Forensics Division

AGAT Laboratories

Forensic Services

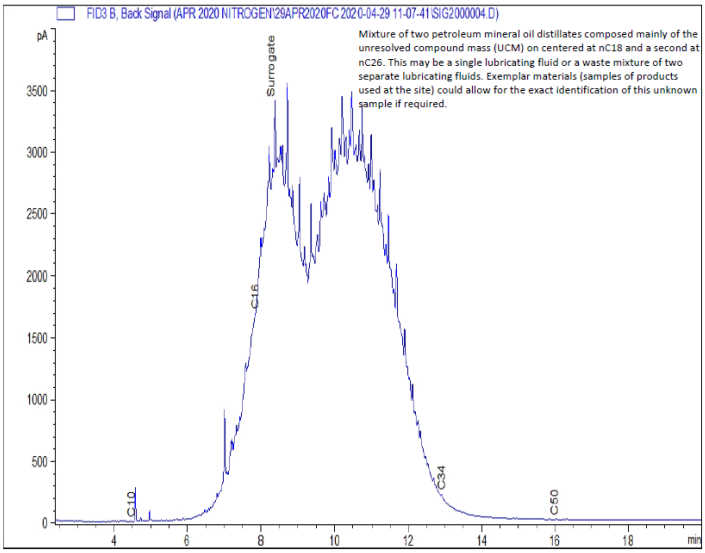
You've discovered hydrocarbon impacts and don't know the source – now what?

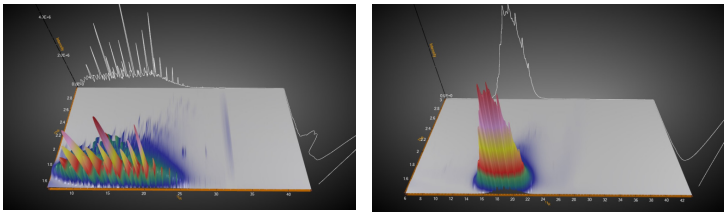
Hydrocarbons are often discovered in soil and groundwater with no known source based on site history. Chromatograms included by the laboratory as part of standard BTEX, C6-C50 analysis can identify the carbon range, but making a definitive assessment as to the type of petroleum product present can be more difficult. In an effort to produce high quality, but rapid quantitative results for standard hydrocarbon analysis chromatograms are condensed due to shortened analysis times making fingerprinting and forensic assessment much more difficult.

To assist our clients assess PHC impacts, AGAT offers the following additional testing packages.

Fuel Identification – C10-C50 Range

Samples are extracted following standard hydrocarbon methods and analyzed by GC/FID with an extended run time to allow for better peak separation and more detailed chromatograms. The results are presented alongside reference material (such as diesel, motor oil, kerosene, and other petroleum distillates) with basic interpretation comments from an experienced chemist.

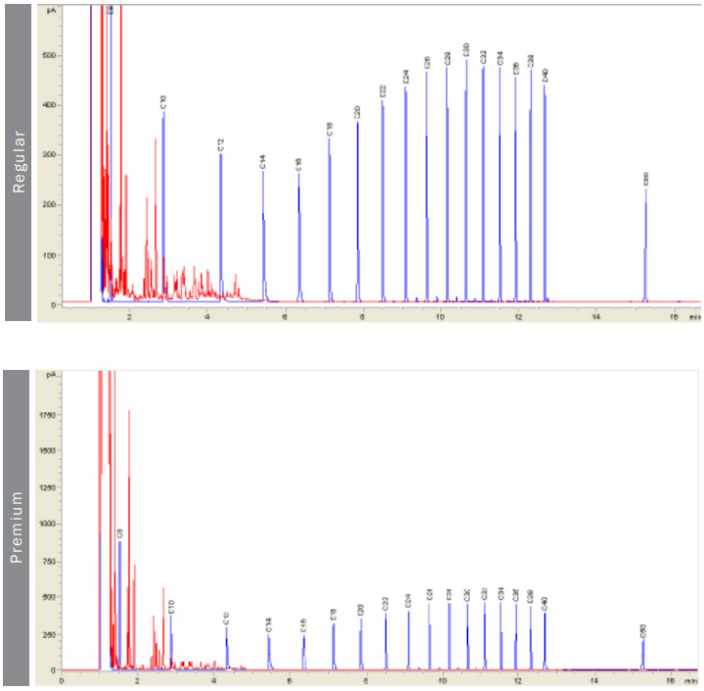




2D GC Chromatograms for Unweathered and weathered diesel. The differences are obvious in both the first dimension (x-axis) as well as the second dimension (y-axis). Typical projects looking at weathered products will utilize only the first dimension, but if additional inspection is required the option for an in-depth review is available.

