

# Applications of Forensic Chemistry to Environmental Work

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## Abstract

Recent trends in environmental remediation have increasingly employed the use of environmental chemistry techniques to decipher the source(s) and fate of the contaminants and, in some cases, to determine their age or apportion them to sources. An extensive database of pyrogenic and petrogenic “chemical fingerprints” has been constructed by the Gas Technology Institute (GTI) and META Environmental, Inc. using gas chromatography/flame ionization detector (GC/FID) or with a mass spectrometer (GC/MS). The use of these chemical fingerprinting techniques have been highly successful in discerning wastes from wholly different sources as well as among Manufactured Gas Plant (MGP)-type wastes from different plant operations. However, these techniques have been limited when low-level polycyclic aromatic hydrocarbon (PAH) discernment is required. Specifically, these techniques often do not provide data with sufficient conclusive discriminating power between the “urban background” PAH sources and those from MGP-operations, which is pertinent for meeting low-level, stringent site-cleanup standards. GTI has been developing a new analytical method for the measurement of “urban background” PAH contamination. This method measures the compound-specific carbon isotope ratio (CSIR) with a GC/IRMS (isotope ratio mass spectrometer). The GC/IRMS technique is a relatively new analytical tool that has great potential as an environmental forensic method at former MGP sites. This paper focuses on the applications of both chemical and isotopic analysis of samples to discern PAH contamination in the environment.

## Introduction

Recent trends in environmental remediation have increasingly employed the use of environmental forensic techniques to decipher the source(s) and fate of the constituent chemicals and, in some cases, to determine their age or apportion them to sources [3, 12, 14]. Current environmental forensic methodologies have been especially effective in discerning Manufactured Gas Plant (MGP) derived coal-based wastes, primarily containing polycyclic aromatic hydrocarbon (PAH) compounds, from other waste mixtures. Environmental forensic techniques and databases were originally developed in the oil industry, and were initially applied to environmental work with the Exxon Valdez incident. Since that time, the techniques have been refined for identification of both petrogenic and pyrogenic materials. It has only been in the past few years that these techniques have been applied to tar identification, specifically tars associated with MGP processes [5, 6].

Most environmental forensic work is carried out using only a few analytical techniques. An extensive database of pyrogenic and petrogenic “chemical fingerprints” has been constructed by the Gas Technology Institute (GTI) and META Environmental, Inc. using

gas chromatography coupled with a flame ionization detector (GC/FID) or with a mass spectrometer (GC/MS). To be successful, chemical fingerprinting requires the identification of specific compounds or patterns of compounds that provide distinguishing or discriminating information. Further, the information must be reproducible and consistent with basic principles of chemistry. Analysis of the database provides indicator chemical parameters which are indicative of a specific waste or source of waste. These parameters may include specific compound ratios, the presence/absence of biomarkers or general trends in the chromatogram pattern.

The use of GC/FID and GC/MS chemical fingerprinting techniques have been highly successful in discerning wastes from wholly different sources [13] or even between MGP-type wastes from different plant operations [5, 6]. However, the reliability of GC/FID and GC/MS forensic methods decreases when multiple sources are present in a sample and when the sample composition becomes extensively altered by environmental weathering processes. This is the situation for many background surface soil locations where the PAHs have accumulated over many years, are present at relatively low concentrations, and have been subjected to long periods of weathering. GTI has been developing a new analytical method to provide the additional data needed for reliable source identification of "urban background" PAH contamination. Recently developed instruments are capable of measuring the ratio of the two natural isotopes of carbon in individual PAH compounds [7, 10]. This method is called compound-specific carbon isotope ratio (CSIR) determination and is done with a GC/IRMS (isotope ratio mass spectrometer). The GC/IRMS technique is a relatively new analytical tool that has great potential as an environmental forensic method at former MGP sites. This paper focuses on the applications of both chemical and isotopic analysis of samples to discern PAH wastes in the environment.

