FINGERPRINTING PETROLEUM PRODUCT SPILLS

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Fingerprinting of petroleum products may be defined as finding those unique properties or compositions that positively identify the product or the oil. If the product is found in the environment it may be possible to identify, and estimate how long the product has been in the environment. Unfortunately the materials are modified by biodegradation, water solubility, and evaporation based upon the environment the spill is exposed to, and the length of time in that environment. This usually means that the composition and the properties are not the same at the time of sampling as they were at the time of the event.

It is therefore not unreasonable to ask, why even attempt to run fingerprint analysis? The answer seems rather obvious. Experience has shown that without some chemical analysis data, the analyst is forced to rely on verbal reports, incomplete records, geological data defining the nature of the soil and direction of the ground water plume. These are all important, but analysis of that data only suggests possible sources and does not identify the product.

This paper looks at spills from the view of the petroleum chemist and in general is limited to free product. With this limitation, the analyst will rely upon his knowledge of the composition and properties of petroleum and it's refined products to establish a regimen of tests for the sample. The test results will be vital to guiding the investigator to a final identification. The following table lists a number of tests that have been useful to this author.

USEFUL TESTS FOR FINGERPRINTING

CAPILLARY G C

- Piano Analysis
- Composition
- Component Ratios
- Property Calculations

METALS ANALYSIS

- Lead
- Manganese
- Barium
- Nickel
- Vanadium
- Others as needed (Lube Oil Metals)

HALOGENATED ORGANICS

Ethylene dichloride
Ethylene dibromide
Others as needed (dry cleaning fluids and industrial de-greaser)

OXYGENATES

Alcohols
Ethers

MISCELLANEOUS

Octane number
Sulphur content
Nitrogen content
Hydrocarbon type (FIA)
Simulated distillation or D-86
Infrared
MS/GC
Noise

It is probable that no particular sample will have all of the above tests run on it. This may be due to lack of sample or the expense of running all of the tests, or identity may be discovered early in the testing. The capillary GC is the key analysis. It may identify the product without any further testing. This is often the case with refined products that are recent spills and show no significant weathering. Further testing may allow the source to be identified by comparison testing. This technique is valuable on free product, it may have limited value when soil or water is extracted due to loss of key components during extraction, or natural organics being extracted and co-eluting on the GC.

Many spills (perhaps most) will be gasoline or diesel fuel from underground tanks or pipelines. These products will be considered first.

Gasoline is generally manufactured in an integrated refinery by blending components for economy and octane rating (R+M/2). All grades of gasoline from these refineries consists of varying amounts of the following components.

GASOLINE BLEND COMPONENTS

Straight run/Natural gasoline
Naphtha
Alkylate
Olefins
Aromatics
Reformate
Isomate
Oxygenates
Cat Gasoline (polymerized)

Proper blending of these components along with generally proprietary additives for oxidation stability, metal deactivation and inlet valve deposit prevention produces the regular (87 octane), premium (89 octane) and super (92-93 octane) gasolines. The octane ratings or octane index as they are sometimes called are the average of the Research and Motor octane ratings, or R+M/2. The detailed specifications for gasoline may be found in ASTM Designation D4814-93 and titled, Standard Specification for Automotive Spark-Ignition Engine Fuel. Unlike previous specifications this specification includes fuels with oxygenates such as alcohols and ethers.

In order to give the analyst some insight into the nature of gasoline and what key components it may contain a brief discussion of each of the primary blend stocks seems in order.

Straight-run/Natural gasoline is the low boiling material from the crude still consisting of hydrocarbons with carbon numbers from C4 through C7. If the material is condensed or extracted from natural gas the product is referred to as natural gasoline. The product is used to build vapor pressure (quick cold start) based upon the quantity of butane present. The iso-compounds are moderate to good octane builders, but the high normal hydrocarbon content does little for octane. It is equally obvious that limited pentane and lighter may be used in the blend because of EPA vapor pressure limitations.

