www.zymaxforensics.com/index.htm>, or contact Dr. Alan Jeffrey at 805-544-4696.



## Application of Isotopic Analyses in Chlorinated Solvent Investigations

Compound specific isotope analysis represents a mature methodology used in chlorinated solvent investigations to (1) distinguish between different contaminant sources, and/or (2) to demonstrate that biodegradation is occurring. These techniques have been successfully used to examine the biodegradation of chlorinated solvents under either anaerobic or aerobic environments as evidence of natural attenuation, for source differentiation at field sites throughout the world and to distinguish between different sources.

The use of isotopic analyses as evidence of degradation is especially intriguing not only for chlorinated solvents but for other compounds such as MTBE and normal alkanes. This technique is widely used in Europe and the United Kingdom as evidence that natural attenuation is effective in remediating chlorinated solvents in groundwater.

To distinguish between sources of chlorinated solvent releases, the use of isotopic analyses is premised on the assumption that a wide range of isotopic signatures exist for different manufacturers. This assumption implies that carbon isotopic fractionation is not expected to occur during synthesis unless there are incomplete reactions and/or recycling of by-products during the manufacturing process. The primary variability is therefore most likely associated with differences in the isotopic signature of the original carbon materials. Chlorinated solvents are expected to exhibit a wide range of manufacturer dependent isotopic signatures due to various chemical reactions, which may include dehydrochlorination or dehydrogenation reactions and production conditions (e.g., temperature differences, catalysts used, engineering design, etc.) as well as use of different feedstocks.

The isotopes most commonly used for this purpose are  $^{13}\text{C}$  (carbon 13) and  $^{37}\text{Cl}$  (chlorine 37). A number of researchers have analyzed carbon and chlorine isotopes in chlorinated solvents prior to their introduction into the environment. Recent research shows that trichloroethylene (TCE) and

1,1,1-trichloroethane (TCA) have characteristic isotopic signatures associated with their respective manufacturer.

From a forensic perspective, releases of chlorinated solvents from different manufacturers may be difficult to establish due to the precision of the analyses, effects of dissolution, sorption and volatilization whose extent are difficult to quantify as well as significant difference in the carbon and chlorine isotope ratios for product, even if from the same supplier. It is also difficult to reliably interpret small variations in isotopic composition to different sources as viewed from a confidence interval perspective.

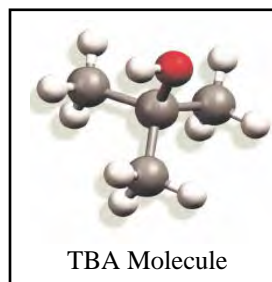
Another issue in interpreting isotopic data for chlorinated solvent source differentiation is the issue of temporal source variation and the assumption that the isotopic characteristics of the released chlorinated solvent(s) is known. In practice, it is rare that a historical sample of a chlorinated solvent is available to provide a baseline isotopic signature.

While the cost and sampling techniques vary for collecting a liquid or gas sample to be analyzed for carbon or chlorine isotopes, most laboratories in the United States charge between \$300 and \$450 per sample.

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### What is TBA?

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TBA (sometimes called gasoline-grade TBA or GTBA) is the acronym for tert-butyl alcohol. TBA has been used by some petroleum refiners since its introduction for use in gasoline in 1969. Initial concentrations of TBA increased from about 2% to eventually about 7% since 1973. The use of TBA increased after the United States Environmental Protection Agency approved its use in 1979. The use of TBA constituted a minor percentage of the oxygen-containing gasoline produced in the United States throughout the 1980's as the use of TBA was generally supplanted by MTBE.



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