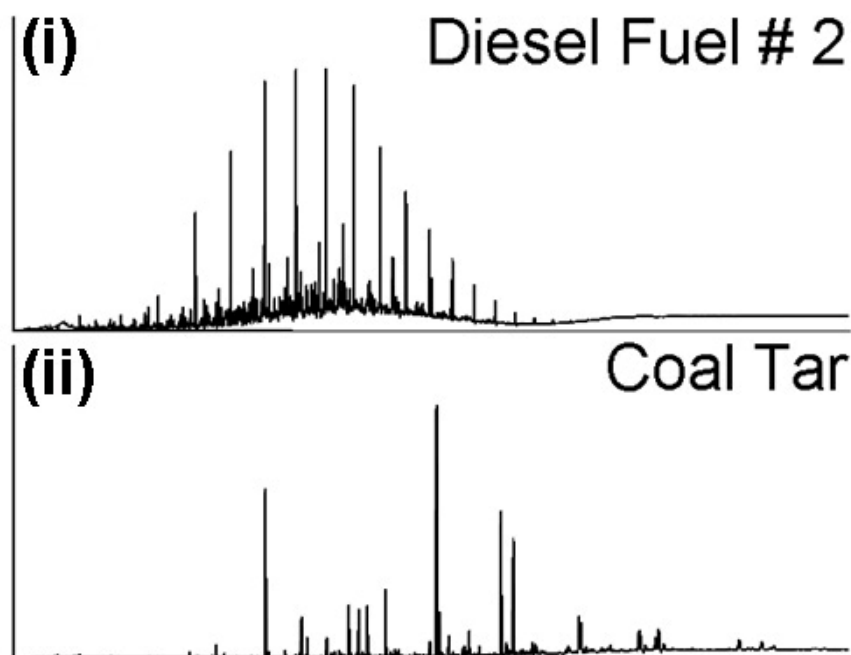
### **PAH Contamination in the Environment**

PAHs have been released into the environment from a number of natural and anthropogenic sources, especially in urbanized areas over the past 150 years. Although PAHs are produced naturally and are widespread in the environment, the most concentrated sources of PAHs found in the environment are from human activity. Fossil fuel burning, petroleum refining and usage, and industrial activities such as coke and steel production have produced and released large quantities of PAHs. Several studies in the U.S. and Europe have indicated that the concentrations of PAHs in urban surface soils can range from the low parts per billion to hundreds of parts per million depending on the proximity to and contribution from significant PAH sources [5, 16]. Forensic chemistry techniques that can be used to measure, characterize, and ultimately differentiate these different types of PAH contaminations are GC/FID, GC/MS, and GC/IRMS.

### **Chemical Analysis of PAH Contamination**

Chemical analysis of PAH contaminated samples can be accomplished with a GC/FID or a GC/MS. Chemical fingerprints generated from GC/FID can be very useful because they show the presence/absence and relative amounts of hydrocarbon compounds. Patterns of individual peaks and their sizes as well as the shapes of any baseline features are examined qualitatively for similarities and differences. Fig. 1(i) shows a GC/FID

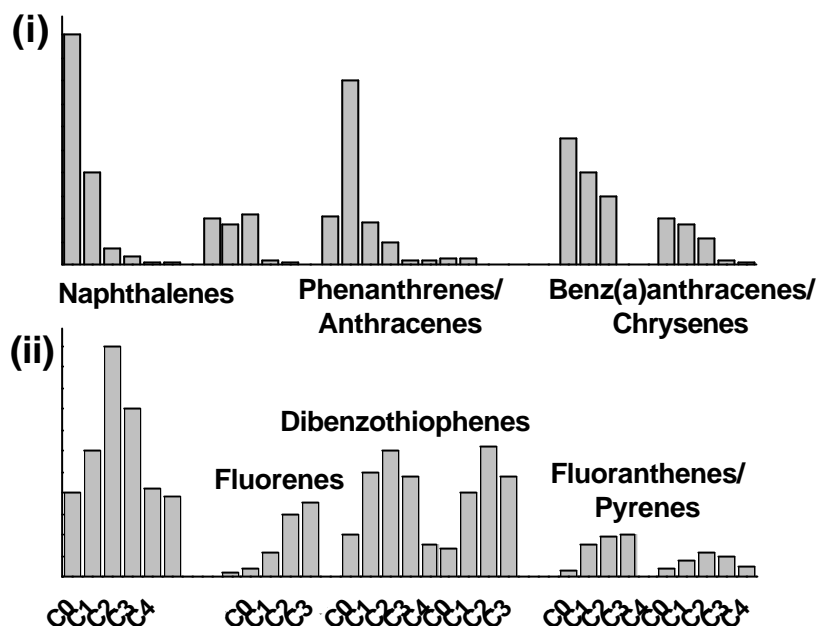
fingerprint of diesel fuel #2. The presence of an unresolved complex mixture (UCM), which is a bell-shaped baseline, is indicative of petrogenic sources (e.g., petroleum products). In addition, the presence of a regular series of normal alkanes and isoprenoid hydrocarbons is also indicative of petroleum products. In contrast, Fig. 1(ii) shows a GC/FID fingerprint of coal tar. The abundance of monocyclic aromatic hydrocarbon (MAHs) and PAHs seen in this fingerprint is a typical pattern found in pyrogenic sources.



