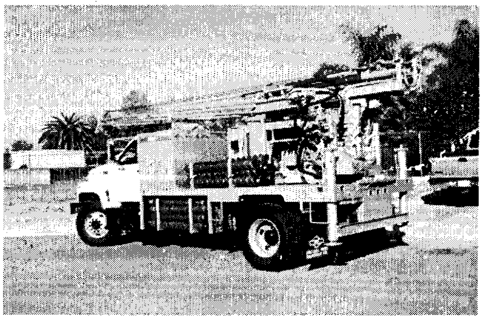
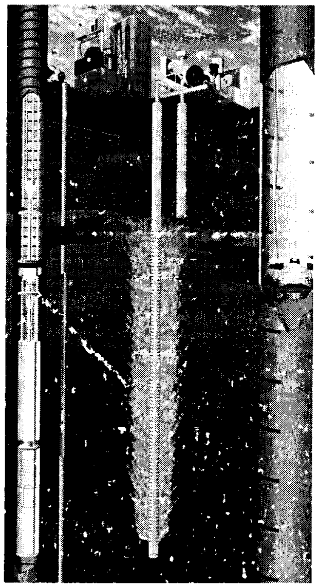
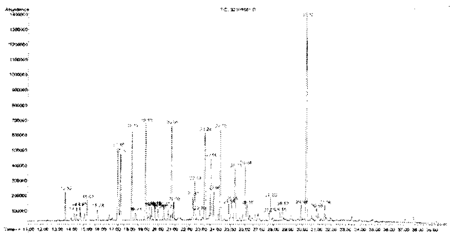
行政院所屬各機關報告書
出國類別：考察

土壤及地下水油汙染調查、檢測新設備、技術及證據保全措施

裝 訂 線







服務機關：中國石油股份有限公司
油品行銷事業部 安環室
出國人職　稱：環境保護師
姓　　名：侯 善 麟
出國地區：美國
出國期間：民國九十二年十月三十一日至十一月七日
報告日期：中華民國九十二年十二月二十九日

系統識別號:C09204873

公 務 出 國 報 告 提 要

頁數: 36　含附件: 是

報告名稱:

考察土壤地下水油污染調查檢測新設備技術及證據保全措施

主辦機關:

中國石油股份有限公司

聯絡人／電話:

葉宇容／87258422

出國人員:

侯善麟　中國石油股份有限公司　油品行銷事業部　環境保護師

出國類別: 考察

出國地區: 美國

出國期間: 民國 92 年 10 月 31 日 -民國 92 年 11 月 07 日

報告日期: 民國 92 年 12 月 29 日

分類號/目: G2／石油礦及石油工業　G2／石油礦及石油工業

關鍵詞: 地下水.土壤.汙染調查.檢測.證據保全.環境法醫學

內容摘要: 爲順應日趨嚴格之環保法令及日漸高漲之環保意識，如何提昇本公司環保技術，建立優良企業形象，是面對激烈競爭及急遽社會變遷形勢時，所必須兼顧之重要議題。本考察行程所獲得的資訊，歸納出目前美國土壤及地下水油汙染調查、檢測新設備、技術及證據保全措施及實務之發展現況，並整理出美國在「環境法醫學」新領域上的最新成果及發展趨勢，供本公司作爲研擬未來環保策略之參考依據。

本文電子檔已上傳至出國報告資訊網

摘要

為順應日趨嚴格之環保法令及日漸高漲之環保意識，如何提昇本公司環保技術，建立優良企業形象，是面對激烈競爭及急遽社會變遷形勢時，所必須兼顧之重要議題。本考察行程所獲得的資訊，歸納出目前美國土壤及地下水油汙染調查、檢測新設備、技術及證據保全措施及實務之發展現況，並整理出美國在「環境法醫學」新領域上的最新成果及發展趨勢，供本公司作為研擬未來環保策略之參考依據。

土壤及地下水油汙染調查、檢測新設備、技術

及證據保全措施

目次

壹、目的

近年來由於工商業發達，各種產業所產生之水污染物、空氣污染物、固體廢棄物，常因不當排放、棄置，導致土壤及地下水受到有機或無機化合物、重金屬、農藥、油料、不明廢棄物及化學品等污染。

自從政府於八十九年二月施行土壤及地下水污染整治法(以下簡稱土水法)以來，確立了污染責任歸屬，污染範圍查證、控制、整治、驗證等執行程序，明定受污染之土地未整治完成不得轉移、開發，且增列民眾檢舉及追溯既往條款，並設置基金以強化污染整治之財務來源，其相關配套措施，如過渡時期之行政規範、個案監督作業要點、施行細則、監測基準、管制標準等亦陸續建立，因此相關業者必須逐步落實執行土壤及地下水汙染調查、檢測及整治復育工作。

土壤及地下水汙染之調查、檢測及整治復育工作往往曠日費、成效不易彰顯，且需花費極高成本；環保署九十年度執行之地下水潛在污染源調查計畫中，針對台灣地區之加油站進行地下環境污染潛勢調查顯示，計有十九座加油站，地下環境偵測出揮發性氣體或苯含量偏高，疑似受油品污染佔調查總數 191 座之 9.9% ，其中並有士香、桃鶯、嘉仁等多座民營加油站遭到環保署依土水法予以停業處分，並公告為污染控制場址，被處分、公告之業者需面對一連串的繁複程序，進行積極之改善，直到地下環境污染改善至符合土水法相關標準，才

得向環保主管機關申請結案、解除列管，其間更須面對巨額營業損失、企業形象受損、受污染事件影響民眾索賠、法律訴訟等各項問題、損失及風險，對企業經營而言具有相當負面的影響。

此行主要之目的是在於藉由拜訪ERM(Environmental Resources Management)公司洛杉磯分公司，研討美國土壤及地下水油汙染調查、檢測新設備、技術及證據保全措施及實務。並出席在美國加州聖地牙哥所舉辦的「美國環境法醫學會專業研討會」的機會，與各先進技術發明人/公司實地研討、學習美國土壤及地下水油汙染調查、檢測新設備、技術及證據保全措施。期能藉此引進美國在土壤及地下水油汙染調查、檢測新設備、技術及證據保全措施方面的實務經驗及觀念，以提昇中油公司環保技術水準，並確保公司永續經營之利基。

貳、過程

本次考察自民國九十二年十月三十一日至十一月七日共八天，過程如下:

九十二年十月三十一日：啟程前往美國

九十二年十一月一日～三日：拜訪ERM(Environmental Resources Management)公司洛杉磯分公司，研討美國

土壤及地下水油汙染調查、檢測新設備、技術及證據保全措施及實務。

九十二年十一月四日～五日：出席美國環境法醫學會專業研討會，學習美國土壤及地下水油汙染調查、檢測新設備、技術及證據保全措施。

九十二年十一月六日、七日：返程

叁、心得

一、美國土壤及地下水油汙染調查、檢測新設備及技術

在拜訪ERM(Environmental Resources Management)公司洛杉磯分公司、出席美國環境法醫學會專業研討會及相關參訪行程之中，來自美國及世界各地的專家學者提出了數十種有關地下環境污染調查、檢測新設備、技術及整治技術、最佳化操作管理方案、新技術實驗等研發成果，其中有關壤及地下水油汙染調查、檢測新設備及技術等方面，彙整如下：

土壤氣體調查

美國超級基金場址之地下水質監測統計資料顯示，揮發性有機物質出現之總數量與美國環保署訂定之優先污染物（priority pollutants）出現之總數量成一線性正比關係，並且在最常出現的

25 種污染物質中，即有 15 種是揮發性有機化合物。因此，調查土壤氣體中所含揮發性有機化合物的成份與濃度，即可反應地下受污染土壤或地下水有機物污染團在水平方向分佈範圍的偵測指標項目。

