Journal of Chromatography, 211 (1981) 95–102
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,760

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC STUDIES OF COAL LIQUIDS BY LASER-BASED DETECTORS

MICHAEL J. SEPANIAK and EDWARD S. YEUNG*
Ames Laboratory and Department of Chemistry, Iowa State University, Ames, IA 50011 (U.S.A.)
(Received February 24th, 1981)

SUMMARY

Four solvent-refined coals were studied by isolating the asphaltene fractions, using reversed-phase liquid chromatography and detecting with three independent spectroscopic detectors. Simultaneous chromatograms from a UV absorption detector, a visible fluorescence detector, and a two-photon excited fluorescence detector provide an abundance of information, even though baseline chromatographic resolution is not achieved. The chromatograms were found to be good fingerprints of the individual solvent-refined coals.

INTRODUCTION

The concern over energy resources in the future has generated renewed interest in the conversion of coal to gas and oil. It is important that the conversion product be in a form suitable for efficient energy production and that it retains little, if any, of the impurities[1] that may eventually pollute the environment. To evaluate various coal liquefaction processes, it is necessary to characterize the liquefied products, as well as various intermediates in the processing stream. Such information can lead to the optimization of the processing conditions, improved quality control, reduced environmental pollution, and the understanding of the fundamental chemical reactions involved. Coal liquefaction products include a fraction known as the asphaltenes, which are operationally defined as the pentane-insoluble, benzene-soluble components. The asphaltenes have been postulated as intermediates in the conversion of coal to oil and contain a high concentration of the coal impurities[2]. It is the goal of this work to characterize the asphaltenes derived from various solvent-refined coals (SRCs)[3], so that similarities and differences between various refining processes can be identified.

Current methods for the characterization of coal-derived samples are not very well developed. Proton magnetic resonance (^{1}H NMR) spectroscopy has been used to quantitate the hydroxyl groups in asphaltene samples[4] and ^{13}C NMR spectroscopy has been used to place aromatic carbon atoms into bridgehead, protonated, or substituted categories[5]. Ether oxygen, basic nitrogen, and non-basic nitrogen contents have been determined using a combination of elemental analysis, infrared spectros-

0021-9673/81/0000–0000/$02.50

copy, ^{1}H NMR spectroscopy, and chemical derivatization[6]. Mass spectroscopy and gel permeation chromatography have been used to obtain molecular-weight profiles of coal liquids[7–10]. Preparative-scale liquid chromatography has been used to fractionate coal-derived samples[10–12], but very few examples of high-resolution chromatography have been reported[7,12].

A typical coal-derived asphaltene sample contains hundreds of components, mostly in the 200–800 molecular-weight range. Considering the complexity of these samples, it is imperative to resolve the components as much as possible, to obtain the maximum amount of information for classification purposes. The low volatility of most of the components and the uncertainty about chemical changes at high temperatures preclude taking advantage of the high separatory powers of gas chromatography. Recent advances in microbore columns[13,14] have resulted in extremely high efficiencies in liquid chromatography. Chromatographic runs however can last tens of hours. Also, the reliability, reproducibility, and useful life of these columns for repeated injections of such complex samples have not been adequately tested. We have therefore chosen for these studies standard commercial reversed-phase high-performance liquid chromatographic (HPLC) columns, which, with the proper eluent gradient, are not much lower in efficiency than those mentioned above. The use of a pre-column switching technique significantly prolonged column life and reduced contamination. The use of multidimensional detectors allows the extraction of a maximum amount of information, and the high sensitivity of the detectors allows small injection quantities and again more reliable separation.