**Fig. 1. GC/FID Fingerprint of (i) Diesel Fuel #2 and (ii) Coal Tar.**

In general, chemical fingerprints generated from GC/MS are similar to the ones generated from GC/FID with the addition of mass spectra information. This additional information is useful for the accurate determination of the concentrations of target compounds such as monocyclic aromatic hydrocarbons (MAHs), PAHs, alkylated-PAHs, and biomarkers. For instance, the ratios of fluoranthene/pyrene (Fl/Py), dibenzofuran/fluorene (D/F), acenaphthylene/acenaphthene (ACY/ACE), and ethylbenzene/m- and p-xylene can be used to confirm patterns that are characteristic of various MGP tars. Specifically, carburetted water gas (CWG) tar commonly has Fl/Py ratios of between 0.5 and 0.9, while coal carbonization (CC) and oil gas (OC) tars have Fl/Py ratios greater than 1.0 [5]. Also, CWG tars commonly have D/F ratios between 0.12 and 0.46, while CC and OC type tars have D/F ratios between 0.39 and 1.11 [5].

Another important distinction between the chemical fingerprints of pyrogenic and petrogenic substances is the distribution of PAHs and their alkylated homologues, which can be seen in Fig. 2. Namely, pyrogenic substances typically contain higher concentrations of the parent PAH than their alkylated homologues, whereas, the opposite is true for petrogenic substances.

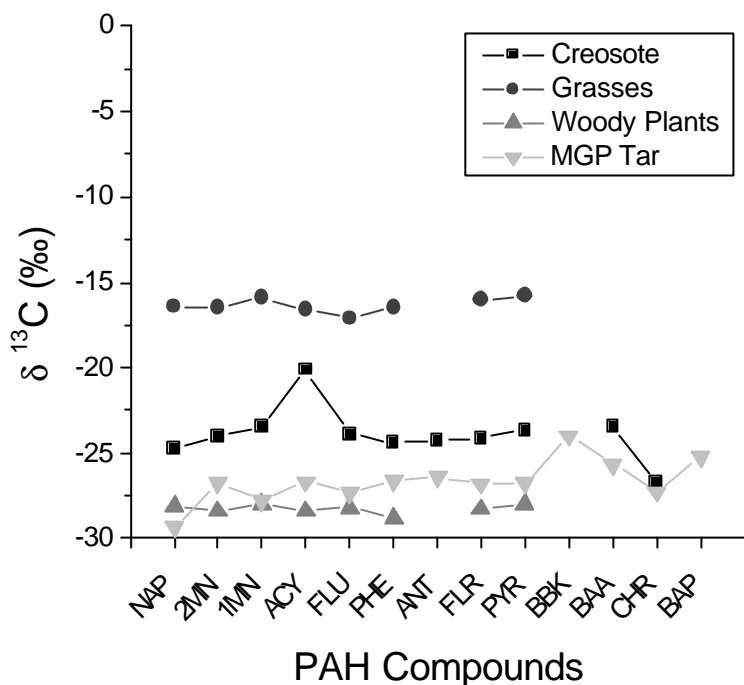


**Fig. 2. Patterns of PAH and Alkylated-PAH in (i) Petrogenic and (ii) Pyrogenic Substances.**

There are, however, some limitations to the use of GC/FID and GC/MS for environmental forensics purposes. The data are less reliable for samples that are contributed by multiple sources as well as samples that are extensively altered by environmental weathering processes. Finally, GC/FID and GC/MS analytical techniques often do not provide data with sufficiently conclusive discriminating power when low-level PAH discernment is required. The analysis of PAH contamination using isotopic techniques described in the next section addresses this limitation.