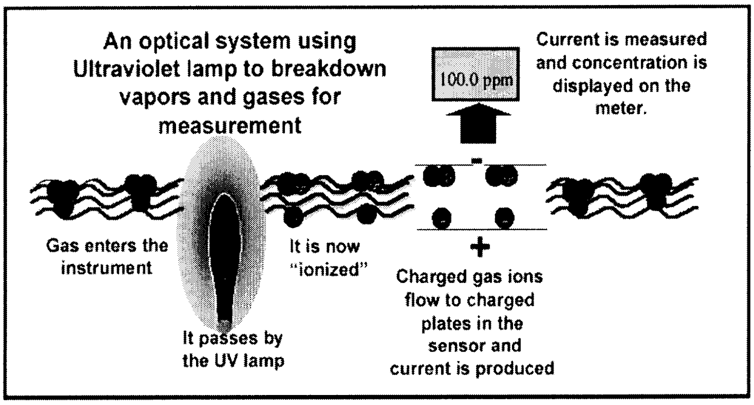
土壤氣體偵測技術是在不擾動地下水文系統、污染團分佈範圍，及不影響地表廠區作業之採樣技術條件下，調查地下土壤及地下水污染現況、污染範圍、可疑污染源分佈位置及污染團遷移方向等項目；尤其是應用在地下儲油槽或輸油管線之偵漏調查方法上最具成效，其偵測流程亦可因調查目的之差異而有不同之步驟與架構。

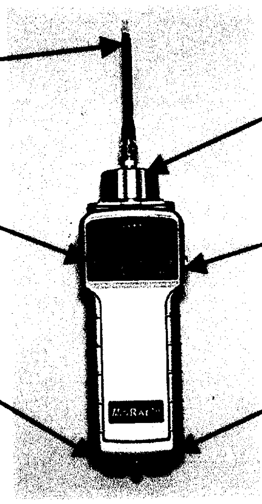
土壤氣體（soil gas）是指介於地表與地下水面上部毛細管帶間之未飽和層內，在其組成顆粒間之孔隙內存在的氣體或空氣；然而此氣相成份在接近地表時與在大氣中性質相近，但在地下深處則受土壤本身或地下水內存在之揮發性有機化合物影響而改變其組成。因此，當液態有機化合物自地表或地下設施向下滲漏時，未飽和層土壤將因滲流路徑之部份殘留油品所污染，而其向下遷移之行為將受油品本身之特性及地下土層自然環境之影響（例如：地層物化特性，孔隙率等）；比重小於水之有機化合物(如汽、柴油等石化油品：LNAPLs)則在地下水面上形成凸鏡狀之浮油，並受重力作用影響立即向四方擴散延伸，此時存在浮油內之揮發性有機化合物氣體（VOCs；如 Benzene、Toluene、Ethyl-benzene、Xylenes、Styrene 等），將自液相界面釋

出經由土壤氣體相通處向地表方向垂直遷移；而可溶性之有機成份在溶入地下水後，則受地下水流梯度控制向下游移動，在地下水面表層浮油消失後，溶於地下水中的 VOCs 才開始向上揮發進入土壤氣體內。

土壤氣體偵測分析設備(光離子偵測器 Photo Ionization Detectors)

光離子偵測器 Photo Ionization Detectors（PID）能測量低的濃度從 PPB 到 PPM 的 VOCs 及其他毒性氣體，是一種非常敏感且具有廣域光譜的監測器。PID 使用紫外光源來瓦解化學物的鍵結及陰離子（即游離化），以便能容易地讓偵測器計量。偵測器測量已離子化氣體的變化並且把信號轉換成電流。然後電流被擴大並在儀錶上以 PPM 顯示（如下圖）。被測量後的離子會改變原有氣體或蒸氣的形式。PID 是一個非常敏感的監視器它能正確地量測氣體和蒸氣在很低微的 ppm 或甚至 ppb 濃度中。然而 PID 不是個有選擇性的監測器，它並未具有區別化學物之間的不同的能力。

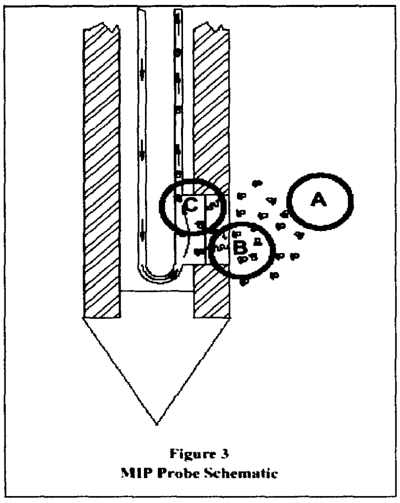




光離子偵測器 Photo Ionization Detectors（PID）構造圖

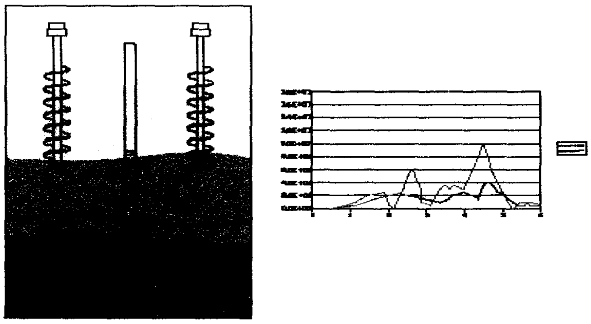
<u>半透性薄膜連續土壤氣體調查技術（Membrane Interface Probe）</u>

半透性薄膜連續土壤氣體調查技術（Membrane Interface Probe－MIP）偵測器之主體為一直徑約3.8 公分、長30 公分之金屬體，其中，MIP探測器部分之薄膜是由金屬與高份子聚合物所組成，藉由加熱之薄膜與土壤中之揮發性有機物接觸，激化後進入薄膜內部，由探測器內部惰性氣體攜帶至地表上移動式實驗車內，藉由氣相層析儀（GC）上之火焰離子偵測器（FID）或光游離子偵測器（PID）進行分析，以了解土壤污染情形。



MIP 偵測器主體剖面圖

MIP 操作方法係採用直接貫入式（Direct Push）鑽機，將半透性薄膜偵測器貫入地表下，偵測器由地面主機控制加熱溫度至 121℃，使得土壤中有機氣體被激化並滲透進入偵測器表面的半透性薄膜，藉由傳輸管內的攜帶氣體（惰性氣體，如氮氣）將有機氣體傳送至地面實驗車內的 GC-FID/GC-PID 分析。



MIP 操作模式示意圖

二、土壤及地下水油汙染證據保全－環境法醫學

環境法醫學（Environmental Forensics）為一全新的新興學術、專業領域，環境法醫學（Environmental Forensics）專有名詞一直到九○年（1990 年）末期才被提出，直到 2002 年美國「國際環境法醫學會 International Society of Environmental Forensics－ISEF」才正式成立。

環境法醫學（Environmental Forensics）領域中涵概了環境工程、化學、化工、地質、水文、航照技術、電腦科技、統計分析、、、等多元學術、專業知識及應用，為一整合型專業領域，有鑑於世界各先進國家對於環境污染事件之責任鑑定、證據調查、保全等需求日趨殷切，環境法醫學相關學門之整合亦加速進行中。

以此次參與研討會之成員而言，包括工程、統計分析、顧問、政府機構、軍方、金融及法律等各行各業專業人士，其研發成果報告及應用實例介紹亦遍及各種廣泛之環境鑑定及證據調查之議題。

有關本次研討會議題，與本公司最具直接關係者，應屬美國貝泰機構 Dr. Allen D. Uhler 所提出的「Geochemical Testing Techniques for Petroleum Hydrocarbons and Related Contaminants」（石油碳氫化合物及相關污染物質的地質化學分析技術）。Dr. Uhler 之報告中提供了許多他個人在油污染鑑定及證據調查方面之寶貴實務經驗。

