Chapter 10
Forensic Characterization of Gasoline Releases Impacting the Environment

Gil Oudijk

Abstract Many different environmental-forensic techniques are needed when investigating the spillage of gasoline to soil or groundwater. An important laboratory analytical technique is known as a PIANO analysis, which can identify hundreds of different hydrocarbons in gasoline. Through interpretation of these results, the origin and age of the gasoline can often be determined and, hence, responsibility for the release can may be identified.

What is environmental forensics? One definition is that it is the use of environmental expertise to resolve disputes, whether or not those disputes might be environmental in nature. But why is this field important in the United States or in any other industrialized country? The United States manufactures about 300,000,000 gallons (about 1,200,000,000 L) of gasoline per day (Dickson et al. 1987), whereas Canada, Europe and Japan are not far behind on a per capita basis. Even if the spillage rate is only 0.01 % of the quantity manufactured, the amount of gasoline released to the environment would still be more than 30,000 gallons (>100,000 L) per day, just for the United States and no one wants to pay for those cleanups. The problem in modern society is that environmental cleanups are quite expensive and no one will pay for them unless they are forced to. It is from this problem that forensic scientists earn their living. Might there be other responsible parties to help pay for these cleanups? Regulatory agencies, who are often left holding the bill for these cleanups, often employ these techniques to help find additional contributors. The forensic techniques described herein can be helpful if other responsible parties do exist.

In general, there are two important types of forensic studies being performed nowadays on environmental cases, especially the ones involving the spillage of gasoline (Oudijk 2005):

- *Fingerprinting*: What type of gasoline was released? Regular? Premium? How was it manufactured? Who manufactured the gasoline? (This question is often very difficult to answer because gasoline is a fungible commodity, meaning that it can be bought, sold and traded between the refining companies) (Oudijk 2007).

G. Oudijk (✉)
Triassic Technology, Inc., 57 Hamilton Avenue, Hopewell, NJ 08525, USA
e-mail: goudijk@triassictechnology.com

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H. Kars, L. van den Eijkel (eds.), *Soil in Criminal and Environmental Forensics*,
Soil Forensics, DOI 10.1007/978-3-319-33115-7_10

For example, the gasoline found in an underground tank owned by Chevron was not necessarily produced by Chevron, and

- *Age dating*: When was the gasoline manufactured and, hence, how old is the release? One should keep in mind that the "shelf life" of gasoline (or how long it might be stored) is commonly less than 2 weeks and the date of manufacture for a gasoline is commonly fairly close to when it was released.

This above information often allows us to determine who was responsible for gasoline releases.

In the United States, the majority of the environmental cases that end up in litigation are civil cases and not criminal cases. In my experience, the majority of the criminal cases are resolved before they ever reach a courtroom. However, the methods explained in this paper should be applicable whether the case is civil or criminal.

10.1 The PIANO Analysis

A PIANO analysis is a laboratory procedure through gas chromatography coupled with mass spectroscopy. PIANO is an acronym for *n*-paraffins (P), *iso*-paraffins (I), aromatics (A), naphthenes (N) and olefins (O), what this analysis can detect (Peters and others 2005). Oxygenates can also be identified through this analysis.

Many or most of our fingerprinting and age-dating questions can be answered through an interpretation of a PIANO analysis. This procedure allows us to identify and quantify 500–1000 different hydrocarbons in gasoline and they are presented in either weight%, volume% or molar concentration. Many of these hydrocarbons would not be identified on the normal scans used for regulatory compliance.

The five hydrocarbon classes in the PIANO analysis are (Kaplan and others 1997; Kaplan 2003):

- paraffins (P) or "normal alkanes": straight-chain saturated ("aliphatic") hydrocarbons (C_nH_{2n+2});
- *iso*-paraffins (I) or "i*so*-alkanes": branched-chain saturated hydrocarbons (C_nH_{2n+2});
- aromatics (A): carbon chains with a double bound after every second carbon (C_nH_{2n-6});
- naphthenes (N) or "*cyclo*-alkanes": saturated carbon chains (C_nH_{2n+2});
- olefins (O) or "alkenes": unsaturated hydrocarbons with double bounds (C_nH_{2n}).