OCTANE AND VAPOR PRESSURE OF SELECTED LIGHT HYDROCARBONS

HYDROCARBON	MOTOR OCTANE NUMBER	RVP
I-butane	97.6	72.5
N-butane	89.6	51.7
I-pentane	90.3	20.4
N-pentane	62.6	15.6
N-hexane	26	4.9
N-heptane	0	1.6

Naphtha is a generalized name for straight run petroleum cuts. Generally they range in boiling points from about 95 to 400 degrees F. for full range naphtha. They are low in olefin and aromatic content. The product is often cut into narrow boiling range materials (30 degrees) and used in specialty solvent applications. Low boiling naphtha boiling 90-190 degrees F. (Carbon number 5-7) have historically found application in motor gasoline as vapor pressure builder. This product is very similar to natural gasoline (NGL).

Alkylate is the name given to the material produced by the alkylation process. This process causes new molecules to be formed generally by the fusion of light olefins such as isobutylene with isobutane to form 2,2,4-trimethylpentane, a material that is not present in significant quantities in nature. Concentrated sulfuric acid or hydrofluoric acid is used as a catalyst in this reaction.

Because some quantities of propylene and pentenes are present in the olefin stream some C7 and C9 branched chain hydrocarbons are also formed. The 2,2,4-trimethylpentane has a motor octane number of 100 by definition. This compound is a key component used to identify gasoline in a spill.

Olefins as a class of hydrocarbons are not generally found in petroleum. They are often called unsaturates because they have a deficiency of hydrogen in the molecule. They are formed in the catalytic cracker and certain dehydration (reformer) reactions. Generally the C2 to C7 olefins are the dominant materials formed. The lighter olefins have fair octane ratings, and are used in most grades of gasoline.

MOTOR OCTANE RATINGS OF SELECTED OLEFINS

OLEFIN	MOTOR OCTANE
Propylene	84.9
i-butane	80.8
cis-2-butene	83.5
i-pentene	77.1
Isoprene (3-me-1,3- butadiene)*	81

* Note that isoprene is a diene and is not a desirable product in gasoline because of its ability to form gums. When two olefins react over a catalyst the product is often called cat-gasoline.

Aromatics are cyclic (ring) unsaturated compounds. They have the general formula CnHn. Benzene is the first of the series followed by toluene, ethylbenzene, xylenes and cumene etc. Aromatics are found in natural gas in low concentrations and in crude oil and condensates. Depending upon their concentrations they may be isolated from the lower boiling fractions of straight run distillate (90-400 degrees F.) by extraction with one of the ethylene glycols (Udex process). Aromatics are also produced by catalytic reforming (platforming, etc) which will be discussed below. Aromatics are the primary source of octane builders in gasoline.

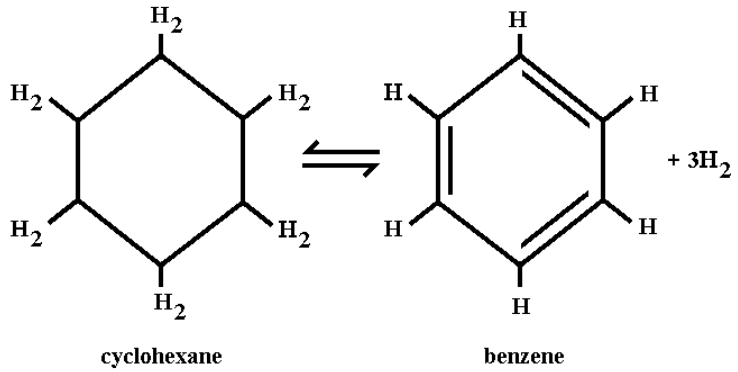
MOTOR OCTANE RATINGS OF AROMATICS

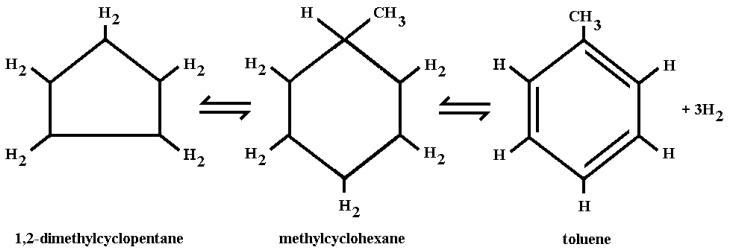
COMPOUND	MOTOR OCTANE
Benzene	+2.7
Toluene	+0.3
Ethylbenzene	97.9
m-Xylene	+2.8
p-Xylene	+1.2
o-Xylene	100.0
Isopropylbenzene	99.3

