

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF COAL LIQUEFACTION
PROCESS STREAMS USING NORMAL-PHASE SEPARATION WITH DIODE ARRAY
DETECTION.

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INTRODUCTION:

Since its introduction as an analytical method in the late 1960s and early 1970s, high performance liquid chromatography (HPLC) has become widely used in environmental studies, especially for the analysis of PAHs^{1,2}. PAHs are widespread environmental contaminants and much effort has been devoted to the development of liquid chromatographic columns which are sensitive to PAH separation. Reverse-phase HPLC on chemically bonded C₁₈ has become the method of choice for the separation of PAHs³⁻⁶, and a review by Wise *et al.*¹ has described general protocols for the separation of PAHs using reverse-phase HPLC. However, direct analysis of PAHs in complex fuel mixtures using reverse-phase HPLC is complicated as sample preparations have become elaborate, due in large part to the fact that most complex organic materials contain compounds that are not usually miscible in acetonitrile, the solvent of choice for reverse-phase HPLC separations of PAHs. These materials routinely are fractionated first into general compound class categories⁷ (i.e. aliphatics, polar compounds, aromatics, resins, and asphaltenes) before separation of PAHs can be performed, and usually normal-phase HPLC is relegated to general cleanup and isolation of the total PAH fraction. The development of "charge-transfer" stationary phases for separation of π -electron rich PAHs⁸⁻¹⁰ allows for the separation of PAHs and their isomers in the normal-phase using solvents which are generally miscible with complex organic systems.

Another problem associated with HPLC analysis of complex fuel mixtures and other extracts of natural samples is that, in the past, normal-phase and reverse-phase HPLC have depended upon either fluorescence detection or monochromatic UV absorbance detection. Fetzer and Biggs² have pointed out, these detection methods are too selective and many compounds go unobserved due to varying optimal wavelengths for different compounds. Developments in the last fifteen years of a full spectrum UV absorbance detector (i.e. diode array detector or DAD) enable full spectrum detection of HPLC eluates. A distinct advantage of the diode array HPLC technique, which provides UV spectra of separated fractions as a function of time, is its ability to identify, by spectral comparisons, the molecular components of the eluates, including the isomers of PAHs.

In this paper, we demonstrate a sensitive method for the detection and analysis of PAHs in coal liquefaction process stream samples. This is accomplished by the normal-phase separation of PAHs and their alkylated derivatives using a TCPP-modified silica column⁸ (Hypersil Green PAH-2) in combination with UV-diode array detection. This method allows for a more sensitive detection and efficient separation of multi-ring PAHs and their isomers without elaborate sample preparations or on-line coupling of a reverse-phase HPLC system.

EXPERIMENTAL:

Instrumentation: The dilute coal liquefaction process stream samples were analyzed and separated using a Waters 600E HPLC and Waters 991 photodiode array detector. The column used for HPLC separations was a Hypersil Green PAH-2 column purchased from Keystone Scientific, Inc.(Bellefonte, PA).

Mass spectral data were collected for each fraction using the solids injection probe of a Kratos MS-80 double-focusing high-resolution mass spectrometer. The ionization mode on the mass spectrometer was electron impact (EI, 70 eV). Instrument control and data collection were accomplished by using a computer-aided Data General DS90 software system.

Sample Description: A standard consisting of a mix of 16 PAH's was obtained from Supelco, Inc., Bellefonte, PA. The coal derived liquids used for two-dimensional, normal phase HPLC separation, were supplied by CONSOL, Inc. and consisted of five liquefaction process streams representing different liquefaction systems, different feed coals, and different degrees of catalytic activity (Table I).

Procedure: The standard PAH mix is subjected to HPLC analysis to derive response factors for internal standard quantitative calculations. The internal standards were benzo[b]fluoranthene and benzo[g,h,i]perylene, which were added to each diluted coal liquefaction stream sample at an appropriate concentration level. The former was used as the internal standard for samples 1, 2, and 3 because the compound elutes in a region containing few intense peaks in the sample eluates. For samples 4 and 5 we used the latter internal standard because some significant peaks were observed in the elution range of benzo[b]fluoranthene and these would co-elute with the standard.

The coal liquids are then filtered through 0.2 μ m filters (Supelco brand ISO-DISC N-32 3mm diameter, nylon membrane, 0.2 μ m pore size filters) in order to remove any insoluble

material. The column, equilibrated with 100% hexane, was operated in the gradient elution mode. Samples are injected onto the PAH-2 column, and following an initial 10 minute isocratic period, a linear gradient from 100% hexane to 100% dichloromethane is used up to 80 minutes followed by a final hold for 5 minutes.