Fuel Identification – Gasoline (C6-C12 Range)

When a light hydrocarbon product such as gasoline, jet fuel or kerosene is suspected, a gasoline range fuel identification can be a valuable tool to determine the potential source. Samples are extracted in a methanol solvent and analyzed by gas chromatography with a dual MS/FID detector. Chromatograms are provided with this package along with an unweathered gasoline as a reference. As with the C10-C50 fuel ID package, AGAT will provide basic chromatogram interpretation comments on the chromatograms.



Two gasoline examples showing the clear difference between grades of gasoline. Similarly, field collected samples can be differentiated quickly and accurately.

How Old Is the Contamination?

This is probably the most common, yet most challenging environmental forensics question asked of the laboratory. AGAT employs specific analytical tools to help provide evidence that when combined with site history and other information often can assess the timeframe when the contamination event(s) began. Not every analysis ends with a definitive answer and it is important to realize that the lab results are just one line of evidence. The tools tools used in thsi work are determined by contamination source: Fuel Oil, Diesel, Gasoline.

When you are dealing with fuel oil or diesel contamination the analysis of isoprenoid compounds such as pristane and phytane can be very useful to assess the the extent of environmental weathering, which can be an indicator of age. It is important to note that isoprenoid analysis is to be used in conjunction with other site evidence, not as a stand-alone tool to determine the age of a release. Christensen-Larson published a model that estimates the age of a diesel/fuel oil release is based on a linear relationship between the biodgredation of n-alkane C17 relative to pristane. The nC17:Pristane ratio in an unweathered or fresh diesel/fuel oil is approximately 2:1. As diesel/fuel oil weathers in the environment through biodegradation, the nC17 alkane is preferentially depleted vs phytane. The lower the nC17:Pristane ratio, the more biodegraded the sample is.

AGAT reports the nC17:Pristane ratio as well as the Pristane to Phytane ratio which can be indicative of crude oil feedstock source. nC18 to Phytane ratio is also reported which can be an additional weathering index.

An example report is below:

AGAT ID	Client ID	nC17/Pr	nC18/Ph	Pr/Ph
20C135447_1234567	Source	0.05	0.07	2.63
20C135447_1234567	MW2-4	0.02	0.10	2.96

Gasoline

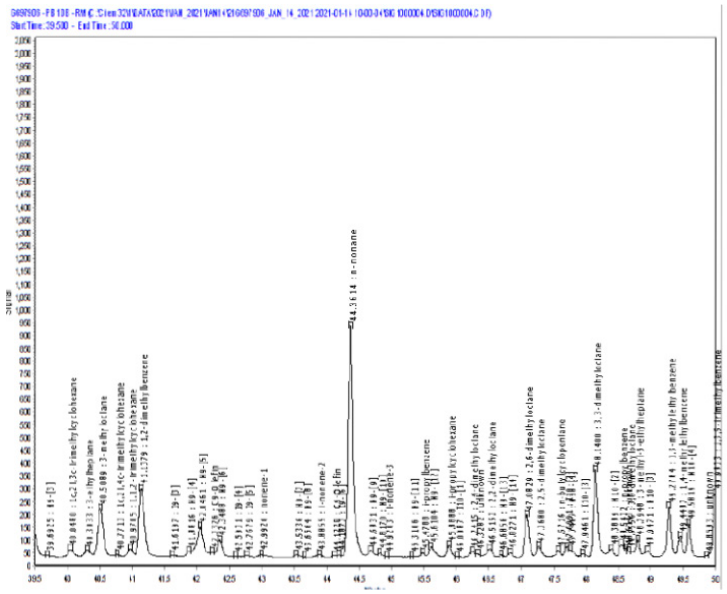
When free phase gasoline is encountered on your site, AGAT offers analytical tools designed specifically for use on free product to assess the degree of weathering and age of the release.