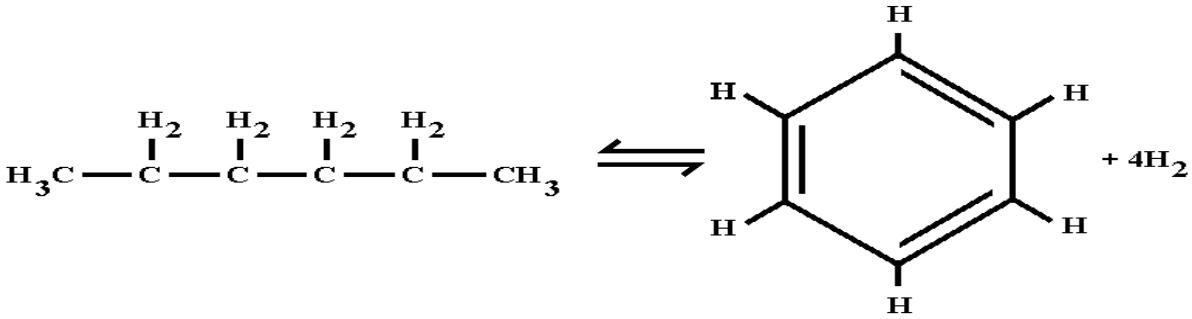
Other heavy C9-C10 aromatics are in the 90-97 octane range. Those components having octane ratings of for example +2.7 indicates that these components have octane ratings equal to 2,2,4-trimethylpentane to which 2.7 grams/gallon of tetraethyllead has been added.

Reformate (platformate, etc.) is the product from catalytic reforming. As the name suggests certain molecules are changed to other molecules in the reformer. This is usually over a platinum catalyst with hydrogen and a trace of an organic chloride to control activity. Molybdenum is also often used as a catalyst. The major reactions in the reformer are naphthene dehydrogenation, naphthene dehydroisomerization, paraffin dehydrocyclization, paraffin isomerization, paraffin hydrocracking, olefin hydrogenation and hydrodesulfurization. The aromatics formed are usually high in C8 and C9 aromatics and give muscle to gasoline. Other reactions may take place in the reformer to a lesser extent, but they are controlled by conditions. The graphics below show some typical reactions taking place in the reformer.

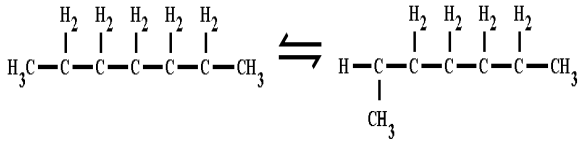
TYPICAL REFORMER REACTIONS



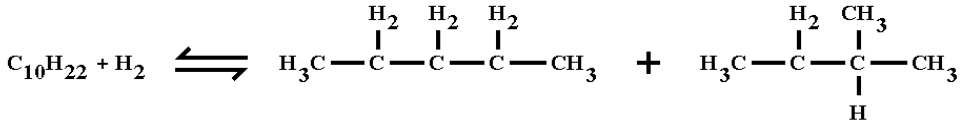




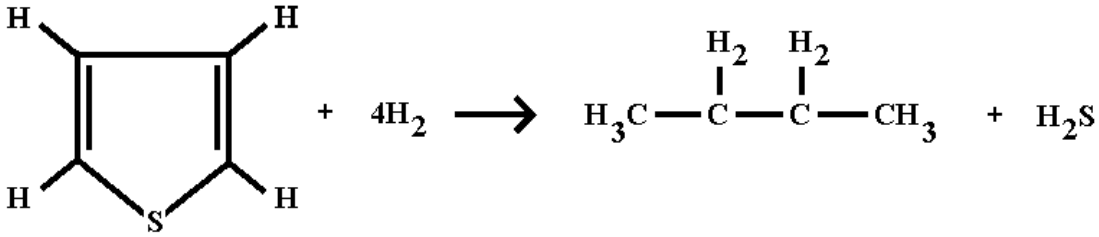
***n*-hexane** **benzene**



n-heptane 1-methylhexane, etc.