These are the predominant hydrocarbons in gasoline (plus the oxygenates). What does the laboratory need to perform this analysis? Separate-phase gasoline, but more than a sheen and at least a film of gasoline, preferably a layer. Can the analysis be performed on soil samples? Yes, the analysis can be performed, but because of hydrocarbon adsorption, it will probably adversely impact the subsequent interpretation of the results.

The laboratory methods used with a PIANO analysis are similar to those used for volatile and semi-volatile analyses that are often required by regulatory agencies. With both, a gas chromatograph is employed equipped with a mass spectrometric detector (GC/MS).

10.2 Data Interpretation

Through the PIANO data, we normally look at three factors impacting the chemical composition of the gasoline:

- the magnitude of environmental weathering;
- refining characteristics: the types of methods used, the grade of gasoline, etc., and
- compliance with regulatory requirements (in the United States: now known as reformulated gasoline or "RFG").

All of this information very often will help us to characterize the gasoline and, hopefully, identify its origin.

Normally, we look at several ratios of hydrocarbons obtained from the PIANO scan. Commonly, they are hydrocarbons of the same molecular weight, but with different environmental characteristics, such as volatility, solubility or biodegradability (Kaplan et al. 1997; Peters et al. 2005). It is commonly helpful to perform the PIANO analysis on known gasoline samples for comparison purposes. For example, samples of premium- and regular-grades of gasoline obtained from a nearby service station.

Provided in the paragraphs below are some of the important ratios of hydrocarbons obtainable from a typical PIANO analysis. These ratios were prepared for gasoline manufactured in the United States, but these principles should be fairly close for other countries where modern refining techniques are implemented and similar environmental regulations are in place.

10.3 Biodegradation Ratios

- *(iso-paraffins + naphthenes)/n-paraffins*: Gives us an approximation of the magnitude of biological alteration ("biodegradation"). The ratio normally ranges from about 2 to 10 in fresh gasoline, but it increases as biodegradation proceeds because the *iso*-paraffins and naphthenes (*cyclo*-alkanes) are more resistant to biological alteration compared to the *n*-paraffins, and
- *methyl-cyclo-hexane/n-*C_7 *(n-heptane):* Normally, this ratio is around 0.5–2.0 in fresh gasoline, but it can vary. The ratio increases as biodegradation proceeds because methyl-c*yclo*-hexane is more resistant to biological alteration compared to *n*-heptane.

10.4 Dissolution Ratios

- *[Benzene + Toluene]/[Ethylbenzene + o,m,p-xylenes]:* In fresh gasoline, this ratio normally ranges from about 0.8 to 1.1 (Kaplan et al. 1997). The ratio then declines as dissolution of the aromatics proceeds because benzene and toluene are more water soluble compared to ethylbenzene and the *o,m,p*-xylenes. However, this ratio is highly dependent on the geochemical conditions or the type of microbes present (Alvarez et al. 1998). Under anaerobic conditions, the ratio could reverse;
- *Benzene/cyclo-hexane:* This ratio provides an approximation of the magnitude of dissolution or "water washing". The ratio is normally, between 0.5 and 2.0 in fresh gasoline and it declines as dissolution proceeds because benzene is more water soluble compared to *cyclo*-hexane, and
- *Toluene/methyl-cyclo-hexane:* Normally, the ratio ranges from about 2 to 10 in fresh gasoline. The ratio declines as dissolution proceeds because toluene is more water soluble compared to methyl-*cyclo*-hexane.

10.5 Evaporation Ratios

- *n-pentane (n-C_5)/n-heptane (n-C_7):* This ratio provides an approximation of the magnitude of evaporation of the gasoline. Normally, the ratio is around 0.5–2 in fresh gasoline and it declines as evaporation proceeds because *n*-pentane is more volatile compared to *n*-heptane, and
- *2-methylpentane/2-methylheptane:* Normally, the ratio is between about 3 and 8 in fresh gasoline. The ratio declines as evaporation proceeds because 2-methylpentane is more volatile compared to 2-methylheptane.