### **Isotopic Analysis of PAH Contamination**

Researchers have noted that the carbon isotope ratios of PAHs from different hydrocarbon sources are often different [10]. Further, other studies indicate that the carbon isotope ratios of PAHs from different industrial products and by-products, such as refined petroleum products, coal tar products, and vehicle exhaust will vary because of the disparate sources coal or oil [9, 15]. Stable isotope ratios have been used in geochemistry for many years [2]; and recently, carbon, hydrogen, sulfur, and oxygen isotope ratios have been found useful for environmental studies [11]. The ratios of two stable isotopes of carbon can be measured for each individual PAH compound with a GC/IRMS. Fig. 3 shows the carbon isotope ratios of PAHs in creosote, combusted grasses, combusted wood, and an MGP tar samples. The result suggests that PAHs from different sources have different carbon isotope ratios.



**Fig. 3. CSIR of Creosote [1], Grasses [8], Woody Plants [8], and MGP Tar.**

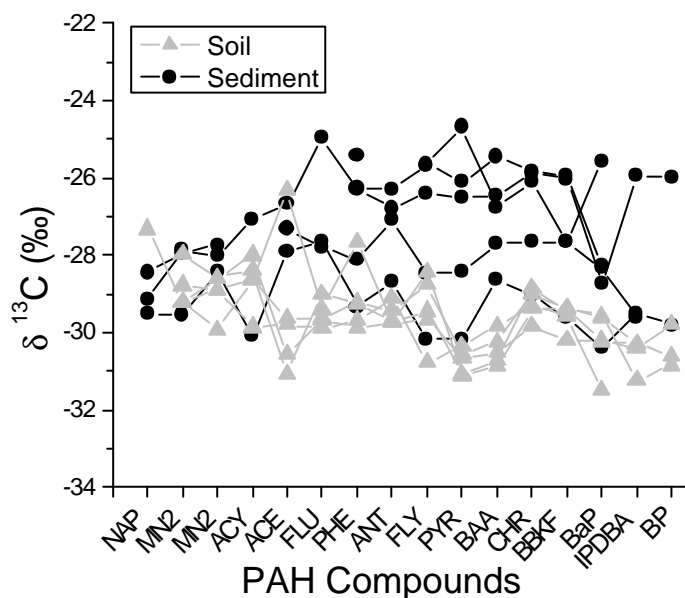
Stable carbon isotope ratios were also found not change as significantly as the molecular composition as a substance weathers in the environment [1, 4, 8, 10]. Therefore, as oil products or tars weather over time, the carbon isotope ratios of the constituent PAHs will stay relatively constant. For this reason, GC/IRMS can connect contaminated samples to their source materials even after their chemical composition has degraded so extensively that other techniques such as GC/MS cannot provide confident source matches.

The isotopic composition was expressed relative to a reference standard that can be traced to the PDB standard of the University of Chicago (Belemnite from the Peedee Formation, Cretaceous, South Carolina). Results, in per mil (‰), are expressed as:

$$d^{13}C = \frac{\left[ \left( \frac{^{13}C}{^{12}C} \right)_{\text{sample}} - \left( \frac{^{13}C}{^{12}C} \right)_{\text{standard}} \right]}{\left( \frac{^{13}C}{^{12}C} \right)_{\text{standard}}} \times 1000$$

The following case study is an example of a situation where GC/FID and GC/MS chemical fingerprinting techniques were not able to fully identify the source(s) of

contamination in the samples with confidence due to their low PAH concentrations; and GC/IRMS was used to clarify this ambiguity. A survey of a riverbed sediment found elevated PAH levels. And it was assumed that the source of the elevated PAH concentrations in the sediment was a nearby former MGP site. Although data from GC/FID and GC/MS analyses were not able to provide conclusive evidence for the source(s) of contamination, CSIR values provided some insights. Specifically, results from the isotope studies, shown in Fig. 4, displayed a good agreement among the on-site soil samples, having isotope ratios between about -28 and -32 ‰. In contrast, most of the sediment samples appear to be different, having isotope ratios between about -25 and -28 ‰. These differences are significant given the typical precision of this method. The PAHs at the storm sewer outfall were also measured. And one of the sediment samples was measured to have an intermediate isotope composition that may represent a mixture of sources. The overall results from the isotope studies, therefore, suggested that at least some of the PAH content in the sediments was from a source other than the MGP.