***n*-decane** ***n*-pentane** **isopentane**



thiophene **butane(s)**

Metals in gasoline are generally limited to lead or manganese. The source of lead is from tetraethyllead, tetramethyl lead or the equilibrium mix of these compounds. The source of manganese is Methylcyclopentadienyl manganesetricarbonyl (MMT) which for a short time was sold mixed with TEL. Neither of these are currently used in U.S. fuels except in some very limited situations such as farm vehicles in parts of the country, racing fuels and perhaps in some aviation gasoline. Canada does allow the use of MMT. The EPA phase-out of lead calendar may give the analyst a handle on the time of a spill based upon the lead content of the sample. Caution must be used when using this approach for early lead numbers were averages for the gasoline pool from a given refinery, and lead may go through reactions in the soil and water that may reduce it's concentration. Nevertheless the table below is given for information on the EPA phase out order for lead. (EPA LEAD FACTS)

LEAD PHASE OUT CHRONOLOGY **Regulatory Chronology**	
Date	**Key Event**
12/6/73	Five step “phasedown” regulation, final step equals 0.5 gram per total gallon.
3/19/76	D.C. Circuit Court of Appeals up holds regulation (Ethyl vs EPA).
9/28/76	EPA extends final compliance date for 0.5 gptg to 10/01/79.
8/7/79	EPA establishes “sliding scale” standard for small refineries effective until 10/01/82.
9/12/79	EPA extends compliance date for 0.5 gptg to 10/01/80 (provided unleaded production increased).
10/1/80	Effective date of 0.5 gptg for large refiners.
2/22/82	EPA publishes NPRM requesting comments on whether 0.5 gptg standard should be rescinded or relaxed; indefinite suspension of 10/01/82 effective date of 0.5 gptg std.for small refineries proposed.
4/15/82 to 4/16/82	81 witnesses testify at public hearing on 02/22/82 notice.
8/27/82	EPA publishes three *Federal Register* notices: (1) Withdrawal of 02/22/82 proposal. (2) Proposal of 1.10 gplg std.for large refineries and importers. 2.5 gplg for small refiners (interrefinery averaging also proposed).

LEAD PHASE OUT CHRONOLOGY Regulatory Chronology	
Date	**Key Event**
	(3) Small refinery compliance with 0.5 gptg suspended until 11/01/82.
9/7/82 to 9/8/82	Public hearing on 08/27/82 proposal.
10/29/82	EPA promulgates 1.10 gplg standard, effective 11/01/82 effective 11/01/82 for large refiners and importers, 07/01/83 for small refiners (1.90 gplg interim standard - 11/01/82 through 06/30/83); inter-refinery averaging allowed; calculation of compliance based upon leaded gallons produced vs total gallons produced.
11/1/82	Large refiners and importers subject to 1.10 gplg std.
1/26/83	D.C. Circuit Court of Appeals vacates 1.90 gplg small refiner interim standard, upholds other challenged portions of regulations.(SRTF vs EPA)
2/1/83	EPA Promulgates interim small refinery standards of 2.15 gptg and 2.65 gptg effective until 07/01/83.
7/1/83	All refiners and importers subject to 1.10 gplg std.
8/2/84	EPA publishes NPRM proposing a 0.10 gplg std. effective 01/01/86, also proposed two approaches to long term lead use (ban in mid 1990's and no regulatory action).
8/30/84 to 8/31/84	Public hearing on 08/02/84 proposal.
1/4/85	EPA publishes NPRM proposing the banking of lead rights to be effective on 01/01/85 if promulgated (for use through 12/31/87).
1/15/85	Public hearing on 01/04/85 proposal.
3/4/85	EPA announces final lead regulation with two standards: 1) 0.50 gplg effective 07/01/85 2) 0.10 gplg effective 01/01/86 EPA also issues supplemental NPRM soliciting comments on a soliciting comments on a total ban of lead as early as 1988.