With the evaporation ratios, we can often assess whether the gasoline release was aboveground or underground; for example, from (1) an underground tank or subsurface pipeline or (2) an aboveground tank. Gasoline from releases that had any residence time in contact with the atmosphere will normally be more evaporated, especially near sea level where the atmospheric pressure could be much higher. Based on this knowledge, better insight into who may be responsible for a particular spill event may be more easily achieved.

One should compare the results to a PIANO analysis of a local and recent gasoline for that particular area (keep in mind that the octane rating of gasoline and, hence, the chemical composition will be dependent on elevation). For example, do not compare the recent results from a sea-level site to 1980 gasoline from Switzerland (in the mountains) (Table 10.1). The original chemical compositions of these gasolines could be radically different and this type of comparison would not tell us much.

Table 10.1 Example of a comparison of PIANO analyses of gasoline separate-phase samples from two gasoline service station sites in 2008 to a sample collected from a spill site in New Jersey

Method	Formula	NAPL sample MW - 8	*Compariso:* 2008 Exxon regular unleaded gasoline[1]	2008 Gulf regular unleaded gasoline[2]	Significance	Explanation
Environmental:						
Biodeg	$\left(iso\ \ \text{paraffins}+\text{naphthenes}\right)/\ n\ \ \text{paraffins}$	4.61	2.29	8.54	Biodegradation minimal	Ratio increases s biodegradation proceeds because the *iso*-paraffins and naphthenes are more resistant to biological alteration compared to the *n*-paraffins.
Biodeg	$\text{MCH}/n-\text{C}_7$	0.70	0.57	0.84	Biodegradation minimal	Ratio increases as biodegradation proceeds because methyl-*cyclo*-hexane is more resistant to biological alteration compared to *n*-heptane.
R_b	$\left(\text{B}+\text{T}\right)/\left(\text{E}+\text{X}\right)$	0.04	1.12	1.07	Dissolution significant	The ratio declines as dissolution of the aromatics proceeds because benzene and toluene are more water soluble compared to ethylbenzene and the *o*, m, p-xylenes.

(continued)

Table 10.1 (continued)

Method	Formula	NAPL sample MW - 8	*Compariso:* 2008 Exxon regular unleaded gasoline[1]	2008 Gulf regular unleaded gasoline[2]	Significance	Explanation
Water wash	$B\,/\,cyclo - \text{hexane}$	0.00	0.45	1.41	Dissolution significant	The ratio declines as dissolution proceeds because benzene is more water soluble compared to *cyclo*-hexane.
Water wash	toluene/MCH	0.22	9.25	5.6	Dissolution significant	The ratio declines as dissolution proceeds because toluene is more water soluble compared to methyl*cyclo*- hexane.
Evap	$n - \text{pentance}\,/\,\text{n}\quad\text{heptane}$	0.00	0.13	0.23	Evaporation significant	The ratio declines as evaporation proceeds because *n*-pentane is more volatile compared to *n*-heptane.
Evap	$2 - \text{methylpentane}/2 - \text{methylheptane}$	0.62	7.49	4.83	Evaporation significant	The ratio declines as evaporation proceeds because 2-methylpentane is more volatile compared to 2-methylheptane.

Table 10.2 Conventional versus reformulated parameters in the United States and Canada

	Limit	US	Canada
Benzene	<1 %	1995	1998
Oxygenates	>2 %	1995	1998
Total aromatics	<35 %*	1995	1998

These parameters are for North America only. There are similar regulations in Europe.
* Not a regulation, but vapor-pressure limit normally cannot be met with total aromatics at >35 %.