PIANO

A PIANO analysis is a gasoline component analysis that identifies as many as 70 key constituents in gasoline. Originally used as a product test to ensure gasoline meets quality specifications, this test has tremendous application for environmental forensics. AGAT reports the relative concentration by % for 70 compounds and a breakdown of the total for Paraffins, Isoparaffins, Aromatics, Naphthenes and Olifens (PIANO).

AGAT also reports gasoline additives and oxygenates such as MTBE in this package. Of particular value in the AGAT report are the diagnostic weathering ratios and interpretation guide which provides data to assess the degree of weathering from: evaporation, biodegradation and water washing.

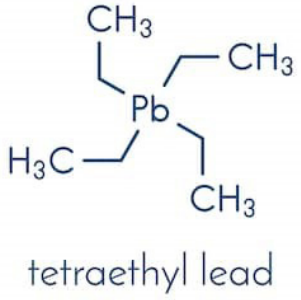
An example report is below:



Example of a crude petroleum product indicating the various compounds that can be identified and utilized as markers.

Tetraethyl Lead (TEL)

Historically, lead was used in Canadian gasoline as an anti-knock agent to improve performance. After the environmental effects were discovered, it was phased out in Canada until a complete ban (with some minor exceptions such as race cars) in 1990. With this very specific time marker, TEL can be an important indicator of the age of gasoline. If present, it indicates that the contamination began at least before 1990. AGAT offers TEL in product, soil and groundwater by GC/MS.



tetraethyl lead

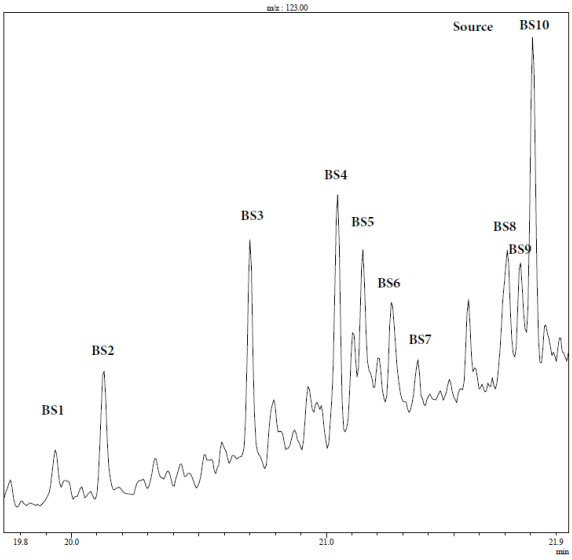
Are there Multiple Sources or a Single Source?

Once the contamination type is identified, often there is evidence that suggests there may have been multiple release events over time or contamination from a neighbouring property is co-mingling with another plume. AGAT offers two packages to help compare impacts between samples or suspect source to determine if there is a match.

Biomarkers

Environment Canada has published several peer reviewed journals on the use of biomarkers to differentiate source and suspect samples for middle distillate and crude oil contamination. Biomarkers are chemical fossils present in all crude oil that survive the refining process and their signature is specific to the geology and source of the crude oil. The signatures resulting from these biomarker compounds can be used in environmental forensics as a means to determine if samples are from a consistent crude source, which often can be used to link a spill to a suspect source. The most documented and useful biomarkers are a class of compounds called bicyclic sesquiterpanes. There are 10 diagnostic compounds and their relative abundance is what produces the signature.

In this package, AGAT will report the ratio of the 10 compounds using Environment Canada ratios and a chromatogram identifying the signature. When the ratios are consistent between source and suspect, it suggests the hydrocarbon came from the same crude oil feedstock. This type of forensic chemistry has been widely used on high profile spills, including claims as a result of the Deepwater Horizon spill and many other crude oil releases from tankers.



