

Separation and Characterization of Polycyclic Aromatic Hydrocarbons
and Alkylphenols in Coal Derived Solvents

R. J. Hurtubise, T. W. Allen, and A. Hussain

Chemistry Department

H. F. Silver

Chemical Engineering Department, University of Wyoming
Laramie, Wyoming 82071

Introduction

Polycyclic aromatic hydrocarbons (PAH) and alkylphenols in coal derived solvents are important in the conversion of coal to solvent refined coal (1). A knowledge of the composition of coal derived solvents used in coal liquefaction will allow the adjustment of processing conditions to improve the solvent effectiveness in liquefying coal and thus improve the overall yield of coal derived liquids. Selective and efficient methods are reported for the separation and characterization of PAH and alkylphenols in coal derived solvents.

Experimental

The coal derived solvents were obtained from Wilsonville, Alabama and Tacoma, Washington. The Wilsonville sample was a Wyodak coal derived recycle solvent from which a light distillate (533K-) and a heavy distillate (533K+) were obtained. The Tacoma sample was a Kentucky recycle solvent.

The liquid chromatograph used was a Waters model ALC/GPC 244 equipped with a model 6000-A pump, a U6K injector, a free standing ultraviolet detector set at 254 nm, and a 10-mV strip chart recorder. For normal-phase work, a μ -Bondapak NH₂ column and n-heptane:2-propanol mobile phases were used. For reversed-phase work a μ -Bondapak C₁₈ column was used with methanol: water mobile phases.

All corrected fluorescence excitation spectra were obtained with a Farrand MK-2 spectrofluorometer, a Farrand excitation correction module, and a Farrand Autoprocessor I.

Results and Discussion

Polycyclic Aromatic Hydrocarbons

Dry-column chromatography with an aluminum oxide (activity II-III) stationary phase and a n-hexane-ether (19:1) mobile phase was used to separate PAH by ring size (3-, 4-, 5-, and 6-ring). Prior to the dry-column chromatography step, the coal derived solvents were added to an acid

treated silica gel column and eluted with chloroform. This step removed pyridine-type nitrogen heterocycles (2). Snyder (3) has shown that PAH can be separated according to ring size by using an aluminum oxide stationary phase and a relatively weak mobile phase. These concepts were applied in developing the dry-column chromatographic method for PAH in coal derived solvents. After separation of the individual ring fractions, the fractions were further separated by either thin layer chromatography (TLC) or high performance liquid chromatography (HPLC).

If TLC was used, then after separation fluorescence profiles of each PAH ring fraction distributed on 30%-acetylated cellulose chromatoplates were obtained with a spectrodensitometer. The fluorescence profiles were essentially a plot of fluorescence intensity for a given PAH ring fraction versus distance on the chromatoplate. The profiles were simple in that only one or two fluorescence peaks were obtained. Measurement of fluorescence peak heights gave an approximate measure of the amount of the 3-, 4-, 5-, and 6- ring PAH.

For HPLC separation, the 3- and 4- ring PAH fractions obtained from the dry-column chromatography step were separated with a μ -Bondapak C₁₈ column. Figure 1 shows a typical HPLC chromatogram of a 3-ring PAH fraction from a Wyodak coal derived solvent using a μ -Bondapak C₁₈ column and methanol:water (65:35) mobile phase. Identical separation steps were carried out with the Kentucky coal derived solvent and differences with the Wyodak coal derived solvent were compared. The HPLC separated PAH were characterized by chromatographic correlation factors and corrected fluorescence excitation spectra. The chromatographic correlation factors were described earlier (4). Corrected fluorescence excitation spectra were obtained because they are identical to absorption spectra and allow for ready comparison with literature spectra. In addition, the corrected fluorescence excitation spectra of substances can be obtained at very low concentrations. This is important when small amounts of material are obtained in the several fractions collected in a separation scheme. Figure 2 shows fluorescence excitation spectra for standard fluoranthene and fluoranthene isolated from a Wyodak coal derived solvent using the dry-column chromatography and HPLC steps. Several 3- and 4- ring PAH in coal derived solvents were separated and characterized by the approaches described above. Similar approaches will be used for the 5- and 6- ring PAH.

