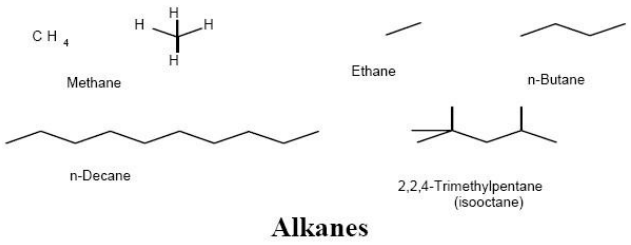
HYDROCARBON ANALYSIS FOR ENVIRONMENTAL SAMPLES

What is a hydrocarbon?

"Compound containing only hydrogen and carbon atoms"

Sources



Alkanes

Hydrocarbons in the environment may come from two main sources;

- **petroleum oil based hydrocarbons**, such as natural gas**,** LPG, petrol, kerosene, jet fuel,diesel, fuel oils, bunker oils, lubricating oil, transformer oil, greases, asphalt, and bitumen
- **natural living sources,** such as terpenes (eg rubber, pinene, limonene, camphor), phytane, pristane, squalane and squalene.

Uses

Hydrocarbons are used principally as either fuels (the petroleum based hydrocarbons) or industrial chemicals (both petroleum based and natural). Industrial chemicals may be used as solvents and degreasing agents (toluene, xylene, Stoddard's Solvent, petroleum spirits/ethers, mineral turpentine, limonene) or as precursors for the synthesis of a wide range of chemicals such as polymers (from styrene) and detergents (from alkyl benzenes).

Hydrocarbons in the environment

Hydrocarbons can enter the environment either naturally, from spills, by leakage from storage facilities or from deliberate application (oils spread on unsealed roads, diesel as a solvent for herbicide application).

Importance of hydrocarbons in the environment

Hydrocarbons can affect the environment in a number of ways:

1. They provide an energy source for microbiological activity and so can add to the oxygen demand loading ie. they contribute to CBOD.
2. They can add to an odour problem eg cyclopentadiene.
3. They are flammable (explosive in confined spaces) and so increase the risk of fires.
4. Some are toxic

   a) Neurotoxic eg hexane

   b) Carcinogenic eg benzene, benzo[a]pyrene
5. Most are insoluble in water and they are also less dense than water, so they float on water bodies and may coat earth, animals, birds and other surfaces.

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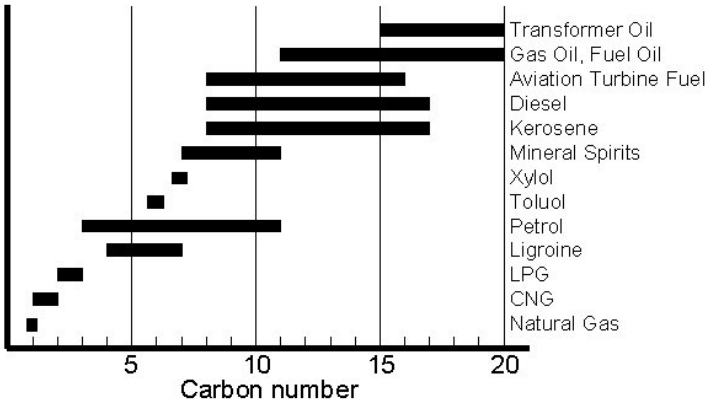
Chemical Classification

Hydrocarbons (HCs) are classified chemically as:

- saturated HCs (**alkanes**, only single bonds between carbon and/or hydrogen atoms)
- unsaturated HCs (alkenes or **olefins** - which contain at least one carbon-carbon double bond and alkynes, which have a carbon-carbon triple bond, acetylene is the only common alkyne)
- aromatic HCs (both **monoaromatic** such as benzene, toluene and xylenes, and **polycyclic aromatic**, the PAHs, such as naphthalene, benzo[a]pyrene and fluorene).



Because hydrocarbon properties depend on the size of th**e** molecules, it is often useful to refer to the number of carbon atoms contained in a hydrocarbon. Volatility (and flammability risk) decreases with increasing size eg C1-C4 are gases, C5-C16 are liquids and higher ones are solids.