Lead may be determined in gasoline by ASTM method D-3237.

Halogenated compounds may be found in gasolines that contain TEL or TML. Ethylene dibromide (EDB) and ethylene dichloride (EDC) are usually both present in quantities sufficient to convert all the lead to lead chloride or lead bromide. DuPont for example, added one theory of chloride and 0.5 equivalent of bromide. Their package for aviation fuel contained one equivalent of EDB. An antioxidant 2,6-ditertiarybutyl-4-methylphenol is added to prevent sludges from forming in storage. EDB and EDC may be determined by gas chromatography with an electron capture detector. The presence of both compounds may be an excellent indicator of leaded gasoline even if lead is not found. The data below from an unknown source gives data for water solubilities, and half-life in water.

SOLUBILITY AND HALF-LIFE OF EDB AND EDC IN WATER

COMPOUND	SOLUBILITY IN WATER	REMARKS
EDB	0.4 %/wt.	Half-life @ 7 pH and 20 deg. C. is 7-14 years. Ethylene is formed in soil.
EDC	0.83-0.87 %/wt.	Half-life @ 7 pH and 25 deg. C. is 50,000 years. It may form vinyl chloride with air and water.

Other halogenated materials found in gasoline should be investigated as impurities, biodegradation products or illegal dumps of degreasing solvents, or dry cleaning solvents.

Isomate is the product from an isomerization reactor when C4-C8 normal hydrocarbons are converted to iso-hydrocarbons. These materials have improved motor octane ratings over the normal hydrocarbons. Another process uses mol sieves to separate the isos from an iso/normal mix. The resulting isos are also called isomate.

Oxygenates in gasolines of the United States are a relatively new component, dating from the EPA lead phase-out originating in the 70's and finding wide use in the reformulated gasoline of mid 90's. One should not ignore the politics of the renewable fuel, ethanol as a major source of oxygenates (gasohol).

The major oxygenates expected to be found in reformulated gasoline are listed in the table below.

MAJOR OXYGENATES IN REFORMULATED GASOLINE

OXYGENATE	R+M/2	WEIGHT % OXYGEN
Methanol	116	49.9
Ethanol	113	34.7
Isopropanol	108.5	26.6
n-propanol	104	26.6
t-butanol	101	21.6
i-butanol		21.6
sec-butanol		21.6
n-butanol	87	21.6
diisopropylether	104.5	15.7
MTBE	109	18.2
ETBE	110	15.7
TAME	104.5	15.7

Regulations of the Clean Air Act of 1990 will demand 41 cities with carbon monoxide (CO) problems use oxygenated gasoline during the winter months starting 1992-93. In addition 9 cities with severe ozone must use reformulated gasoline by 1995. In addition 87 cities may opt into the reformulated gasoline program. The law requires that the high CO (41 cities) areas have 2.7% oxygen by weight (not oxygenates) during the winter months. Reformulated gasoline will contain an average oxygen content of 2.1% oxygen. The table below is likely going to be the specifications for reformulated gasoline.

Reformulated Gasoline	
Item	**Specification**
Benzene	1.3%/vol avg. gal
RVP	7.4 psia
Oxygen	2.1%/wt
Sulphur	40 ppm/wt
Olefins	6.0 vol%
Distillation	
T90 ? F	300
T50 ? F	210

It should be noted that oxygenates show substantial water solubility with a partition coefficient highly in favor of water solubility. This means that if oxygenates are found in free gasoline product the release is very likely quite recent. It is also quite useful to know that MTBE was not commercially available until 1979 when ARCO made it available. Since 1980, production has increased at a rate of 40% per year. MTBE is added at the point of gasoline manufacture. Methanol and ethanol are blended at the terminals and sometime in the retail tank.

