HYDROCARBON FORENSICS - OVERVIEW

TECHNICAL BULLETIN

To assist customers in the process of fuel spill delineation and the evaluation of multiple spill sources or potential weathering scenarios, Maxxam offers a wide range of Hydrocarbon Forensic analyses, depending on the type of sample, suspected contaminant and the level of qualitative and quantitative investigation required. Each analysis method is accompanied by validation and verification of the data by senior staff, followed by basic data reporting. Available as an extra to each analytical package are in-depth data analyses, reporting and specialized consulting services by senior scientists and chartered chemists. All analysis options are outlined below.

CCME Hydrocarbon Analysis (Btex and F1 to F4)

The F1 to F4 chromatograms provide quantitative information for compliance purposes, applicable in Ontario, Prairie provinces and Federal properties. Given the specificity of the FID detector towards hydrocarbon compounds, this method can also provide valuable qualitative information for product characterization by comparing chromatograms to a library of standard reference materials that Maxxam maintains. This analysis can be applied for both volatile and semi-volatile constituents in solid, water and product samples.

An outline of analysis benefits and prices is provided in the table below.

Test Name: PHC Quantitative Assessment		
Suspected Contaminant	**Matrix**	**Parameter**
General Hydrocarbons	Soils	BTEX and F1
	Water	
	Product	
	Soil	F2 to F4
	Water	
	Product	

Gasoline and Light Distillates

For samples impacted by gasoline or other light distillates, Maxxam provides forensic fingerprinting of volatile components. This analysis involves an open characterization for VOCs followed by a detailed evaluation of individual parameters that can be used to establish fingerprinting and diagnostic BTEX ratios, and the presence of gasoline additives

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such as MTBE and lead scavengers. Comparison of this data with other volatile hydrocarbon impacts can lead to establishing a source of contamination and assessing weathering. A standard Certificate of Analysis for the list of volatile parameters is provided. This data can be compared for similarities or differences between multiple samples to identify any patterns.

An outline of analysis benefits and prices is provided in the table below.

Test Name: Gasoline VOCs		
Suspected Contaminant	**Matrix**	**Parameter**
Volatile hydrocarbons (gasoline and other light distillates)	Soils, Water, Product	VOC Open Characterization

Further to the VOCs full scan Maxxam provides specific analysis for NAPL samples in the gasoline range (up to C_{14}) using a GC/MS analysis based on ASTM protocols. A characterization of non-additive components found in gasoline by classes, including paraffins, isoparaffins, aromatics, naphthenes and olefins, provides an efficient fingerprinting tool for establishing degree of weathering (e.g. biodegradation, solubilization and evaporation); providing an indication of octane rating or fuel grade; and potentially determining refining method and/or origin. This information is derived by assessing diagnostic ratios of a variety of parameters. The data is provided in a standard Certificate of Analysis for the list of parameters specified.

An outline of analysis benefits and prices is provided in the table below.

Test Name: Gasoline Components (PIANO)		
Suspected Contaminant	**Matrix**	**Parameter**
Gasoline components by classes (> C_{14})	Product	Paraffins, isoparaffins, aromatics, naphthalene and olefins (PIANO), as well as specific hydrocarbon compounds

Heating Oils and Heavy Distillates

The two most predominant hydrocarbon classes in fuel oil and diesel fuel are the straight-chain and branched alkanes (aliphatics), and the aromatic hydrocarbons. The ratios of certain straight-chain aliphatics ("normal" or *n*-alkanes) versus specific isoprenoid compounds (pristane and phytane) can be used as a numerical proxy for weathering, in particular to determine biodegradation. Under aerobic conditions, *n*-alkanes can be quite susceptible to biological alteration, whereas isoprenoids can be much more resistant. The ratios include: *n*-C_{17} (*n*-heptadecane) versus pristane (*n*-C_{17}/Pr) and *n*-C_{18} (*n*-octadecane) versus phytane (*n*-C_{18}/Ph). However, the *n*-C_{17}/Pr ratio is considered to be a better proxy for biological weathering than the *n*-C_{18}/Ph ratio. The magnitude of environmental weathering increases as both of these ratios decline. In addition to assessing biological weathering, Pr/Ph ratios are used to differentiate between crude sources.

For fuel oils and heavier distillates, Maxxam offers extended run GC/FID and extended run full scan GC/MS analyses of compounds present in the hydrocarbon material. The extended run GC/FID method provides information on specific compounds, including *n*-alkanes and isoprenoids. The data for specific diagnostic hydrocarbon compounds can be used to establish ratios that are used to evaluate degree of weathering and potentially estimate age.