**Fig. 4. Comparison of CSIR of MGP-Contaminated Soil Samples and Sediment Samples.**

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## References

1. Hammer B, Kelley C, Coffin R, Cifuentes L, and Mueller J (1998)  $\delta^{13}\text{C}$  values of polycyclic aromatic hydrocarbons collected from two creosote-contaminated sites. *Chem. Geol.* 152:43-58
2. Hoefs J (1997) *Stable Isotope Geochemistry* (4th edition). Springer-Verlag, Berlin, Germany, pp 244
3. Johnson MD and Morrison RD (1996) Petroleum fingerprinting: dating a gasoline release. *Environ. Protection* September:37-39
4. Mansuy L, Philp R, and Allen J (1997) Source identification of oil spills based on the isotope composition of individual components in weathered oil samples. *Environ. Sci. Technol.* 31:3417-3425
5. Mauro DM (2000) *Chemical Source Attribution at Former MGP Sites*. EPRI, Palo Alto, CA, NYSEG, Binghamton, NY, and RG&E, Rochester, NY. 1000728
6. McCarthy KJ, Emsbo-Mattingly S, Stout SA, and Uhler AD (2000) Identifying Manufactured Gas Plant residues in industrial sediments. *Soil Sediment & Groundwater* Oct/Nov:1-3
7. McRae C, Snape CE, Sun C-G, Fabbri D, Tartari D, Trombini C, and Fallick AE (2000) Use of compound-specific stable isotope analysis to source anthropogenic natural gas-derived polycyclic aromatic hydrocarbons in a lagoon sediment. *Environ. Sci. Technol.* 34:4684-4686
8. O'Malley V, Burke R, and Schlotzhauer S (1997) Using GC-MS/Combustion/IRMS to determine the  $^{13}\text{C}/^{12}\text{C}$  ratios of individual hydrocarbons produced from the combustion of biomass materials – application to biomass burning. *Org. Geochem.* 27:567-581
9. Okuda T, Takada H, and Naraoka H (2003) Thermodynamic behavior of stable carbon isotopic compositions of individual polycyclic aromatic hydrocarbons derived from automobiles. *Polycyclic Aromatic Compounds* 23:219-236
10. O'Malley V, Abrajano Jr. TA, and Hellou J (1994) Determination of the  $^{13}\text{C}/^{12}\text{C}$  ratios of individual PAH from environmental samples: can PAH sources be apportioned? *Org. Geochem.* 21:809-822
11. Philp R, Kombrink M, and Allen J (1995) An investigation into the potential of GCIRMS as a technique for the correlation of weathered oil spill samples to their source. Amherst Scientific Publishers, Amherst, MA, pp 363-380
12. Sauer TC and Uhler AD (1994) Pollutant source identification and allocation: advances in hydrocarbon fingerprinting. *Remediation* 5:25-50
13. Stout SA, Uhler AD, and McCarthy KJ (1998) PAH can provide a unique forensic "fingerprint" for hydrocarbon products. *Soil & Groundwater Cleanup* October:1-4
14. Stout SA, Uhler AD, Uhler RM, Healey EM, and McCarthy KJ (2003) Detailed chemical fingerprinting of gasoline for environmental forensic investigation, Part 3. Applications to environmental forensics investigations. *Soil Sed. Water* March/April:16-18
15. Sun C, Snape CE, McRae C, and Fallick AE (2003) Resolving coal and petroleum-derived polycyclic aromatic hydrocarbons (PAHs) in some contaminated land samples using compound-specific stable carbon isotope ratio measurements in conjunction with molecular fingerprints. *Fuel* 82:2017-2023

16. Taylor BB, Mauro DM, Maxwell SS, and Quinn A (2000) Literature Review of Background Polycyclic Aromatic Hydrocarbons. EPRI, Palo Alto, CA. TR-114755