綜合彙整 Dr. Uhler 報告之重點如下：

1. 欲判別地下環境污染之石油碳氫化合物種類（油品種類），通常可藉由 GC(氣相層析儀)分析之結果（圖譜）加以印證。
2. 若需進一步瞭解污染源來自何處，並鑑定責任歸屬，則更進一步的詳細分析（如氣相層析/質譜儀－GC/MS），配合環境、地質、化學等相關專業知識的應用，才能較為準確地提供科學化證據。
3. 根據經驗顯示，美國環保署所提供之標準檢驗方法（如 EPA8045－分析 TPH、EPA8260 分析 BTEX）並不足以提供鑑定石油碳氫化合物來源及種類的充足證據。
4. 相關輔助技術如特定化合物（多環芳香烴化合物 PAH）濃度配比、生物指標、同位素分析等可大幅提升調查、鑑定之精確性。
5. 配合資深專業人員，整合不同專業領域，共同擬定適於個別場址的調查計劃，並運用先進的電腦分析軟體技術，才能準確做好油污染鑑定及證據調查工作。

有關 Dr. Allen D. Uhler 所提出的「Geochemical Testing Techniques for Petroleum Hydrocarbons and Related Contaminants」（石油碳氫化合物及相關污染物質的地質化學分析技術）簡報內容，詳如附錄。

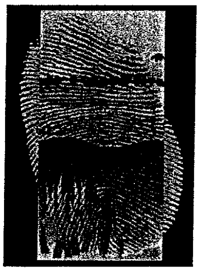
肆、建議

1. 有關美國土壤及地下水油汙染調查、檢測新設備及技術，近年來已漸趨於成熟，土壤氣體調查技術、光離子偵測器 Photo Ionization Detectors（PID）及半透性薄膜連續土壤氣體調查技術（Membrane Interface Probe－MIP）偵測器等皆已普遍地應用於土壤及地下水油汙染場址的調查、檢測。
2. 國內受各種條件限制，無法自行相關進行技術開發，但上述壤及地下水油汙染調查、檢測設備及技術已由國內相關業者及本公司引進使用；唯設備技術之應用涉及許多實務經驗之累積，以目前國內使用情況而言，尚處於初步試驗期，其熟練度仍稍顯不足，然而國外相似技術設備之演進日新月異，本公司應隨時留意最新發展資訊，隨時提升汙染調查、檢測技術能力。
3. 我國環保趨勢，一向跟隨歐美等國腳步，對於本次考察所獲得之美國技術資訊及發展趨勢，本公司應及早妥善規劃，採取適當措施（如更新儀器設備、加強同仁土壤及地下水油汙染調查、檢測專業技能訓練）以趕上世界之潮流與趨勢。
4. 環境法醫學為未來環境污染事件污染責任鑑定，及證據調查之主流專業領域，為謀求本公司最大利益，建議積極培訓環境法醫學相關專業技術人才以為因應。

附錄

Overview of Forensic Analytical Methods:

Geochemical Testing Techniques for Petroleum Hydrocarbons and Related Contaminants – GC, GC/MS, GC-IRMS



Allen D. Uhler, Ph.D.
Battelle Memorial Institute
Duxbury, MA

Environmental Forensics Workshop
November 4-5, 2003
San Diego, VA

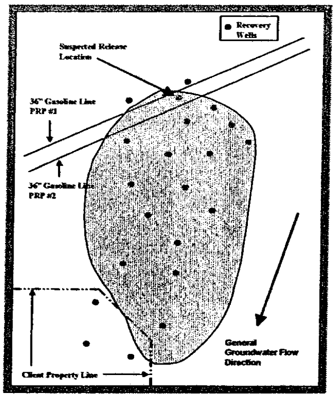
Presentation Outline

- Environmental Forensics, and the Role of Advanced Chemistry
- Hydrocarbon Chemistry
  - Petroleum
  - Tars
  - Combustion Residues (Urban Runoff)
- Analytical Methods
  - Gas Chromatography
  - GC/Mass Spectrometry
  - GC/Isotope Ratio Mass Spectrometry
- Illustrative Examples, Where Appropriate

Questions welcomed throughout!

Environmental Forensics

"The systematic investigation of a contaminated site(s) or an event(s) focused on defensibly allocating liability for the contamination." [1]



[1]Stout, S.A., A.D. Uhler, T. G. Naymik and K.J. McCarthy. 1998. Environmental Forensics: Unraveling Site Liability. *Environ. Sci. Technol.*, 32: 260A-264A.

Overview of Forensic Analytical Methods 3

Questions Addressed in Environmental Forensic Studies

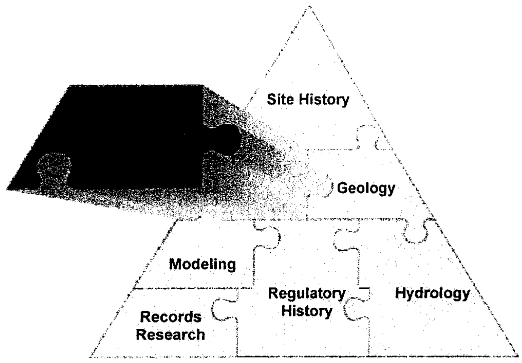
- **WHAT, WHERE, & WHEN?**
  - Unambiguous contaminant identification(s)
  - Well-defined spatial extent of contaminant(s)
  - Age-constraints on release(s) of contaminant(s)

    Detailed Site Assessments
    Remedial Design/Monitoring
    Risk Assessments
- **WHO?**
  - Defensible Allocation of Responsibility

    Due Diligence Investigations
    Toxic Torts
    Spills & Leaks
    NRDA Assessments

Overview of Forensic Analytical Methods 4

Advanced Chemical Analyses are a Critical Element in Integrated Environmental Forensics Investigations

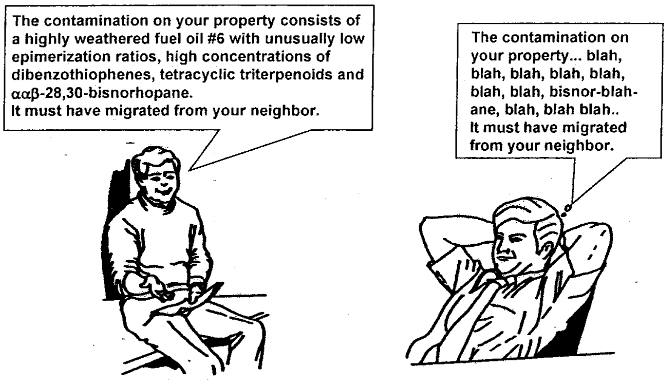


Reduce Technical Uncertainty ⇒ ***Greater Defensibility***

Detailed Chemical Analysis in Environmental Forensics

- A suite of analytical tool(s) by which the molecular distributions within complex organic pollutants are assessed
- Advanced methods are designed "drill down" to unravel the complex mixture of hydrocarbons that comprise source materials and environmental contamination
- Advanced methods almost always involve modified EPA or proven, but non-regulatory methodologies
- Robust and defensible quality control, data quality objectives, and quality assurance is imperative in developing high quality, defensible data
- Information-rich data from such measurement programs can be used to support the identification and differentiation of site contamination

Communicating Technical Information

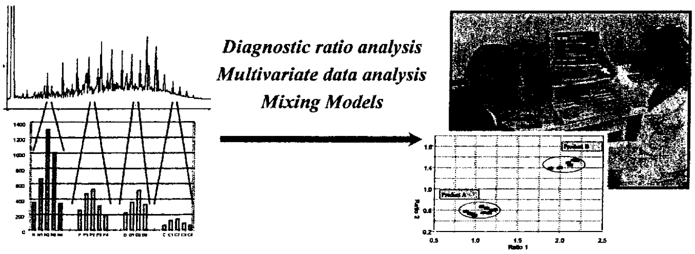


What the chemist says — What interested parties hear

Overview of Forensic Analytical Methods 7

Chemometrics

- Utilizes a quantitative chemical data set to numerically compare chemical signatures and either **correlate** or **differentiate** samples and suspected sources
- Expresses complex chemistry data in more understandable graphic representations of site conditions



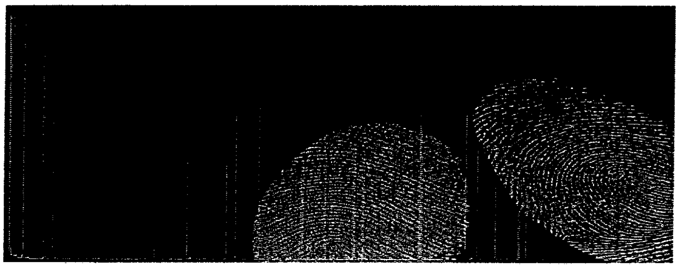
Overview of Forensic Analytical Methods 8