Bicyclic Sequiterpanes areas m/z=123

Name	Peak #	Ion	Source	MW2-4	MW2-7	Perdue
Sesquiterpane 1	1	179				
Sesquiterpane 2	2	179				
Sesquiterpane 3	3	193				
Sesquiterpane 4	4	193				
8β (H)-drimane	5	193				
Sesquiterpane 6	6	193				
Sesquiterpane 7	7	207				
Sesquiterpane 8	8	193				
Sesquiterpane 9	9	193				
8β (H)-homodrimane	10	207				

Bicyclic Sesquiterpane ratios

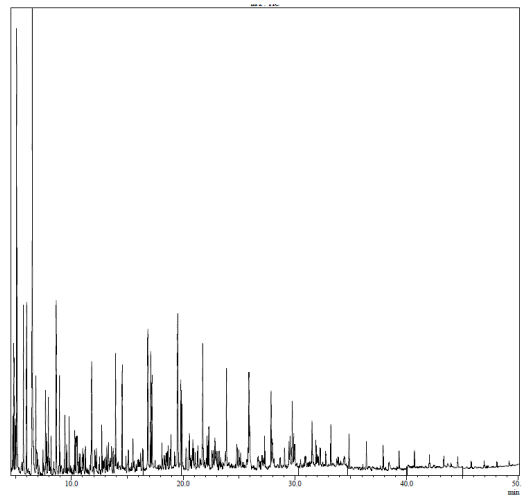
Ratios	Source	MW2-4	MW2-7	Perdue
10/(5+10)				
3/(3+5)				
10/sum(6 to 10)				
(4+6)/(4+6+10)				
1/(1+2)				
5/(5+1)				

Multi-Dimensional Gas Chromatography (2DGC)

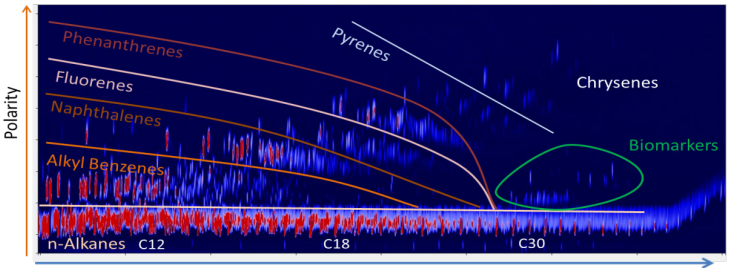
Two dimensional gas chromatography represents an advancement in chromatography allowing for a more complete separation of the individual components of hydrocarbon products compared to conventional GC analysis.

The techniques uses two columns that separate based on different physical characteristics of the compounds, generally mass and polarity and separating in two dimensions instead of one dimension. The result is a dramatic increase in peak resolution resulting in a much more detailed chromatogram improving the ability to separate and compare features from multiple samples, particularly characteristic/distinguishing features of different samples. By using this technique, multiple hydrocarbon functional groups are able to be well resolved and quantified in a single gas chromatographic run, whereas a conventional analysis would require multiple GC runs and different samples preparation steps to acquire the same data.

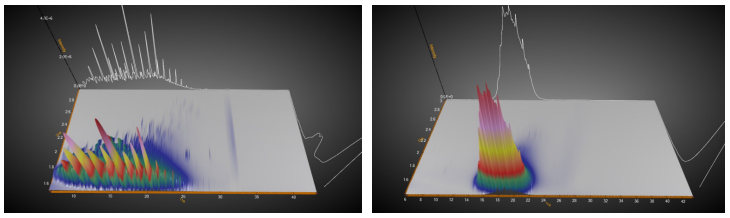
AGAT has instruments equipped with both flame ionization detectors as well as TOF-MS. The use of TOF-MS with the resolving ability of 2D-GC provides very powerful tools with applications for both qualitative and quantitative determination of a variety of sample types.



1D and 2D Chromatograms of the same sample. The 2D chromatogram is able to resolve many peaks that are overlapping and co-eluting. This results in improved quantitative data as well as improved chromatograms for fingerprint comparisons.



2D Chromatogram detailing the separation of various groups commonly present in hydrocarbon products. Note the ability to separate and quantify using a single gas chromatographic run



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