Environmental Forensics: Employing 2-Dimensional Gas Chromatography/Mass Spectrometry (GCxGC/MS) to Predict Environmental Weathering of Oil and Tar

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I. Introduction

Pollution from petroleum sources and coal tar is the result of naturally occurring and unintended seepages; collection, transport, storage and manufacturing activities; and from incomplete combustion sources. When these products are released into the environment, they are subject to a number of weathering factors including physical (evaporation, adsorption, dissolution, and emulsification), biological (microbial degradation), and chemical (photo- and oxidative degradation), all of which can significantly change the chemical composition of the source material over time. Understanding how local environments impact weathering is critical to determining if natural attenuation is sufficient to reduce pollutant impact on the environment or if active remediation is required. To make this determination, the compositional effects of dissolution, organic phase partitioning, and evaporation must be known; each of which can be examined by studying the aqueous solubility (S_W), octanol-water partition coefficient (K_{OW}), and vapor pressure (V_P) of sample components, respectively.

A novel approach for estimating these physical properties from comprehensive 2-dimensional gas chromatography/mass spectrometry (GC×GC/MS) retention data is presented. A polyparameter linear free energy relationship (LFER) model was developed to correlate each compound's retention index with the aforementioned physical properties. The model employs isovolatility curves to generate accurate and precise retention indices for families of homologous compounds, leading to better estimates of their physical properties. Findings indicate that the physical property estimates produced by this approach have the same error on a logarithmic-linear scale as previous researchers' log-log estimates, yielding marked improvement in their property estimates. A new software program was developed that automates the determination of these properties for each compound in the sample from a single GC×GC analysis of that sample. This process produces component maps that we use to discern the mechanism and progression of how a particular site weathers due to dissolution, organic phase partitioning, and evaporation resulting from local conditions. Outcomes support hazardous waste site investigation and cleanup projects by providing quantitative data of pollutants by GC×GC/MS. This approach can be used by researchers in a wide range of disciplines, including toxicology (bioaccumulation and toxicity studies) and restoration (ecological and urban planning studies).

Compound/Homologue	GC×GC/MS (µg/g)	GC/MS (µg/g)	% RPD	2.5×AL (µg/g) and [1](RPD)
Naphthalene	0.7	0.7	0	5 (100)
C_1 Naphthalenes	8.0	10	-20	
C_2 Naphthalenes	15	19	-21	
C_3 Naphthalenes	11	11	0	
C_4 Naphthalenes	4.4	2.1	110	
Fluorene	25	23	9	35 (100)
C_1 Fluorenes	24	21	14	
C_2 Fluorenes	13	9.7	34	
C_3 Fluorenes	2.9	0.8	263	
C_4 Fluorenes	1.6	ND	N/A	
Phenanthrene/Anthracene	93	84	11	355 (100)
C_1 Phenanthrenes	78	87	-10	
C_2 Phenanthrenes	20	24	-17	
C_3 Phenanthrenes	5.5	6.8	-19	
C_4 Phenanthrenes	1.3	0.5	160	
Benzo(a)anthracene/Chrysene	29	34	-15	0.25 (60)
C_1 Chrysenes	27	37	-27	
C_2 Chrysenes	3.0	3.3	-9	
C_3 Chrysenes	0.8	ND	N/A	
C_4 Chrysenes	ND	ND	N/A	
Pyrene/Fluoranthene	73	72	1	262.5 (100)
C_1 Pyrenes	61	76	-20	
C_2 Pyrenes	17	22	-23	
C_3 Pyrenes	4.2	1.9	121	
C_4 Pyrenes	1.1	ND	N/A	
C_1 2-Ring PASH	2.0	2.3	-13	
C_2 2-Ring PASH	3.6	4.3	-16	
C_3 2-Ring PASH	4.3	4.7	-9	
C_4 2-Ring PASH	1.4	1.3	8	
Dibenzothiophene	22	20	10	
C_1 3-Ring PASH	30	29	3	
C_2 3-Ring PASH	22	19	16	
C_3 3-Ring PASH	9.7	7.3	33	
C_4 3-Ring PASH	1.9	0.6	217	
C_1 4-Ring Fused PASH	17	14	21	
C_2 4-Ring Fused PASH	7.3	6.6	11	
C_3 4-Ring Fused PASH	0.7	ND	N/A	
C_4 4-Ring Fused PASH	0.6	0.8	-25	
C_1 4-Ring Condensed PASH	7.3	6.1	20	
C_2 4-Ring Condensed PASH	3.5	3.2	9	
C_3 4-Ring Condensed PASH	6.7	6.0	12	