Hydrocarbon Contamination

- Hydrocarbons of environmental concern
  - Petroleum-derived
    - Fuels (gasoline, diesel, Jet, etc.)
    - Wastes
  - Coal-derived
    - Tars (Manufactured Gas Plant wastes)
    - Tar products (creosotes, oils, fuels)
  - Urban runoff
    - Combinations of residual fuel, lubrication oil, combustion products
    - Enriched in polycyclic aromatic hydrocarbons (PAH)
    - Focus on sediments
- Each of these classes of hydrocarbons have unique chemistries that can be leveraged in environmental forensics investigations

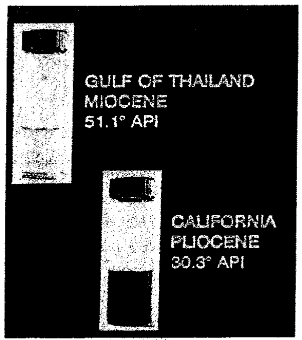
Processes Affecting the Chemistry of Hydrocarbons

- Feedstock (Crude Oil, Tar)
- Refining (Crude Oil, Tar)
- Weathering



Crude Oil/Petroleum

- A naturally occurring fluid mixture of:
  - Aliphatic hydrocarbons
  - Aromatic hydrocarbons
  - NSO-derivatives
  - Asphaltenes

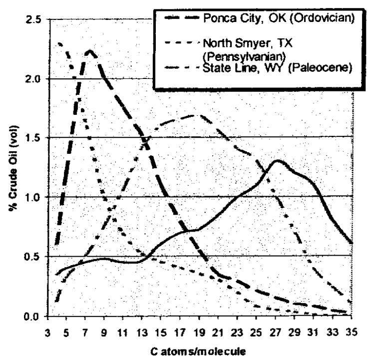


$$°API = \frac{141.5}{RD\ (^{60}/_{60}°F)} - 131.5$$

Overview of Forensic Analytical Methods 11

Crude Oil Chemistry in Forensics

- Crude oils from different geologic basins, fields, and reservoirs can be chemically distinct
- Chemistry is influenced by
  - Source rock type/maturity
  - Reservoir temperature
  - Reservoir degradation

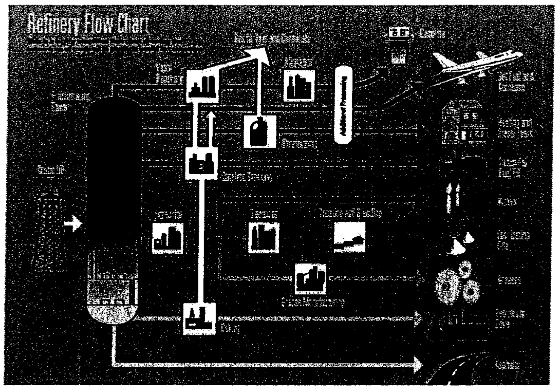


"Feedstock chemistry affects Product chemistry"

Overview of Forensic Analytical Methods 12

Crude Oil Refining in Forensics

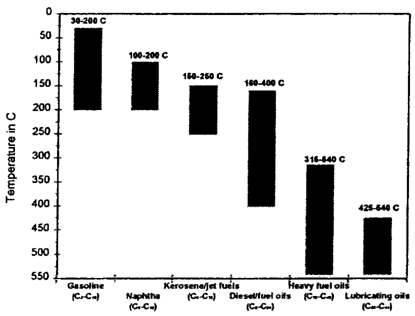
- Distillation
- Cracking
- Extraction
- Reforming
- Isomerization
- Alkylation
- Hydrogenation
- Blending
- Coking



Overview of Forensic Analytical Methods 13

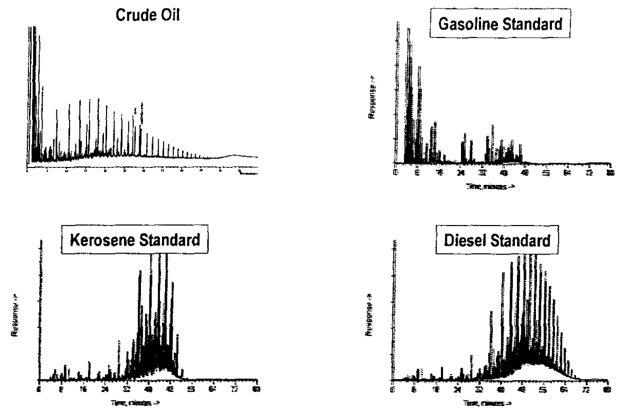
Petroleum Product Chemistry

- Each class of petroleum products have distinct chemical compositions by virtue of their refining characteristics
- Distinguishing differences in the subtle chemical features among similar products is often the central theme in many environmental forensics investigations



Overview of Forensic Analytical Methods 14

Unique Chromatographic Features of Petroleum

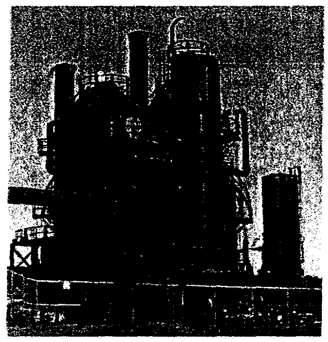


Overview of Forensic Analytical Methods 15

Tar Products – Unique Hydrocarbon Contaminants

Pyrolysis product produced from coal, oil, or mixtures of coal and oil, including:

- Manufactured Gas Plant (MGP) Wastes
- Coal Carbonization Plants
- Tar Processing Facility Products
  - Dozens of intermediate distillation products
- Wood Treating Facilities



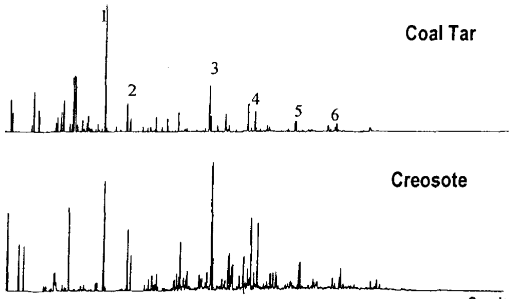
Tar products are distinguished by:

- (Relatively) simple chromatographic signatures
- Compositionally dominated by PAH
- PAH patterns dramatically different than petroleum

Overview of Forensic Analytical Methods 16

Tar Products – Unique Hydrocarbon Contaminants

The unusual composition of tar-derived wastes and products result in distinct gas chromatographic features that are dominated by non-alkylated PAH compounds.



<u>Selected PAH</u>
1 Naphthalene
2 Methylnaphthalenes
3 Phenanthrene
4 Pyrene
5 Chrysene
6 Benzofluoranthenes

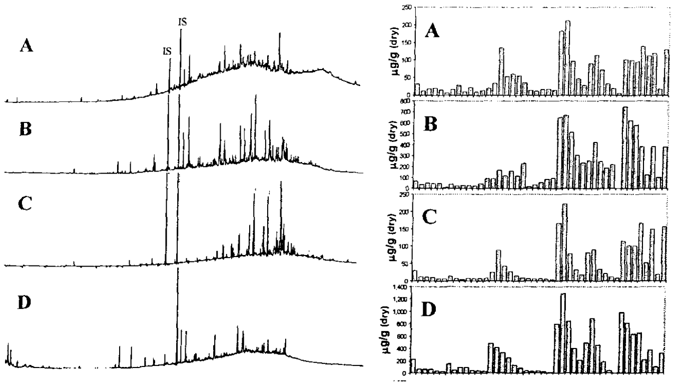
Overview of Forensic Analytical Methods 17

Urban Runoff

- ◆ Unique form of hydrocarbon contamination
- ◆ Complex mixture of non-point source contamination
- ◆ Comprised of residual petroleum and PAH-enriched combustion residues

Overview of Forensic Analytical Methods 18

Hydrocarbon Characteristics of Urban Runoff



GC/FID chromatograms and PAH distributions for sediments impacted by urban background (A) Thea Foss Waterway, WA (B) Eagle Harbor, WA (C) Portland Harbor, OR and (D) Elizabeth River, NJ sites.