Hydrocarbons have a low solubility in water, with solubility decreasing as size increases. A rough idea of relative solubility is given by:

monoaromatic (benzene>toluene>ethylbenzene,etc) > olefins > alkanes

Analytical Methods

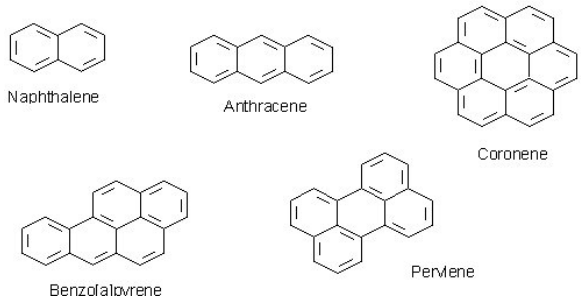
These fall into three groups; total, screening and specific.

1. **"Total":** (Not a true "Total" as the HCs determined are restricted by the method used. Similar to the "Oil & Grease" test)
   a) **Gravimetric**. US EPA Method 1664 "Silica Gel Treated n-Hexane Extractable Material". This measures HCs which extract into n-hexane. Volatile HCs (more volatile than toluene) and very heavy HCs which are not soluble in the solvent are not determined.
   b) Infrared. APHA 5520C & G. This involves Freon extraction, followed by infrared determination. As the Freon used is no longer obtainable, this test is not now available.
2. **Screening**
   a) **In field**. A number of methods are available for use in the field. These include vapour monitoring (PID), portable GC eg GC-PID, portable GC-MS and antibody techniques. Further discussion of these is outside the scope of this technical note.
   b) **In laboratory.** Samples collected from the field may be screened by the laboratory using either a gravimetric method (see Total above) or by gas chromatography using a flame ionisation detector (GC-FID). The latter technique will provide a report with the amount of HC in specific carbon ranges along with a chromatogram which can offer useful information about the source of the hydrocarbon [See example report].
3. **Specific tests:**

   Either after the results of screening tests are available, or for other reasons, it may be necessary to carry out more specific HC testing. The specific tests provide quantitative information, not available from the screening tests, which can be used for risk assessment calculations for example. The specific tests include;

   BTEX (benzene, toluene, ethylbenzene and xylenes). Used mainly for petrol contamination, but also where solvents such as toluene and the xylenes have been used. Usually carried out using a headspace technique with gas chromatography-mass spectrometry (GC-MS).

PAH (polycyclic aromatic hydrocarbons, also called polynuclear aromatics, PNA). These come principally from diesel, heavy petroleum fractions and from coal sources. The term "Total PAH", which is sometimes used, should be discouraged as there is no method which measures this. All methods separate out the individual PAHs and so any "Total" value reported will reflect however many individual compounds the method determines before they are added to give a "Total". Different methods will, therefore, give different "Totals". Analysis for PAH is done by gas chromatography-mass spectrometry (GC-MS).



Polycyclic Aromatic Hydrocarbons (PAH)

Suggested approach for hydrocarbon analysis in soils

A possible plan for investigating HC contamination in soils is shown in the table. To reduce the amount of field work involved, two samples can be collected from each sampling point. All samples should be collected with minimum headspace, cooled and transported cold to the laboratory as soon as possible.

Source	Petrol	Diesel – heavy fractions	Unknown
Determine area involved	BTEX	TPH-GC	TPH-GC (possibly VOC and/or SVOC
For risk analysis calculations	from above results	PAH, possibly BTEX	BTEX, PAH, possibly VOC and/or SVOC

The jam jar sample is then screened using the GC method with the results reported within a few days. The client then confirms immediately with the laboratory any samples to be analysed for BTEX so that the test can then be carried out using the second unopened jar.

Contact

For further information contact one of our Environmental Client Services Managers:

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Christchurch	03 377 7176

A typical hydrocarbon analysis laboratory report is shown on the next pages.

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ANALYSIS REPORT

Client:		**Lab No:**	885996 SPv2
Contact:		**Date Registered:**	07-Apr-2011
		Date Reported:	14-Apr-2011
		Quote No:	
		Order No:	25730
		Client Reference:	
		Submitted By:	

Sample Type: Aqueous

Sample Name:						
Lab Number:		885996.1	885996.2	885996.3	885996.4	
BTEX in Water by Headspace GC-MS						
Benzene	g/m³	0.0024	< 0.0010	< 0.0010	0.0032	-
Toluene	g/m³	0.043	0.32	< 0.0010	0.104	-
Ethylbenzene	g/m³	0.0064	0.042	< 0.0010	0.0165	-
m&p-Xylene	g/m³	0.042	0.38	< 0.002	0.129	-
o-Xylene	g/m³	0.029	0.28	< 0.0010	0.097	-
Total Petroleum Hydrocarbons in Water						
C7 - C9	g/m³	0.14	1.33	< 0.10	0.29	-
C10 - C14	g/m³	24	2.3	< 0.2	0.5	-
C15 - C36	g/m³	210	< 0.4	< 0.4	< 0.4	-
Total hydrocarbons (C7 - C36)	g/m³	240	3.6	< 0.7	0.8	-