References

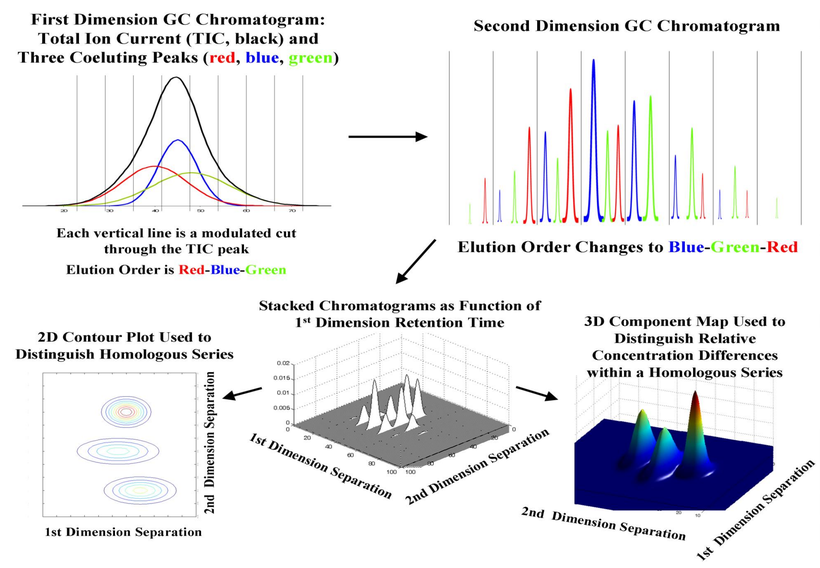
New Spectral Deconvolution Algorithms for the Analysis of Polycyclic Aromatic Hydrocarbons and Sulfur Heterocycles by Comprehensive Two-Dimensional Gas Chromatography-Quadrupole Mass Spectrometery, P.M. Antle, C.D. Zeigler, Y. Gankin, and A. Robbat, Jr., Analytical Chemistry, 85, 10369-10376, 2013

Two-dimensional gas chromatography/mass spectrometry, physical property modeling and automated production of component maps to assess the weathering of pollutants, P.M. Antle, C.D. Zeigler, D.G. Livitz, A. Robbat Jr., Journal of Chromatography A. 1364: 223-233, 2014.

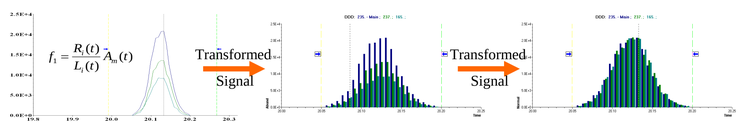
Using comprehensive two-dimensional gas chromatography retention indices to estimate environmental partitioning properties for a complete set of diesel fuel hydrocarbons, J.S. Arey, R.K. Nelson, L. Xu, C.M. Reddy, Anal. Chem. 77 (2005) 7172–7182

II. Technology

Comprehensive GC/MS, GCxGC/MS, is a leading-edge separation technique. All of the effluent from the first-dimension column is focused in many narrow fractions at regular intervals and subsequently injected onto a second capillary column.



Ion Analytics™ software visualizes extracted ion abundances as a histogram and normalizes them to the expected ion ratio of the target compound. Compound identity confirmation is automatically achieved according to spectral deconvoution algorithms that subtract background noise and match sample with library spectra.