Due to the lack of selectivity of the FID detector, certain hydrocarbon biomarkers such as steranes, hopanes, terpanes and adamantanes can be difficult to identify. Therefore, an extended full scan GC/MS analysis can be used to target specific aliphatic and aromatic hydrocarbon groups as well as characteristic biomarkers. This method provides qualitative information and greater detail into the composition of the hydrocarbon source by looking for patterns (or "signatures") of the specific compound groups mentioned. This data can be used to determine the source of contamination. For any particular biomarkers or set of biomarkers not offered in our routine packages we offer a Custom Biomarkers package.

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An outline of analysis benefits and prices is provided in the table below.

Suspected Contaminant	Analysis	Parameters	Matrix
Heating oils and heavier distillates	Test Name: Oils/Diesels Weathering Package		
	Extended GC/FID Analysis	Diagnostic Ratios (acyclic alkanes and isoprenoid biomarkers only)	BTE
	Test Name: Oils/Motor Oils Biomarkers Package		
	Full Scan GC/MS Qualitative Analysis	Patterns for Specific Compound Groups; basic reports will contain Extracted Ion Current Chromatograms for aliphatics (*n*-Alkanes,) bicyclic sesquiterpanes, hopanes and steranes.	Soils, Water and Product
	Test Name: Heavy Distillates Custom Biomarkers		
	GC/FID or GC/MS	Non-routine biomarkers	Soil, Water and Product

Crude oils contain primarily alkylated PAHs with relatively smaller concentrations of the unsubstituted parent compounds. Diesel and fuel oil products contain up to 40% aromatic components. The determination of both parent and alkylated PAH compounds provides an additional useful fingerprinting tool, particularly when the alkane pattern of the product has been extensively impacted by weathering processes.

Using a modified EPA analysis method (SW-846 Method 8270D) Maxxam can provide an analysis method that complements and enhances conventional fingerprinting capabilities.

An outline of analysis benefits and prices is provided in the table below.

Test Name: Alkylated-PAHs		
Suspected Contaminant	**Matrix**	**Parameter**
Heating Oils and Heavier Distillates	Product, Solids, Liquids	Parent and Alkylated PAHs

Specialized and Specific Forensics

Organolead compounds were used beginning in the 1920s as anti-knock additives in automotive gasoline until they were phased out in Canada beginning in 1973. Analysis of Tetramethyl Lead (TML) and Tetraethyl Lead (TEL) can help identify old gasoline releases and differentiate them from recent or current releases. Analysis is conducted by solvent extraction, GC/MS using a modified SW846 8270C method.

An outline of analysis benefits and prices is provided in the table below.

Test Name: Gasoline Leads		
Suspected Contaminant	**Matrix**	**Parameter**
Gasoline (lead components)	Product	Tetramethyl Lead (TML) and Tetraethyl Lead (TEL)

Over the last decade, developments in analytical techniques for the determination of stable isotopes have introduced stable carbon isotopes as a key forensic tool to differentiate gasoline sources and to evaluate biodegradation at contaminated sites. Maxxam currently subcontracts this analysis. We have invested in an Isotope Ratio Mass Spectrometer (IRMS) for the determination of $^{13}C/^{12}C$ ratios and we are in the process of validating this method.

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The ratio of ^{13}C to ^{12}C in the key gasoline components such as BTEX compounds can vary between gasoline based on factors such as the crude oil source or the degree of biodegradation. This ratio provides a "fingerprint" to help identify and differentiate petroleum products from a variety of sources.

An outline of analysis benefits and prices is provided in the table below.

Test Name: Carbon Isotopes		
Suspected Contaminant	**Matrix**	**Parameter**
Gasoline sources	Product	Carbon isotopes (^{12}C and ^{13}C)

Forensics Reporting and Consulting Services

Upon completion of the forensic analysis, the data can be analyzed and a determination made whether the results provide sufficient information for a definitive response to the issue or whether more detailed analyses and forensics evaluation is required. If more evaluation is required, Maxxam provides scientific and consulting services, including written summaries of preliminary findings and recommendations for forensic evaluation, such as hydrocarbon resemblance comments based on the review of the FID chromatograms by senior chemists. Analysis includes rationalization of follow-up analysis while determining methods for minimizing unnecessary costs.

Additionally, Maxxam can provide a letter report summarizing all testing associated with a particular hydrocarbon forensic evaluation and a thorough interpretation of the results to aid in decision making. All data provided is certified by a Chartered Chemist.

Consulting Services	
Scientist	Forensics Consultation
Manager	
Director	
Chartered Chemist	Detailed Analytical Report

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