RESULTS AND DISCUSSION:

Knowing that coal liquefaction process streams contain numerous amounts of polynuclear aromatic hydrocarbons and that the PAH-2 column successfully separated PAHs in a known standard, we had reason to be optimistic about its use for coal process stream liquids. The separation obtained for liquefaction process stream samples is demonstrated by 1-D maxplots in Figure 1. Peak identifications listed in Table II were made by comparison of retention times with the PAH standard and by fraction collection combined with heated probe/mass spectrometry. The use of the latter method was deemed necessary, because many peaks did not have retention times that coincided with those of compounds in the standard, notably the alkylated PAHs.

In general, the HPLC traces are characterized by both sharp peaks identified in Table II and broad regions representing unresolved components. The broad region of unresolved peaks between 0 and 20 minutes is constituted predominantly by two and three ring aromatics as determined by mass spectrometry. Most of the compounds are alkylated PAHs having very similar UV spectra, and some compounds are alkylated hydronaphthalenes. The second broad region of absorbance extends from 20 minutes retention time through to the end of the run, containing multiring PAHs and alkylated PAHs having from three to nine condensed rings. The most notable peaks (7, 8 and 9) are those of pyrene and its multialkylated homologs, the internal standard, benzo(b)fluoranthene (peak 11), benzo(g, h, i)perylene (peak 12), and coronene (peak 16).

We can ascribe several important features to each chromatogram, but basically three samples (sample 1 and sample 2), the pressure filtered liquids, show very similar characteristics and differ markedly as a group from the chromatograms of the composite heavy distillates, samples 4 and 5.

Although the three pressure filtered liquid (PFL) samples from the HRI facility generally show similar features, there are subtle differences in the relative distributions of compounds reflecting process conditions. The chromatogram of sample 1, a PFL from the liquefaction of the Wyodak/Anderson coal, differs from those of sample 2 and sample 3 which were obtained from liquefaction conditions using the Illinois #6 coal as feedstock. While pyrene and alkylated pyrenes are major components of all three samples, the two process streams from the Illinois #6 coal contain relatively larger amounts of PAHs with more than four rings, compared with the sample from the Wyodak/Anderson coal. This is perhaps due to the fact that the Illinois #6 coal is of higher rank. All three samples contain significant chromatographic intensity in the two broad unresolved regions described previously. Compared with sample 3, sample 2 appears to contain more intensity in the broad unresolved region in the early eluting portion of the chromatogram ascribed to two and three-ring PAHs. This could indicate that there is a relative build up of more refractory multi-ring material as Run CC-16 progressed.

The chromatograms (maxiplot) for the two high temperature distillates shown in Figure 1 differ from the chromatograms of pressure filtered process streams in that they contain a predominance of compounds with generally fewer than five rings and virtually no compounds with more than five rings other than coronene. This data is consistent with the gc/ms data presented elsewhere¹³. The dominant peaks are those of pyrene and its alkylated homologs (peaks 7 and 8) and dihydro-benzopyrene and its alkylated homolog (peaks 9 and 10). Wyodak coal (sample 5) appears to yield a higher proportion of dihydro-benzopyrene than Illinois #6 coal (sample 4) in its high temperature distillate. This is also consistent with the gc/ms data¹³. Unresolved components dominate the early part of the chromatogram but not the later retention time range. Unlike the pressure filtered process streams, the distillates contain no significant "hump" for unresolved components between retention times of 40 and 80 min. Obviously, the samples from the Wilsonville facility, comprised of distillates boiling below 850°F, contain lower boiling PAHs, in contrast to the samples obtained from the HRI facility which were not subjected to distillation. This is also demonstrated by the solubility data (Table I), in that samples 1, 2, and 3 have lower solubilities, consistent with higher molecular weight components, compared to the higher solubilities of samples 4 and 5, consisting of lower molecular weight components.