Overview of Forensic Analytical Methods 19

Environmental Weathering

- Hydrocarbons released into the environment are altered by the combined effects of:
  - **Evaporation**
  - **Dissolution/water-washing**
  - **Absorption**
  - **Biodegradation**

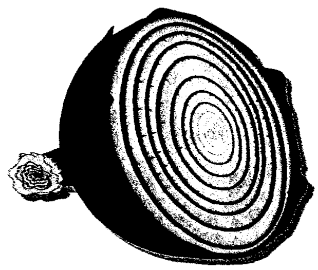
***T/V Erika*, Dec. 1999 released 3MM gallons of heavy fuel oil off coast of France**

- The environmental chemist must understand the implications of these processes in the measurement and interpretation of advanced chemical characterization of hydrocarbons.

Overview of Forensic Analytical Methods 20

Analytical Strategies – Hydrocarbons

- Often a gas chromatographic analysis (e.g. product 'fingerprint') is sufficient to answer the question at hand, "what kind of hydrocarbon product is found at the site?"
- More often than not, more detailed chemical analyses are warranted to differentiate among sources or track hydrocarbon residues in the environment
- Standard EPA Methods of analysis are generally insufficient to address petroleum identification



Peel the Onion!

Limitations Of Standard EPA Methods in Forensic Studies

Method	Utility	Limitations
EPA 413.1 Gravimetric	• Screening tool for TPH	• Total extractables • Subject to multiple interferences • Detection limit limitations
EPA 418.1 Infra-red	• TPH	• Total extractable hydrcarbons • Subject to multiple interferences • False positives and negatives very common • Detection Limit limitations
EPA 8015 GC/FID	• TPH • Product type ID • Initial weathering information	• Product ID subject to interpretation • Similar product types cannot be differentiated • False positives are common (i.e. biogenic hydrocarbons)
EPA 8260 GC/PID GC/MS	• BTEX	• BTEX only; misses 100+ important hydrcarbons • Provides little/no diagnostic source information • Detection Limit limitations
EPA 8270 GC/MS	• Hazardous waste site assessments	• Reports only 16 Priority Pollutant PAH s • Ignores the most important petroleum-related PAHs • Provides little/no diagnostic qualitative information • Detection limit limitations

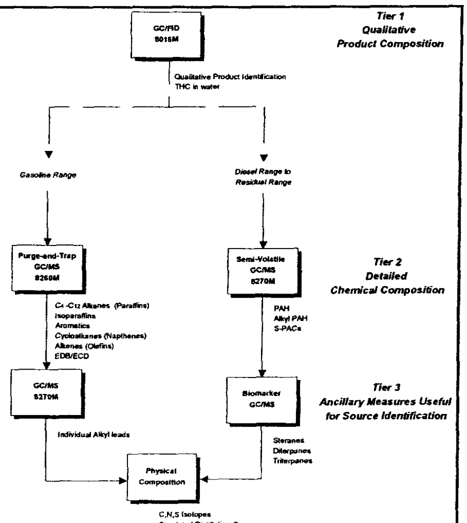
Recommended Measurements and Target Compounds in Forensic Studies

Measurement	Target Compounds	Utility
TPH and Product ID Screen EPA 8015M (GC/FID, GC/MS)	Extractable hydrocarbons Total petroleum hydrocarbons (TPH) C_8-C_{40} satuurates	• Concentration of Petroleum • Primary Product ID, weathering state
Volatile Organic Compounds EPA 8260 M (GC/MS)	C_5 to C_{12} PIANO Paraffins Isoparaffins Aromatics Naphthenes Olefins	• Product ID and differentiation • Product alteration • Evaporation • Water washing • Biodegradation indices
PAH and other heteroatomic AH EPA 8270M (GC/MS)	Petroleum-diagnostic PAH 2- to 4- ring petrogenic PAHs Diagnostic C_1 to C_4 alkyl homologues S-containing PAH	• Long-term product/source ID • Long-term weathering • Biodegradation indices • Petroleum vs other sources
Ancillary measurements	C and H stable isotopes Pb speciation Dyes Density	• Source/manufacturer differentiation • Mix models

Overview of Forensic Analytical Methods 23

A Tiered Strategy

- Logical flow of analysis dictated by hydrocarbon type
- Additional degrees of analytical complexity added commensurate with data needs
- Ancillary measurements or techniques should be used as needed to build the case



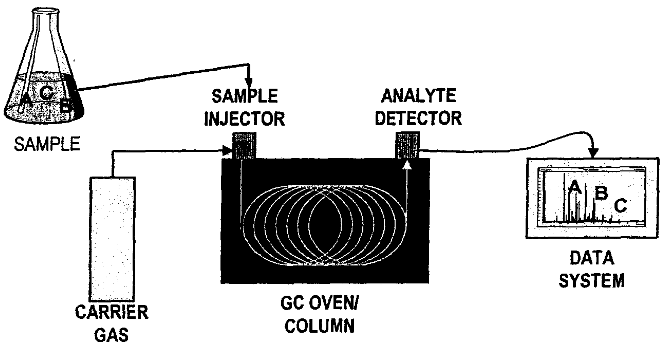
Overview of Forensic Analytical Methods 24

Gas Chromatography

- An analytical chemistry technique used to separate and identify hydrocarbon chemicals in a complex mixture such as a petroleum product or environmental sample
- Various detection systems – simple to complex
- Forensic methods founded on petroleum geochemistry and environmental chemistry literature
- Optimized for hydrocarbon characterization

Overview of Forensic Analytical Methods 25

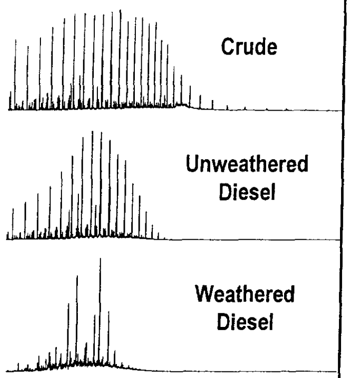
Gas Chromatography



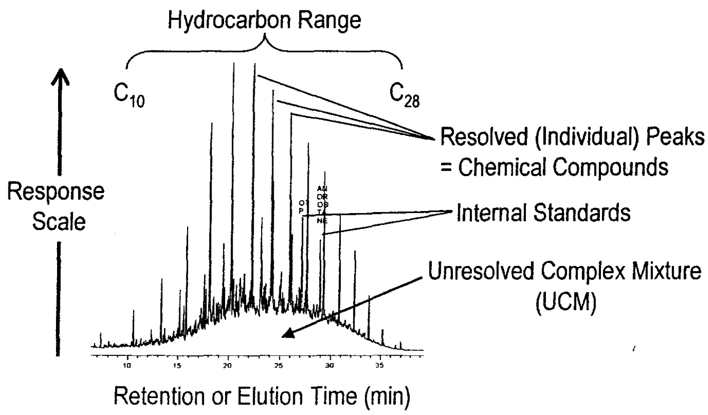
Overview of Forensic Analytical Methods 26

Applications of Optimized GC with Flame Ionization Detection (GC/FID)

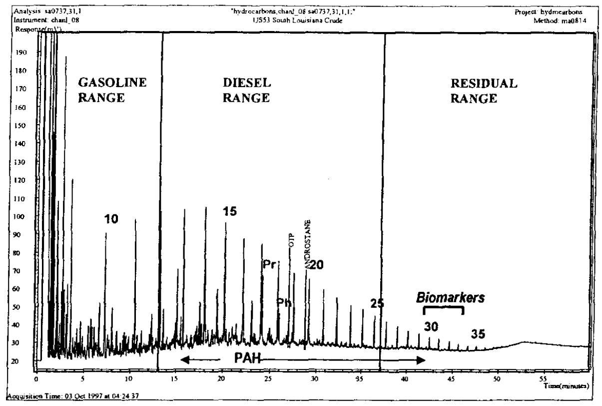
- Hydrocarbon product identification
- Measurement of n-alkanes, isoprenoids
- Measurement of total petroleum hydrocarbons
- Hydrocarbon fraction-specific analysis for risk assessment