Analysis for oxygenates may be performed by ASTM D4815, a GC method. This method may be used until 1997; at that time a method using the Oxygen Flame Ionization Detector (OFID) must be used. This detector consists of a catalytic reactor where the oxygenates are converted to carbon monoxide then to methane where they are detected by a flame detector.

Other tests often used to identify a product may require a large volume of sample. These same tests may not be of any help in aging the product. The listing below may not be complete, but it does list tests that may help to identify not only the product, but may aid in determining the source.

1. Infrared spectroscopy analysis requires only a few microliters of sample and will supply insight into the presence of oxygenates and perhaps other additives with key functional groups.

2. Simulated distillation may be substituted for D-86 or TBP distillation. A very small sample is required. ASTM D-3710 for gasoline or ASTM D-2887 for heavier petroleum products are the methods of choice.

3. Fluorescent Indicator Analysis (FIA) ASTM D-1319 requires about 1 cc of sample. This test groups saturates, olefins and aromatics. When diesel fuel is expected it may be necessary to change the eluting alcohol from isopropyl to isoamyl alcohol. Oxygenates in samples submitted to FIA will cause erroneous results that must be adjusted by correction numbers. See the latest D-1319 for those numbers and how to use them.

4. Nitrogen containing compounds such as polyalkyl amines, polyether amines, poly-alkylsuccinimides and polyalkylaminophenols are now or must be added latter (1995). These materials function as intake valve deposit inhibitors. They must have a molecular weight of at least 900.(CAA 211 (1)) Nitrogen may be determined at low PPM levels using chemiluminescence (ASTM D4629). A few microliters of sample are required. Higher nitrogen levels may be done by instrumental C,H,N analysis or Kjeldahl analysis.

5. Sulphur analysis may be useful, and may be determined by a number of methods. ASTM D-3120 (Oxidative Microcoulometry) has been very popular for the determination of total sulphur at low PPM levels. Specific sulphur groups may be determined by flame photometric detector (FPD)/GC. Remember that H2S may be formed by sulfate reducing bacteria and may not have originally have been in the sample.

6. Octane rating is very useful if gasoline is expected. A large volume is required if octane is to be determined directly on knock engines. Octane may be estimated by FT-IR in the near IR region, and by GC. A recent article in TODAYS CHEMIST AT WORK, May/June 1993, Julian Feldman, and Milton Orchin, Univ. of Cincinnati suggests plotting the sum of 2,2,4-trimethylpentane, toluene, ethylbenzene, and the three xylene isomers against posted R+M/2 to yield a straight line. I have found this useful, but not true with all gasolines in our area. I suspect that it is geography dependant

One who practices the art of fingerprinting must be fully aware of the similarity of petroleum products, and that the products shipped in our national pipeline systems are fungible. This means that even branded stations may very well be selling fuels refined and blended by a different company.

Diesel fuel is perhaps the second most common fuel that may be found in spills. Diesel may be produced in several grades, but the most common is number 2 diesel fuel. Diesel fuel is highly aliphatic with the normal isomers being predominant. Carbon numbers range from trace

C7 to a maximum concentration at C12 to C13 and with a near gausian distribution of carbon numbers to C19 and a tailing of carbon numbers to C23-25. All diesel fuels contain pristane and phytane; they are easily spotted on a cap GC run as the two predominant peaks after n-C17 and n-C18. The ratio of pristane to phytane may be a significant marker for diesel fuel.

The new formulated diesel fuel must contain no more than 500 PPM (wt) of total sulphur and lower aromatic content (< 20% by vol.).

Since diesel is so predominately aliphatic biodegradation may be severe. Bacteria show a preference for the n-hydrocarbons and sometimes show even a stranger preference for odd or even numbered chains. Several tests should be performed in order to identify diesel fuel. Cap GC may be the most informative for a small volume of sample followed by FIA, simulated distillation, total sulphur, total nitrogen and perhaps other specification properties such as cloud point, cetane number or index and flash point.

The following table lists the ASTM D975 specifications for diesel fuels.