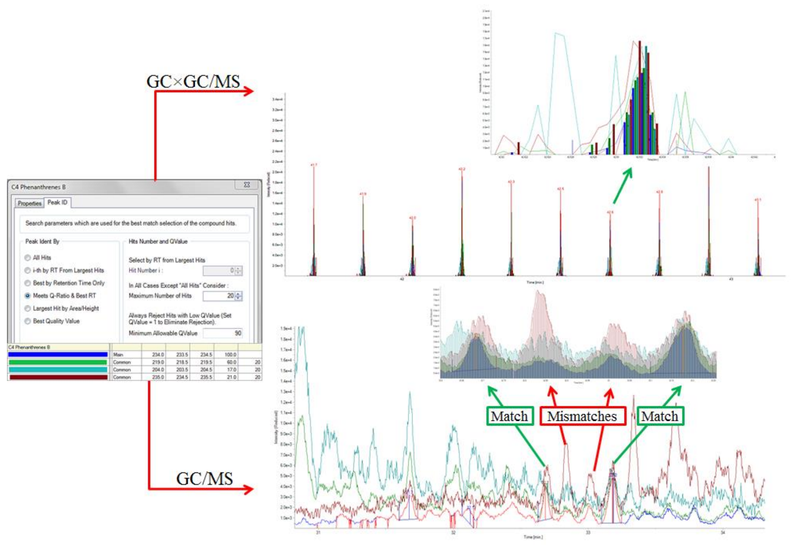


$$F_1(t) = \max_{i \le N}[f_i(t)] - \min_{j \le N}[f_i(t)] \qquad F_2(t) = \frac{\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}|f_i(t) - f_j(t)|}{\sum_{i=1}^{N-1} i} \qquad F_3(t) = \max_{i \le N}\frac{df_i(t)}{dt} - \min_{j \le N}\frac{df_j(t)}{dt}$$

Target Compound Identities Confirmed When

Equations Produce Scan-to-Scan Relative Errors Less Than Analyst Established Values

The combination of spectral deconvolution software with modern fast-scanning quadrupole mass spectrometers has allowed the first quantification of pollutants by GCxGC/qMS. A minimum of three modulations-per-compound and five scans-per-modulation was found to produce results in agreement with GC/MS analysis of parent PAH within 20% RPD, however sensitivity was increased 5-fold and GCxGC/MS provided much higher resolution.



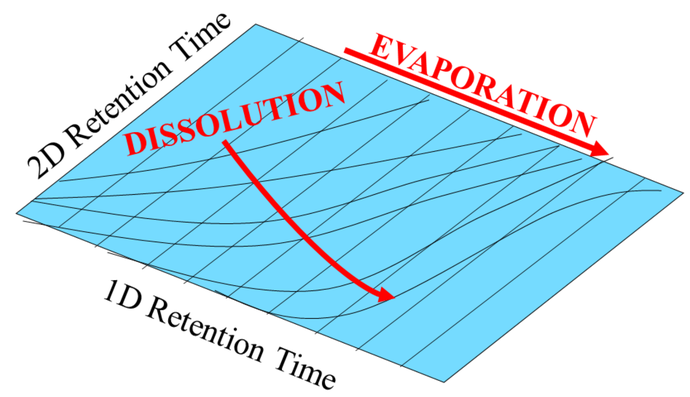
PAH	*RF*		r^2		LOD (ng/g)	
	1D	X	1D	X	1D	X
Naphthalene	0.89	1.04	1.00	0.99	56.7	5.7
Acenaphthylene	1.18	1.19	0.99	0.99	69.8	10.7
Acenaphthene	0.86	1.09	1.00	0.99	24.3	5.7
Fluorene	0.92	0.65	0.99	1.00	171.0	7.5
Dibenzothiophene	0.77	0.68	1.00	1.00	91	19.3
Phenanthrene/Anthracene	0.88	0.93	0.99	1.00	26.5	7.3
Fluoranthene	0.80	0.88	0.99	1.00	92.5	5.5
Pyrene	0.88	0.95	1.00	0.99	105.4	6.3
B(a)A/Chrysene	0.75	1.10	0.99	1.00	86.4	22.3
Benzo(b/k)fluoranthene	0.74	0.73	0.99	0.99	125.9	13.5
Benzo(a)pyrene	0.75	0.74	0.99	0.99	102.0	17.7
Indeno(1,2,3-c,d)pyrene	0.76	0.76	0.99	1.00	149.1	34.2
Dibenz(a,h)anthracene	0.66	0.53	0.99	1.00	161.6	28.0
Benzo(g,h,i)perylene	0.79	0.76	0.99	1.00	117.1	35.8