Anatomy of a GC/FID Chromatogram – Hydrocarbon Analysis



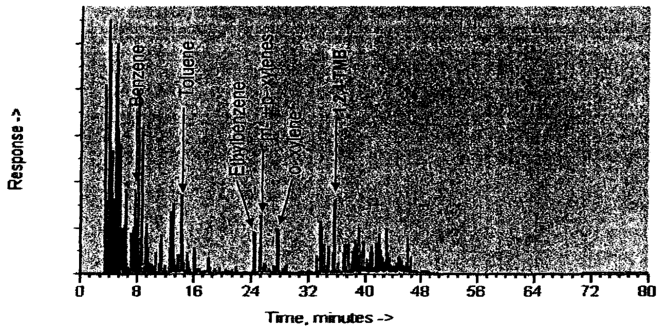
GC/FID Provides a Synoptic Analysis over the C_3-C_{40} Hydrocarbon Range



Overview of Forensic Analytical Methods 29

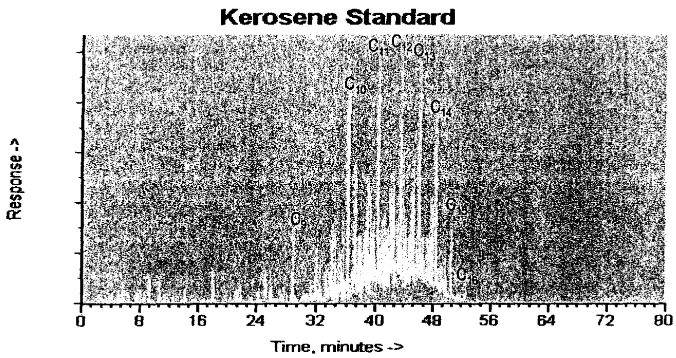
Hydrocarbon Products Can Be Easily Identified by Properly Optimized GC/FID

Gasoline Standard



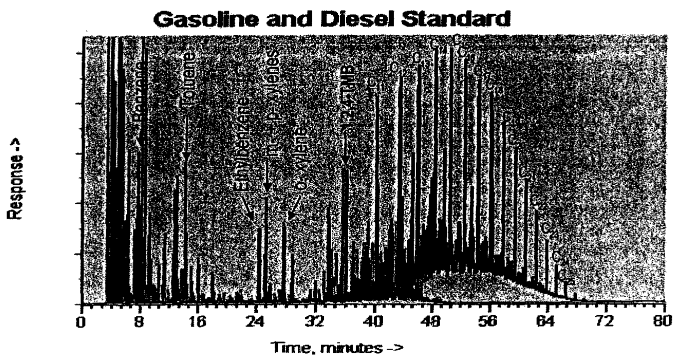
Overview of Forensic Analytical Methods 30

Hydrocarbon Products Can Be Easily Identified by Properly Optimized GC/FID



Overview of Forensic Analytical Methods 31

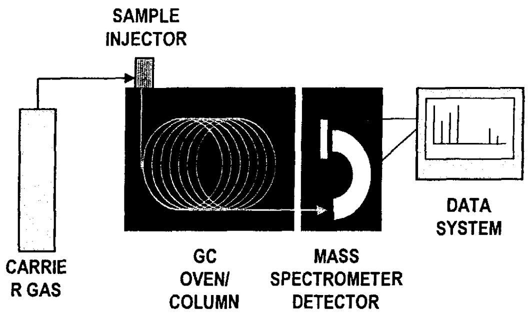
Hydrocarbon Products Can Be Easily Identified by Properly Optimized GC/FID



Overview of Forensic Analytical Methods 32

Gas Chromatography-Mass Spectrometry

A powerful analytical tool to separate and identify chemicals based on their characteristic molecular structure and fragmentation pattern



Overview of Forensic Analytical Methods 33

Applications of GC/MS

Advanced measurement of diagnostic, often low-level, constituents of hydrocarbon products or residues

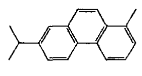
Semivolatile Range
- Homo- and hetrocyclic PAH and alkyl PAH
- Biomarkers
- Alkyl cyclohexanes
- Adamantanes

Volatile Range
- 100s of important gasoline constituents
  - Paraffins
  - Isoparaffins
  - Aromatics
  - Naphthenes
  - Olefins
  - Additives (MTBE, TBA, TAME, etc.)
- Alkyl lead compounds

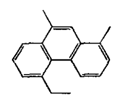
Overview of Forensic Analytical Methods 34

Semivolatile GC/MS: Diagnostic Homo- and Heterocyclic PAH

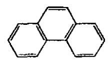
- Diagenic Sources
  - Biologically Mediated
  - Natural
- Petrogenic Sources
  - Petrogenesis
  - Refining
- Pyrogenic Sources
  - Partial Combustion
  - Carbonization (Coal Tars)
  - Pyrolysis
  - Pyrosynthesis



Retene



1,9-Dimethyl-
7-ethyl phenanthrene



Phenanthrene

Overview of Forensic Analytical Methods 35

Compound	Surrogate/ Internal Standard Reference	Compound	Surrogate / Internal Standard Reference
Naphthalene (C0N)	1, A	Benzo[a]anthracene (BAA)	3, B
C1-Naphthalenes (C1N)	2, A	dihydroabietane	
C2-Naphthalenes (C2N)	2, A	Chrysene (C0C)	3, B
C3-Naphthalenes (C3N)	2, A	C1-Chrysenes (C1C)	3, B
C4-Naphthalenes (C4N)	2, A	C2-Chrysenes (C2C)	3, B
		C3-Chrysenes (C3C)	3, B
Acenaphthene (ACE)	2, A	C4-Chrysenes (C4C)	3, B
Acenaphthylene (ACEY)	2, A		
Biphenyl (BIP)	2, A	Benzo[b]fluoranthene (BBF)	4, B
Dibenzofuran (DF)		Benzo[k]fluoranthene (BKF)	4, B
Fluorene (C0F)	2, A	Benzo[a]pyrene (BAP)	4, B
C1-Fluorenes (C1F)	2, A	Benzo[e]pyrene (BEP)	4, B
C2-Fluorenes (C2F)	2, A	Perylene (PER)	4, B
C3-Fluorenes (C3F)	2, A	Indeno[1,2,3-c,d]pyrene (IND)	4, B
		Dibenzo[a,h]anthracene (DAH)	4, B
Dibenzothiophene (C0D)	3, A	Benzo[g,h,i]perylene (BGP)	4, B
C1-Dibenzothiophenes (C1D)	3, A		
C2-Dibenzothiophenes (C2D)	3, A	Benzo[j]fluoranthene (BJF)	4,B
C3-Dibenzothiophenes (C3D)	3, A	Benzo[a]fluoranthene (BAF)	4,B
C4-Dibenzothiophenes (C4D)			
Phenanthrene (C0P)	3, A	**Surrogate Compounds**	
Anthracene (C0A)	3, A	Naphthalene-d8 (D8N)	1, A
C1-Phenanthrenes/Anthracenes (C1P/A)	3, A	Acenaphthene-d10 (D10ACE)*	2, A
C2-Phenanthrenes/Anthracenes (C2P/A)	3, A	Phenanthrene-d10 (D10PH)	3, A
C3-Phenanthrenes/Anthracenes (C3P/A)	3, A	Benzo[a]pyrene-d12 (D12BAP)	4, B
C4-Phenanthrenes/Anthracenes (C4P/A)	3, A	*or Chrysene -d12	
Retene	3,A	**Recovery Standards**	
tetrahydroretene		Fluorene-d10 (D10FL)*	A
Fluoranthene (FLANT)	3, A	Chrysene-d12 (D12C)*	B
Pyrene (PYR)	3, A	*or Acenaphthene-d10(D10ACE)	
C1-Fluoranthenes/Pyrenes (C1F/P)	3, A	* or Fluorene-d10 (D10FL)	
simonellite		* or Benzo[a]pyrene-d12 (D12BAP)	
dehydroabietin			