ASTM D975 Diesel Fuel Specifications

Property	ASTM Test Method[a]	Grade Low Sulfur No. 1-D	Grade Low Sulfur No. 2-D	Grade No. 1-D[c]	Grade No. 2-D[c]	Grade No. 4-D? [C]
Flash Point, ?C, min.	D 93	38	52	38	52	55
Water and Sediment, %vol, max	D 1796	0.05				
Distillation and Temperature, ?C90 % %vol, Recovered min max	D 86	 ... 288	 282[D] 338	 ... 288	 282[D] 338	 ... ...
Kinematic Viscosity, mm^2/S at 40? C min max	D 445 ...	 1.3 2.4	 1.9 4.1	 1.3 2.4	 1.9 4.1	 5.5 24.0
Ash% mass, max	D 482	0.01	0.01	0.01	0.01	0.10
Sulfur, % mass, Max[E]	D 2622[F] D 129	0.05 ...	0.05 ...	... 0.50	... 0.50	... 2.00
Copper strip corrosion rating max 3 h at 50? C	D 130	No. 3	No. 3	No. 3	No. 3	...
Cetane number, min[G] One of the following properties must be met: (1) Cetane index, min (2) Aromaticity, %vol, max	D 613 D 976[F] * D 1319[F]	40[H] 40	40[H] 40	40[H] ...	40[H] ...	30[H] ...
Cloud point, ?C, max	D 2500	'	'	'	'	...
Ramsbottom carbon residue on 10% distillation residue, % mass, max	D 524	0.15	0.35	0.15	0.35	...

[A] To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller and manufacturer.
[B] The test methods indicated are the approved referee methods. Other acceptable methods are indicated in 4.1.
[C] Grades No. 1-D, No. 2-D and No. 4-D are required to contain a sufficient amount of 1,4-dialkyl amino anthraquinone (blue dye) so its presence is visually apparent.
[D] When a cloud point less than -12?C is specified, the minimum flash point shall be 38?C, the minimum viscosity at 40?C shall be 1.7 mm^2/s and the minimum 90% recovered temperature shall be waived.
[E] Other sulfur limits can apply in selected areas in the United States and in other countries.
[F] These test methods are specified in CFR 40 Part 80
[G] Where cetane number by Test Method D613 is not available, Test Method D 4737 can be used as an approximation.
[H] Low ambient temperatures as well as engine operation at high altitudes may require the used of fuels with higher cetane ratings.
[I] It is unrealistic to specify low temperature properties that will ensure satisfactory operation at all ambient conditions. However, satisfactory operation should be achieved in most cases if the cloud point (or wax appearance point) is specified at 6?C above the tenth percentile minimum ambient temperature for the area in which ambient temperatures for U.S. locations are shown in Appendix X2. This guidance is general. Some equipment designs or operation may allow higher or require lower cloud point fuels. Appropriate low temperature operability properties should be agreed upon between the fuel supplier and purchaser for the intended use and expected ambient temperatures.
* Editorially corrected.

Biodegraded samples often show a sawtooth pattern in the n-alkanes. This is due to a selectivity of the even numbered alkanes over the odd numbered ones as food for the microorganisms. A characteristic of high sulphur diesel (>500 PPM) may be a blue color. The new clean air act rule requires that sufficient 1,4-dialkyl aminoanthraquinone be added to give a perceptible blue color to the fuel. Fuels spilled into the environment may have the color removed by absorption in soil. Other additives may be added to diesel at the terminal, but they are not generally added if transported by pipeline.

DIESEL ADDITIVES

Additive	**Purpose**
Amyl Nitrate (0.1-0.5%/vol)	Cetane Improver
Micro crystaline wax	A Pour point depressant
Barium	Smoke reduction

There are a host of other refined petroleum products transported by the petroleum industry in various modes and therefore subject to spills into the environment. Fuels such as;

- Jet fuels
  - Jet A
  - JP 4
  - Kerosine
  - others
- Burner fuels
  - 4, 5, and 6 oils
- Lubricating oils
- Crude oils
- Refined solvents such as
  - Petroleum ether
  - Mineral spirits
  - Stoddard solvent
  - Naphthas
- Aliphatic solvents
  - from hydrotreating
  - mol sieve units

In general a battery of physical tests may be used to characterize the products. Cap G. C. is likely the best tool followed by simulated distillation. A list of product specifications and GC. analysis were placed in the appendix for the users information and are intended to instruct the analyst concerning the complexity of petroleum products that may be found in the environment, and to aid in selecting tests for their identification.