- *2,2,4-tmp/(2,2,4-tmp + 2,2,3-tmp + 2,3,4-tmp + 2,3,3-tmp):* Alkylation is the transfer of an alkyl group from one molecule to another. The most important alkylation process is the reaction with a catalyst (normally sulfuric or hydrofluoric acid) of *iso*-butane with olefins to produce *iso*-octane (Beall et al. 2002). Values for this ratio of between 0.54 and 0.73 represent hydrofluoric acid (HF) alkylation, whereas values between 0.39 and 0.45 represent sulfuric acid (H_2SO_4) alkylation. Alkylation is a refining technique used to produce high-octane *iso*-alkanes, like *i*-C_8 and has been used in refining for several decades, and

10.6 A Comparison to Reformulated Gasoline

In the United States, the chemical composition of gasoline was altered in 1995 to lessen air pollution. This gasoline is known as reformulated or "RFG" in the United States. Similar regulations were enacted in Europe and Canada at around the same time (Table 10.2). For the most part, these regulations lowered the vapour pressure of the gasoline, to lessen volatilization to the atmosphere. Furthermore, concentrations of aromatics (in particular, benzene) and olefins were decreased and the concentrations of oxygenates were increased, although there were numerous particular changes.

10.7 Refining Ratios

By identifying several ratios, the types of refining techniques employed to produce the gasoline may be assessed (Gary and Handwerk 1984):

- *2,2,4-trimethylpentane (iso-octane)/methyl-cyclo-hexane:* Values greater than 5 normally represent a premium grade of gasoline (such as 92 octane), whereas values less than 5 normally represent a regular grade. The *iso*-alkane, 2,2,4-trimethylpentane, which is the same as *iso*-octane (*i*-C_8), is the basis for the octane rating index; gasoline with 100 % *i*-C_8 would exhibit an octane rating of 100, whereas gasoline with 100 % *n*-C_7 (*n*-heptane) would have an octane rating of 0;

- *Octane index (OI) = (2,2,4-trimethylpentane + toluene)/(n-C_7 + n-C_8):* The OI value increases with octane rating; however, toluene, n-C_7 and n-C_8 are susceptible to environmental weathering (Schmidt et al. 2002, 2003). As the gasoline becomes more evaporated, it becomes more difficult to identify the octane rating, which is accomplished through a graph given in the Schmidt et al. (2003) article;
- *n-C_4/(n-C_4 + iso-C_4): Iso*-butane is often removed in modern gasolines to be used as a feedstock in chemical manufacturing; however, both butanes are susceptible to volatilization in the subsurface;
- *iso-C_5/(iso-C_5 + n-C_5):* Isomerization is the conversion of straight-chain molecules to higher-octane branched molecules for blending into gasoline or as a feed into alkylation units. It normally imparts on the gasoline a pentane ratio of >0.70;
- *naphthalene/nC_{12}:* This ratio is normally between 1 and 3 in fresh gasoline. Reforming is a refining process used to produce aromatics. Higher values indicate that high concentrations of aromatics are or were in the gasoline.

10.8 Organo-Metallic Compounds

Organo-metallic compounds are not normally identified with a PIANO analysis, but if there is a chance that the gasoline could be older than around 2000, these compounds should also be searched for. Organic lead was banned in automotive gasoline in the United States in 1996, in 1990 in Canada and generally before 2000 in Europe (Oudijk 2010, 2012); however, organic lead is still permitted in aviation gas, racing gas and many off-road fuels. Therefore, the presence of these compounds can be quite helpful in estimating when the gasoline was manufactured.

The organo-metallic compounds commonly detected in gasoline include the organo-leads (tetraethyl lead, tetramethyl lead and several physical and reaction mixes) plus methyl-cyclo-pentadienyl manganese tricarbonyl (MMT).

10.9 Conclusions

The composition of automotive gasoline has changed over the years, but these changes have been known and documented. By identifying the chemical composition of gasoline spilled into the environment, we can often estimate when a particular gasoline was manufactured, which usually helps in identifying responsible parties. In addition to changes brought by the modernization of refining techniques, the composition of gasoline changed because of regulations. The purpose of the regulations was normally to reduce air pollution. By comparing the chemical composition of spilled gasoline to these known changes in regulation, we can further estimate the time frame of when a gasoline was manufactured. To properly identify the chemical composition of spilled gasoline, a PIANO analysis is often quite helpful. This analysis often identifies hydrocarbons that would not be found with the scans normally required by the regulatory agencies.

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