Alkylphenols

HPLC methods developed previously for ortho and nonortho alkylphenols in coal derived solvents were improved (5,6). A theoretical equation developed by Scott and Kucera (7) was applied for the prediction of retention volumes of alkylphenols and mobile phase compositions which improved the resolution of alkylphenols in normal phase HPLC systems.

Acknowledgement

The support of this research by the U. S. Department of Energy under Contract No. DE-AC01-79ET14874 is gratefully acknowledged.

References

1. D. D. Whitehurst, T. O. Mitchell, and M. Farcasiu, "Coal Liquefaction: The Chemistry and Technology of Thermal Processes," Academic Press, New York, 1980.
2. R. J. Hurtubise and J. D. Philip, Anal. Chim. Acta, 110, 245 (1979).
3. L. R. Snyder, "Principles of Adsorption Chromatography, Marcel Dekker, Inc., New York, 1968.
4. J. F. Schabron, R. J. Hurtubise, and H. F. Silver, Anal. Chem., 49, 2253 (1977).
5. J. F. Schabron, R. J. Hurtubise, and H. F. Silver, Anal. Chem., 50, 1911 (1978).
6. J. F. Schabron, R. J. Hurtubise, and H. F. Silver, Anal. Chem., 51, 1426 (1979).
7. R. P. W. Scott and P. Kucera, J. Chromatogr., 112, 425 (1975).

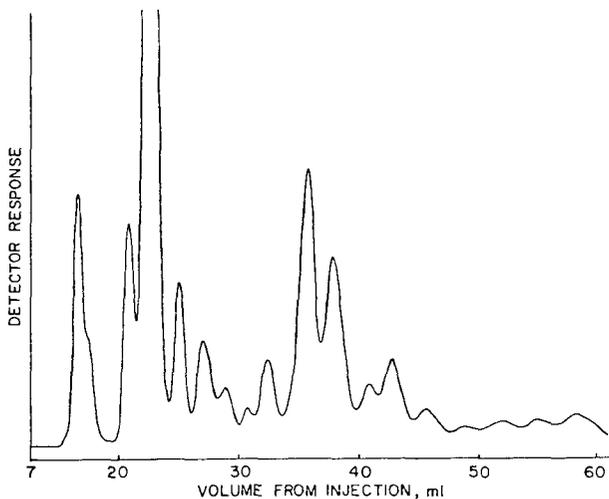


Figure 1. HPLC Chromatogram of 3-Ring PAH Fraction from 533K+ Wyodak Solvent from Willsonville

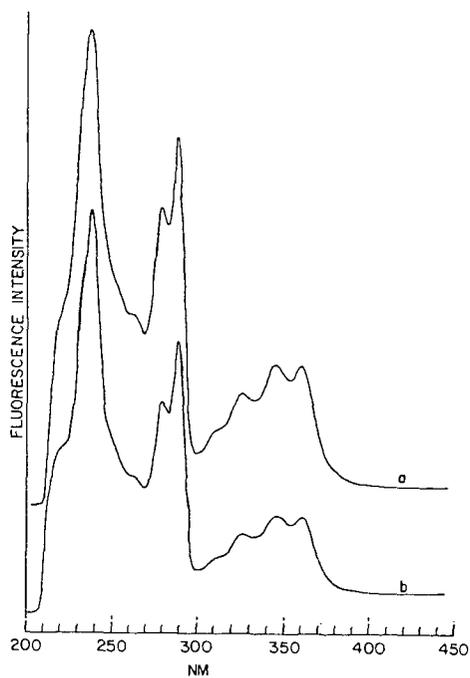


Figure 2. Corrected Fluorescence Excitation Spectra of a Standard Fluoranthene Sample (a) and Suspect Component (b) from HPLC Separation of 533K+ Wyodak Solvent