TRICKS OF THE TRADE

This section of this paper has been purposely separated from the portion above. The first section has dealt with identifying the spill with little regard for suggesting the age of the spill. This section will deal with some techniques that this author uses to attempt to date and identify the source of the spill. Since gasoline and diesel represent the greatest percentage of all hydrocarbon spills, I will limit most of this discussion to them.

The analyst should remember that we are involved in an exercise that is not as exact as we would like. This may be due to changes in the sample composition due to water solubility of some of the products, changes in environmental factors (temperature, soils, etc.) and if time is significant, the actual change in manufacturing of the product and finally regulations that may have changed the use of certain additives (lead). It is obvious that regulatory change will be significant and one must be able to date and document such changes.

Lets assume that a certain spill has resulted in several feet of free product sitting on ground water in a monitor well. Presently, there is no information as to what the product may be. A rapid food place is built on the property, and they do not know what may have been there before. A garage and several gasoline stations are one or two blocks away. An environmental clean up firm has collected samples of the free product and of the water and sent them to you to determine what the product is, and how old do you estimate it to be? You have received the samples and the chain of custody and the samples themselves seem to be in order. What tests do you run and in what order to glean maximum information at minimum expense to the client?

Lets do the water first. Lets analyze for MTBE. We would send this sample to our environmental lab for them to work their magic. The returned results indicated MTBE to be below detection limits.

While the water was being analyzed, a capillary GC analysis was started, and early in the run it became obvious that the material was gasoline. This was indicated by C4 and C5 olefins, 2,2,4-trimethylpentane, benzene, toluene, ethylbenzene and xylenes, an abundance of heavy C9 and C10 aromatics also were present with no carbon numbers heavier than C14. Eureka! Its gasoline. How long has it been in the environment. Total lead was run on the free product and we found O.8 g/gal. We also ran an electron capture GC to check for EDC and EDB. They were positive and we are now sure we are looking at leaded gasoline. A study of the EPA lead phase-out regulations inform us that the nearest date/concentration marker is 07/01/83 when all refiners must have no more than 1.1 g/gal lead in their gasoline. We found 0.8 g/gal and we have already suggested that all lead in gasoline in the environment is likely understated, so the latest probable date for the spill is in mid July of 1983.

Suppose the cap GC did not show the free product to be gasoline. The characteristics of the chromatogram were, trace C7 and C8, some toluene, ethylbenzene, and xylenes. About C9 the normal hydrocarbons began to increase with maximum concentration coming at C11, C12, C13 and then tailing off to a maximum of about C20. Following C17 a significant peak of pristane is present and after C18 a significant phytane peak exists. Bet the farm that you are looking at diesel fuel. Unfortunately I do not have a good way to date a spill of diesel fuel.

The appendix in the back of this paper will help you to identify turbine fuels (JET FUELS), lube oils and of course crude oil/condensates may be identified easily if they are lightly weathered, by the full range of carbon numbers present. I am on the trail of a method that will allow dating of non gasoline spills. When and if I find it I will up-date this paper.

Other facts that may prove useful are:

1. MTBE in water if a recent spill, will be highest at points nearest the source.

2. MTBE is an order of magnitude more soluble in water than any gasoline component. (4.3% vol.)

3. Total BETX/Bz. ratios in water are smaller with time due to greater benzene solubility in water.

4. Most weathering of gasoline is due to volatilization, but the nature of the soil and the ground water flow can effect this.

5. Soil type is important since absorption may play significant role. Components are absorbed inversely proportional to their solubility.

It seems quite obvious that fingerprinting and ageing hydrocarbon spills are a multidisciplined effort between the analytical chemist and the hydrologist/geologist.