Representative PAH Target List For Forensic Applications

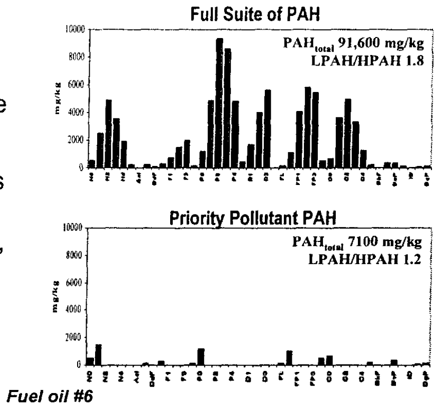
- Priority Pollutant PAH
- Alkyl Homologues
- Other Hetrocyclic PAHs

(Numerous Publications & Federal Register 40CFR Subchapter J, Part 300, Subpart L, Appendix C, par. 4.6.3 to 4.6.5)

Overview of Forensic Analytical Methods 36

Advantages of Measuring an Extended List of PAH and Alkyl PAH Homologues

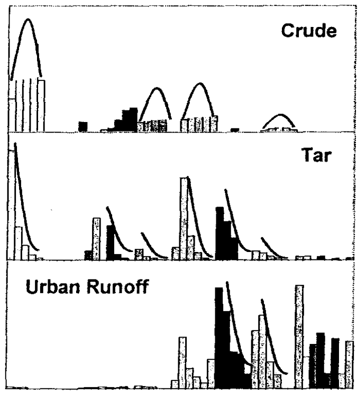
- Standard EPA Method 8270 only measures 16 Priority Pollutant PAH – insufficient to characterize sources of hydrocarbons
- Forensic GC/MS methods focus on >50 PAH, C_1-C_4 alkyl homologues, and S-, N- hetrocyclics



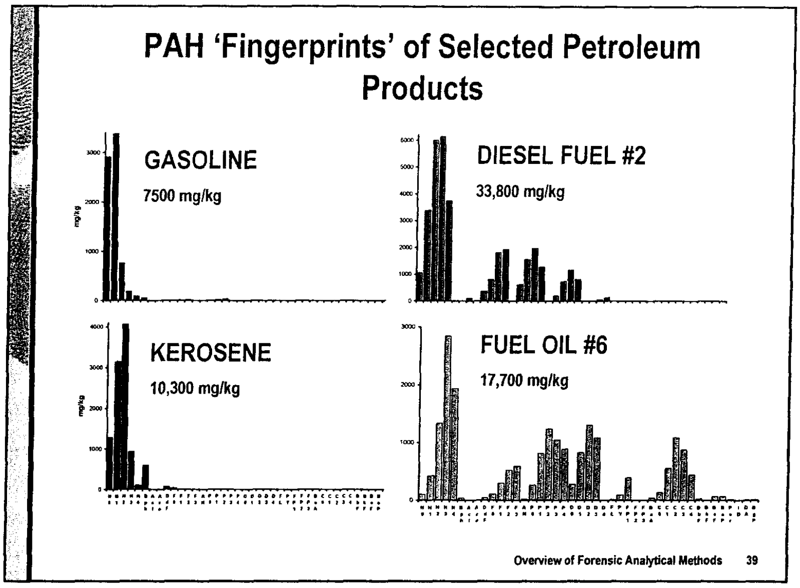
Overview of Forensic Analytical Methods 37

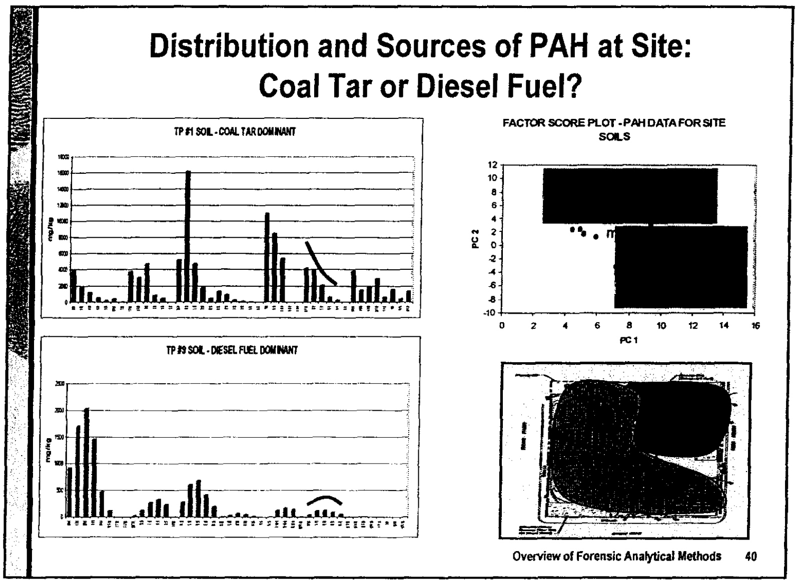
Advanced PAH Analysis Provides Diagnostic "Fingerprint" for Hydrocarbons

- Petrogenic
  - Alkyl > Parent
  - Little 4 to 6 Ring
- Pyrogenic – Type 1
  - Parent > Alkyl
  - High 2 and 3 Ring
- Pyrogenic – Type 2
  - Parent > Alkyl
  - High 4 to 6 Ring



Overview of Forensic Analytical Methods 38

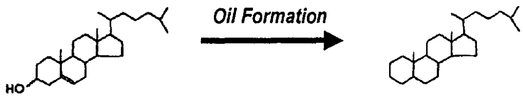

PAH 'Fingerprints' of Selected Petroleum Products
GASOLINE
7500 mg/kg
DIESEL FUEL #2
33,800 mg/kg
KEROSENE
10,300 mg/kg
FUEL OIL #6
17,700 mg/kg
Overview of Forensic Analytical Methods 39


Distribution and Sources of PAH at Site: Coal Tar or Diesel Fuel?
TP #1 SOIL - COAL TAR DOMINANT
TP #9 SOIL - DIESEL FUEL DOMINANT
FACTOR SCORE PLOT - PAH DATA FOR SITE SOILS
PC 2
PC 1
Overview of Forensic Analytical Methods 40

Biomarkers by GC/MS

- *Definition* – organic compounds in oil that structurally resemble biochemical compounds
  - "biomarkers"
  - "biological markers"
  - "molecular fossils"

BIOCHEMICALS **BIOMARKERS**

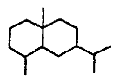


CHOLESTEROL CHOLESTANE

Overview of Forensic Analytical Methods 41

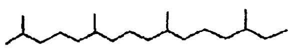
Common Types of Biomarkers

- Sesquiterpanes (C_{15})
  - acyclic & bicyclic



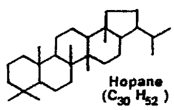
Eudesmane

- Diterpanes (C_{20})
  - acyclic & (bi, tri, tetra) cyclic



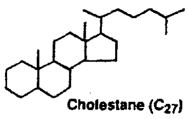
Phytane (C_{20})

- Triterpanes (C_{30})
  - acyclic & (tri, tetra, penta) cyclic



Hopane ($C_{30}H_{52}$)

- Steranes (C_{30})

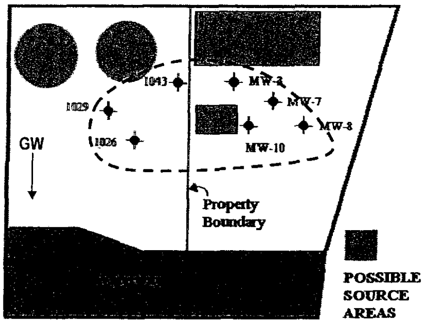


Cholestane (C_{27})

Overview of Forensic Analytical Methods 42

Example –
Using Biomarkers in Contaminant "Mapping"

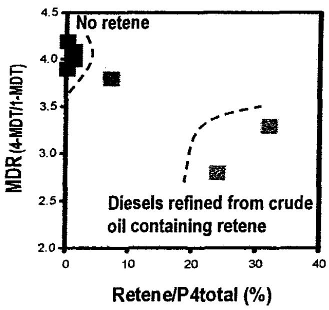
- NAPL(s) exist across adjacent sites
- Exhibit variable degrees of weathering
- Multiple source areas on each site

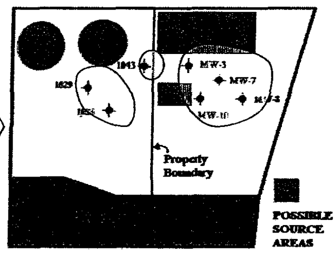


What is the source(s) of NAPL contamination?