Table II contains the quantitative data for the five samples. As mentioned above, the dominant compounds exist as 1-3 ring aromatic/hydroaromatic compounds of undetermined structure. These account for more than half of the products detected. Other multiring PAHs individually account for between 0.05% and 1.3 % of the sample weights of the samples 1-3. Summing of the concentrations of peaks 1-19 in each chromatogram for samples 1-3 reveals that 18% to 32% of the sample weights can be accounted for as detected PAHs. Samples 1 and 2, filtered process streams from two different coals at the HRI facility, appear to have similar overall concentrations of PAHs, even though the distributions are slightly different as mentioned above. The difference between samples 2 and 3, from the same coal, appear to be related to changes in process time, since they represent samples taken from different days. Samples 4 and 5, from the Wilsonville reactor, appear to have significantly lower concentrations of all detected compounds, ranging from 0.007% to a maximum of 2.3%. The significant decrease in concentrations compared to the samples from the HRI facility is indicative of the differences in liquefaction methodology. Not only are the yields of PAHs lower, but the distributions are different, as discussed previously. The low yields initially seemed puzzling, but examination of the gc/ms data presented in a previous report¹³ indicates that significant amounts of unresolved complex materials having intense *m/z* fragment ions characteristic to structures of C_nH_{2n-3} are present. It is likely that the parent compounds of these fragment ions do not yield significant

absorptions in the UV range, thus, explaining why they remain undetected by the HPLC method. If the compounds are undetectable by UV-absorption, then they fall out of our analytical window, a pitfall for this method.

CONCLUSIONS:

The results outlined in this report from experiments performed in our laboratory have proved very encouraging. We were successful in the separation, characterization, and quantification of PAHs of a limited series of select samples which depict a broad range of liquefaction process conditions, using a newly developed normal-phase HPLC column, the Hypersil PAH-2, coupled with a UV-diode array detector. We feel this method has great potential for the characterization of liquefaction process streams along with other extracts of natural products containing high concentrations of PAHs. The success of this method was based on the fact that it enabled us to identify both qualitative and quantitative differences among the limited sample set. Perhaps the most readily observed differences are noted between samples obtained from the HRI facility and the Wilsonville facility. Thus the technique can readily distinguish between sample types from these two liquefaction facilities, regardless of the feed coal used. Those compounds detectable by HPLC from the Wilsonville samples, 850°F distillates, appear to be of lower ring number than samples from the HRI facility, whose samples are composed of the whole process stream.

The HPLC method also allows differentiation among samples from the same facility but differing in their process conditions. For example, a different distribution of PAH's was obtained from the process stream samples in which different coal feedstocks were used. The sample liquefied from the Illinois #6 coal appears to have a higher amount of the multi-ring PAH's than the sample from the Wyodak, consistent with the fact that higher rank of coal is more likely to yield more of the higher condensed ring compounds. Another difference between samples indicative of differences in process conditions is that between samples 2 and 3. The former contains a significantly greater concentration of PAH's and, as a result, more of the sample can be quantified. The PAH distributions are similar, in a relative sense, which is indicative of the fact that the entire spectrum of PAH's is being reduced by the processing and could indicate a build-up of more refractory material as the run progressed. Subsequently, time resolved differences induce an overall decrease in PAH levels, which could be related to increased hydrogenation of the rings due to increased exposure to liquefaction conditions or to deactivation of the catalyst.

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Table I: General information including percent solubilities for samples 1-5.

Sample #	Sample Designation ¹	Source ²	Run Number and Period	Feed Coal	Comments	Percent Solubility (%)
1	PFL	HRI	CC-15 11	Wyodak and Anderson	filtered process stream	91.7
2	PFL	HRI	CC-16 4	Illinois No. 6	filtered process stream	92.9
3	PFL	HRI	CC-16 13	Illinois No. 6	filtered process stream	92.6
4	V-1067 Dist.	W	257 Composite	Illinois No. 6	heavy distillate	96.8
5	V-1067 Dist.	W	262 Composite	Wyodak and Anderson	heavy distillate	97.6

- 1) PFL = pressure filter liquid; V-1067 Dist. = 850°F- distillate of second-stage flashed bottoms
 2) HRI = Hydrocarbon Research Inc.; W = Wilsonville