Analyst's Comments

Appendix No.1 - Total Petroleum Hydrocarbon Chromatograms

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous

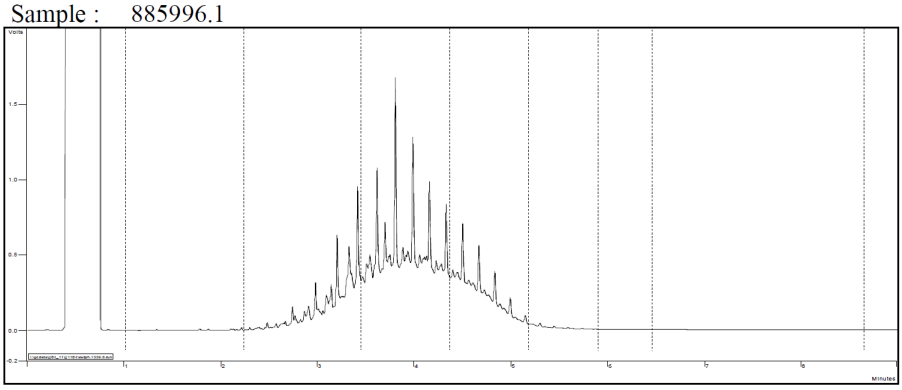
Test	Method Description	Default Detection Limit	Samples
BTEX in Water by Headspace GC-MS	Headspace GC-MS analysis, US EPA 8260B	-	1-4
Total Petroleum Hydrocarbons in Water	Hexane extraction, GC-FID analysis US EPA 8015B/MfE Petroleum Industry Guidelines	-	1-4

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

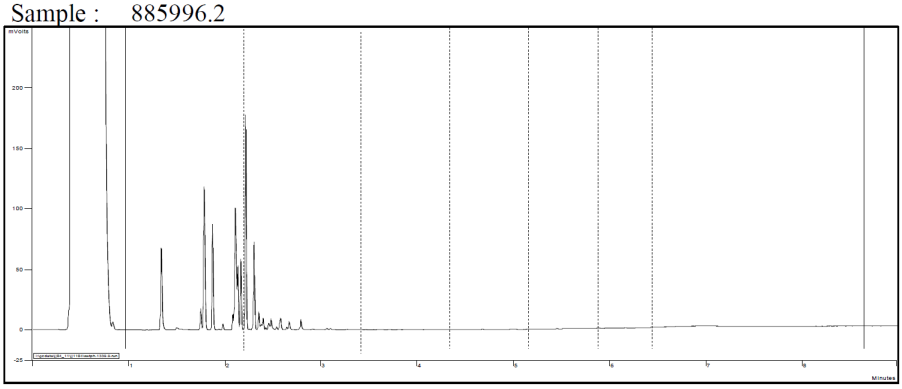
Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

Ara Heron BSc (Tech)
Client Services Manager - Environmental Division

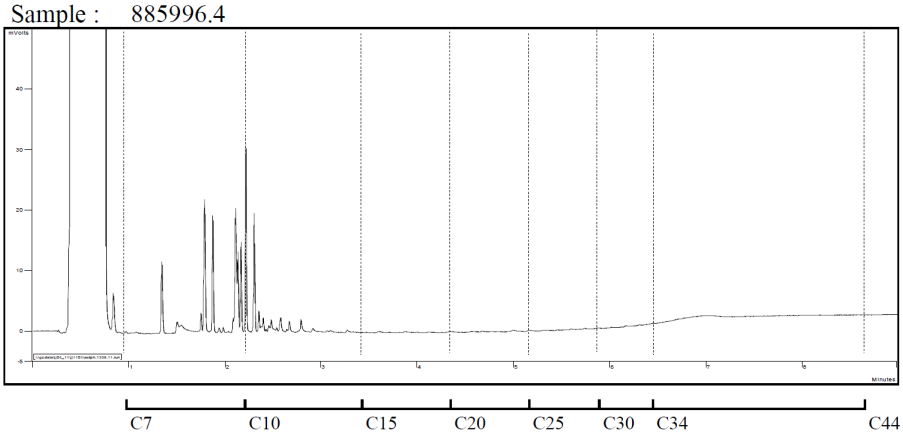
Sample : 885996.1



Sample : 885996.2



Sample : 885996.4



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