Overview of Forensic Analytical Methods 43

Selected Biomarker Ratios Reveal
Three Types of Middle Distillates Exist



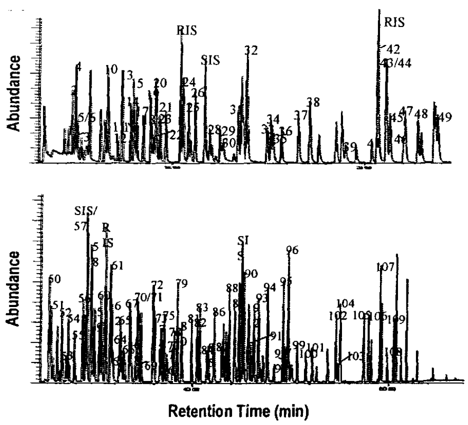


Geographic distribution of NAPL 'types' supports a scenario for distinct source areas and a mixing region near the property boundary.

Overview of Forensic Analytical Methods 44

Volatile Hydrocarbons: Advantages of Measuring >PIANO Compounds by GC/MS

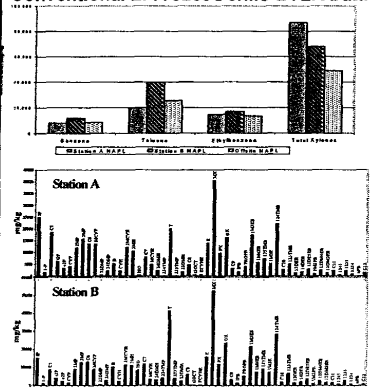
- Standard EPA Method 8260 only measures BTEX Priority Pollutants insufficient to characterize complex gasoline-range hydrocarbons.
- Forensic GC/MS methods focus on >100 Paraffins, Isoparaffins, Aromatics, Napthenes, Olefins (PIANO) and important gasoline additives.
- Forensic data allow compositional differences to be identified.



Overview of Forensic Analytical Methods 45

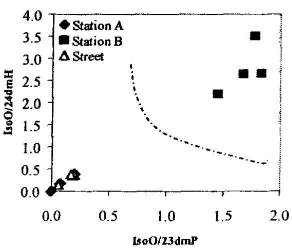
Volatile Hydrocarbons: Advantages of Measuring >PIANO Compounds by GC/MS

Conventional EPA 8260GC/MS BTEX Data



Forensic GC/MS PIANO Data

- Conventional EPA 8260 GC/MS BTEX data unable to depict compositional features among NAPL gasolines.
- Forensic GC/MS PIANO analysis reveals compositional differences (and similarities) among site NAPLs and offsite NAPLs in street.



Isotopic Composition of Hydrocarbons in Environmental Forensics

- The principal "building blocks" of hydrocarbon compounds—carbon and hydrogen—as well as common heteroatoms—e.g., sulfur and nitrogen—exist in nature as mixtures of stable isotopes
- The ratios of these isotopes are a function of the geologic origin of the hydrocarbons
- Isotope ratios are conventionally expressed as delta values (δ) in units of parts per million
- Isotope ratio values are negative if the $^{13}C/^{12}C$ ratio is lower than the standard value (0‰) and positive if the $^{13}C/^{12}C$ ratio is greater than the standard value:

$$\delta^{13}C(‰) = \frac{^{13}C/^{12}C\ \text{sample} - {}^{13}C/^{12}C\ \text{standard}}{^{13}C/^{12}C\ \text{standard}} \times 1000$$

Overview of Forensic Analytical Methods 47

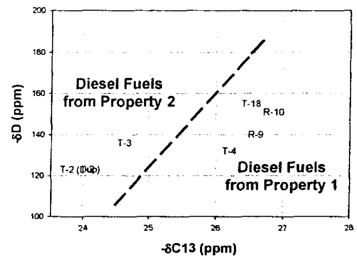
Isotopic Composition of Hydrocarbons in Environmental Forensics

- Traditional applications of isotope composition in forensics has focused on the features of "whole products" (r.e., reference samples or NAPLs)
- Gas Chromatography-Isotope Ratio Mass Spectrometry (GC-IRMS)
  - Measures isotope ratios for individual hydrocarbon compounds after they have been separated by a gas chromatograph
  - Provides a means for developing isotopic source information ("fingerprinting") on a compound-specific basis

Overview of Forensic Analytical Methods 48

Bulk Isotopic Features in Environmental Forensics

- The most commonly measured bulk (whole product) isotope ratios are carbon and hydrogen
- Isotopes measured using a dual collecting mass spectrometer
- Sample is combusted with catalyst to produce CO_2 and H_2O
- Carbon dioxide is measured in the mass spectrometer for masses 44($^{12}C^{16}O_2$), 45($^{13}C^{16}O_2$) and the $^{13}C/^{12}C$ ratio
- The water produced during combustion is converted to hydrogen gas, and measured in the mass spectrometer as ($^1H_2$) and (DH)
- Isotope ratios for carbon can be measured with a precision of ±0.2‰ and for hydrogen with a precision of ± 2.0‰

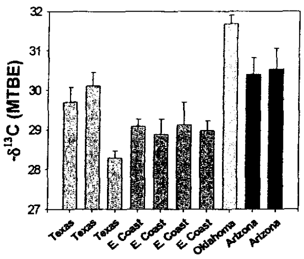


Example: NAPLs found in pools beneath adjoining bulk fuel storage facility sites—both comprised of weathered diesel fuel—were shown to arise from distinct sources, based on bulk isotope features.

Overview of Forensic Analytical Methods 49

Compound-Specific Isotopic Features in Environmental Forensics: GC/IR-MS

- Volatile and semi-volatile organic compounds are amenable to GC/IR-MS
- Compounds in samples separated by GC, then individually combusted with catalyst to produce CO² (for $\delta^{13}C$) and water (for δD)
- Other combustion catalysts available for other isotopes (e.g., N, Cl)
- Precision of better than ±~2%
- Biodegradation results in isotopic fractionation, so isotope measurements of field samples must be used cautiously



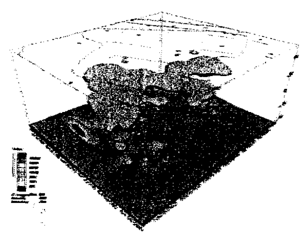
Example: GC/IR-MS was used in a recent investigation to determine that there are regional differences in the isotopic composition of MTBE in dispensed gasolines[1].
The results indicated that that GC/IR-MS has utility in spill-source correlation analysis in MTBE contamination investigations.

[1]Smallwood et al. 2001. *Env. Forensics,* 2:215-221

Overview of Forensic Analytical Methods 50

Summary

- Molecular characterization remain the cornerstone of environmental forensics investigations at hydrocarbon-contaminated sites
  - Gas Chromatography
  - Gas Chromatography/Mass Spectrometry
- Design a Phased Approach
  - Integrate the analytical program with other elements of the investigation (e.g. site geology, records research, regulatory changes)
  - Develop an analytical program that meets the goals of the investigation
  - Understand the Analytical Toolbox and available options
- Consider emerging analytical techniques that allow you to "peel back more of the onion"
  - Isotope ratio mass spectrometry
  - Organic petrographic analysis
  - Multi-dimensional gas chromatography



Overview of Forensic Analytical Methods 51