Table 2: Assignments and weight percents for peaks labeled in Figure 1

Peak Number	Peak Assignment	Weight % in sample #1	Weight % in sample #2	Weight % in sample #3	Weight % in sample #4	Weight % in sample #5
1	one & two ring hydro-aromatics	8.97	12.6	6.43	1.74	2.36
2	two & three ring hydro-aromatics	16.2	14.4	6.72	2.21	1.42
3	C ₁ -anthracene	0.463	0.397	0.656	0.0470	0.0390
4	phenylmethyl-naphthalene* C ₄ -phenanthrene C ₅ -phenanthrene	0.746	0.504	0.698	0.0590	0.0460
5	dihydro-pyrene	ND	0.115	0.0640	0.0220	0.0380
6	hexahydro-benzopyrene	ND	0.0530	0.0220	0.00700	0.0190
7	pyrene	1.29	1.10	0.887	0.111	0.0980
8	C ₁ -Pyrene* C ₂ -Pyrene C ₃ -Pyrene	0.650	0.598	0.498	0.0660	0.0600
9	dihydro-benzopyrene	0.407	0.563	0.379	0.0530	0.123
10	C ₁ -dihydro-benzopyrene* C ₂ -dihydro-benzopyrene hexahydro-benzo[g,h,i]perylene	0.449	0.387	0.200	0.0180	0.0390
11	benzo[b]fluoranthene	internal standard	internal standard	internal standard	ND	ND
12	benzo[g,h,i]perylene	0.326	0.384	0.349	internal standard	internal standard
13	C ₁ -benzo[g,h,i]perylene	0.148	0.169	0.140	ND	ND
14	C ₂ -benzo[g,h,i]perylene* C ₃ -benzo[g,h,i]perylene	0.0660	0.0960	0.0730	ND	ND
15	dihydro-dibenzopyrene* C ₁ -dihydro-dibenzopyrene C ₂ -dihydro-dibenzopyrene	0.0600	0.109	0.0770	ND	ND
16	coronene	0.246	0.276	0.265	ND	ND
17	dihydro-benzocoronene	0.105	0.151	0.133	ND	ND
18	bisanthene* C ₁ -bisanthene	0.0360	0.0370	ND	ND	0.00200
19	benzobisanthene* C ₁ -benzobisanthene	ND	0.0180	0.0160	ND	ND

ND=not detected

* = predominant contributor

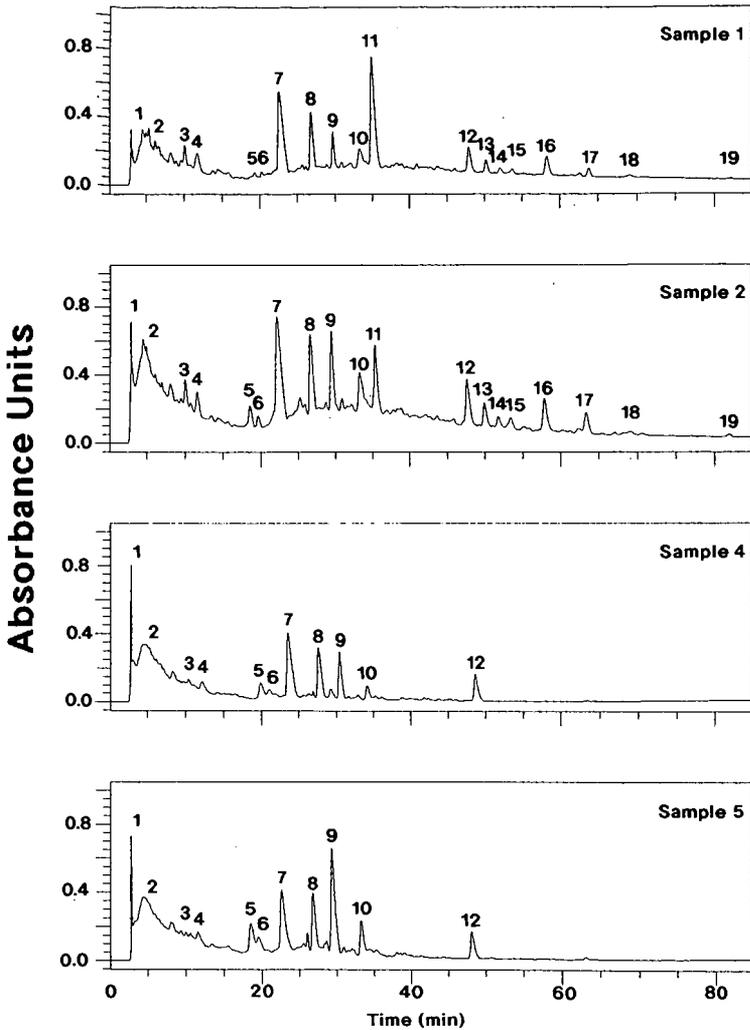


Figure 1. Maxiplots of the HPLC chromatograms for four of the five samples examined. Sample #3 is not included because its chromatogram is similar to that of Sample #2.