III. Weather Maps

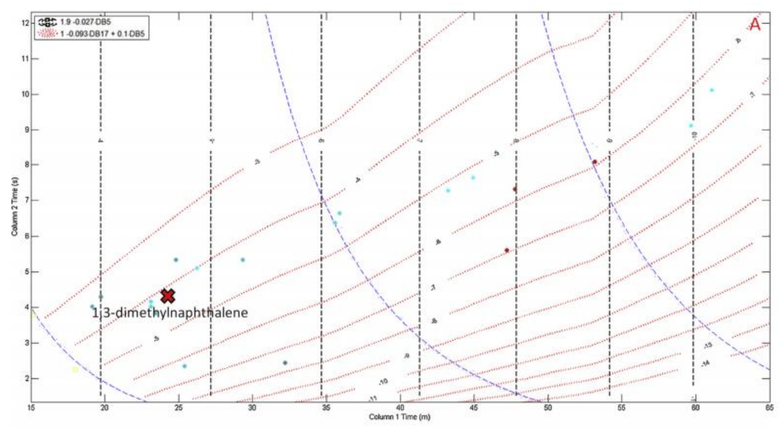
Understanding the impact that weathering processes have on hydrocarbon contamination is essential in risk assessment, forensic analyses and liability studies. GCxGC/MS offers the ability to visualize dissolution and evaporation processes based on retention characteristics on compounds on the 2D chromatogram.

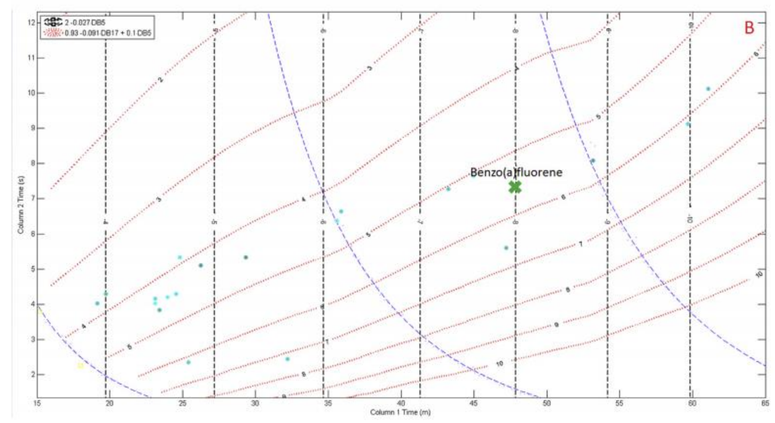
Conceptual Coal Tar Model

- are components volatizing?
- has dissolution stopped?
- what is bioaccessible/available?
- is remediation necessary?



Weathering effects were estimated via LFER based on compound's aqueous solubility (S_W), octanol-water partition coefficient (K_{OW}), and vapor pressure (V_P). These physical properties were linked to a compound's retention index, allowing component maps to be drawn that predict the progression of weathering based on site conditions (e.g. arid climate vs. high soil water content).





GCxGC/MS was used to create the 3D component maps for a "fresh" coal tar, collected from an underground storage tank protected from the environment and from soil contaminated with coal tar outside of the tank. The figures depict changes in volatility and solubility for the sample as it undergoes weathering