Three optical detectors are used for this work, based on the fact that these are sensitive and that they complement one another in the type of information each provides. The first is a conventional UV absorption detector operating at 254 nm. This has a demonstrated detectability in the nanogram range and is a general and versatile detector. The second is a laser-excited fluorometric (LF) detector that has a detectability in the picogram range[15]. In addition to the higher signal levels because of the higher photon fluxes in a laser, the monochromaticity in excitation results in correspondingly narrower Rayleigh and Raman lines and permits larger spectral windows for fluorescence observation[16]. In order to obtain information as different from that in the first detector as possible, visible wavelengths are used in excitation and in emission. This favors the detection of the larger molecules, where conjugation shifts the absorption bands to longer wavelengths. The third is a two-photon excited fluorometric (TPF) detector[17]. A detectability in the nanogram range has been demonstrated with continuous-wave lasers, but picogram levels can be achieved if high-power pulsed lasers are used[16]. The net excitation is into electronic states comparable in energy with those in UV absorption, but the unique selection rules of the TPF process provides complementary information[16]. Furthermore, the TPF process is enhanced when a real electronic state matches the energy of one of the photons, in our case a visible photon. The selectivity again favors the larger molecules with a higher degree of conjugation.

EXPERIMENTAL

Sample preparation

A total of four SRC samples were obtained. Samples of Catalytic Inc. (Wilson-

ville, AL, U.S.A.) SRCs and PAMCO (Fort Lewis, WA, U.S.A.) SRCs were provided by Dr. T. F. Yen of the University of Southern California, and samples of two different Synthoil process SRCs were provided by the DOE Pittsburgh Energy Technology Center (Pittsburgh, PA U.S.A.). The asphaltene fractions were obtained by the procedure of Schweighardt and Thames[18]. The benzene extracts were rotary evaporated to a small volume and then freeze-dried. Solutions were then prepared by dissolving 2 mg of the freeze-dried material per ml of tetrahydrofuran. Appropriate amounts of the internal standards 1,4-diphenyl oxadiazole (TPF standard) and dihydroxyazobenzene derivatized amine (LF standard) were added.

Chromatography

Separations were performed on 25 cm × 4.6 mm C_{18} reversed-phase 10-μm columns (Alltech, Arlington Heights, IL, U.S.A.), and a gradient of 50% to 100% acetonitrile in distilled water was used throughout. The solvent delivery system used consisted of two minipumps (Milton Roy, Riviera Beach, FL, U.S.A.; Model 196-0066-001) and a stirred 50-ml mixing chamber. The mixing chamber initially contained 50% acetonitrile solution and one of the pumps was used to deliver this to the column at a rate of 1.0 ml/min. When the volume in the mixing chamber reached 40 ml the sample was injected through a 20-μl injection loop (Rheodyne, Berkeley, CA, U.S.A.; Model 7010). When the volume reached 35 ml the second pump was turned on to deliver acetonitrile (Burdick & Jackson, Muskegon, MI, U.S.A.; LC grade) to the mixing chamber at a rate of 1.0 ml/min. Using these conditions the mixing chamber compositions at 25, 50, and 75 min after injection were 72, 86, and 93% acetonitrile. An average relative standard deviation in retention time of 2.2% was obtained when several polynuclear aromatic compounds were tested. In the actual studies, contamination from the "dirty" asphaltene samples affects the column backpressure and produces eluent flow-rate variations which limit chromatographic reproducibility and the useful life of the columns.

To improve reproducibility, a 4.5 cm × 2.4 mm pre-column filled with Corasil C_{18} 37-44 μm packing (Waters Assoc., Milford, MA, U.S.A.) was used in the configuration in Fig. 1. A new pre-column was used each time and was switched off-stream 4 min after the injection, thereby trapping components that would be difficult or impossible to elute from the analytical column. The pre-column was kept small in volume to avoid band broadening, but had a capacity sufficient for these sample sizes. After each run, the analytical column was reconditioned by passing in succession 20 ml each of tetrahydrofuran, acetonitrile, and the initial eluent.

Detection

As shown in Fig. 1, three detectors were used in series. The chromatographic effluent first passed into a UV absorption detector operating at 254 nm (Spectra-Physics Chromatronix, Santa Clara, CA, U.S.A.; Model 210). The effluent then entered an optical-fiber-based capillary flow cell described elsewhere[15]. This was chosen over the alternative of suspending a solution droplet on a rod[19] to give better and more stable optical qualities over the eluent gradient. About 2.5 W at 488 nm from an argon ion laser (Control Laser, Orlando, FL, U.S.A.; Model 554) was focused into the flow cell with an 18-mm focal length lens. The laser power was monitored, but was stable enough so that normalization of the signals were not needed. LF from the

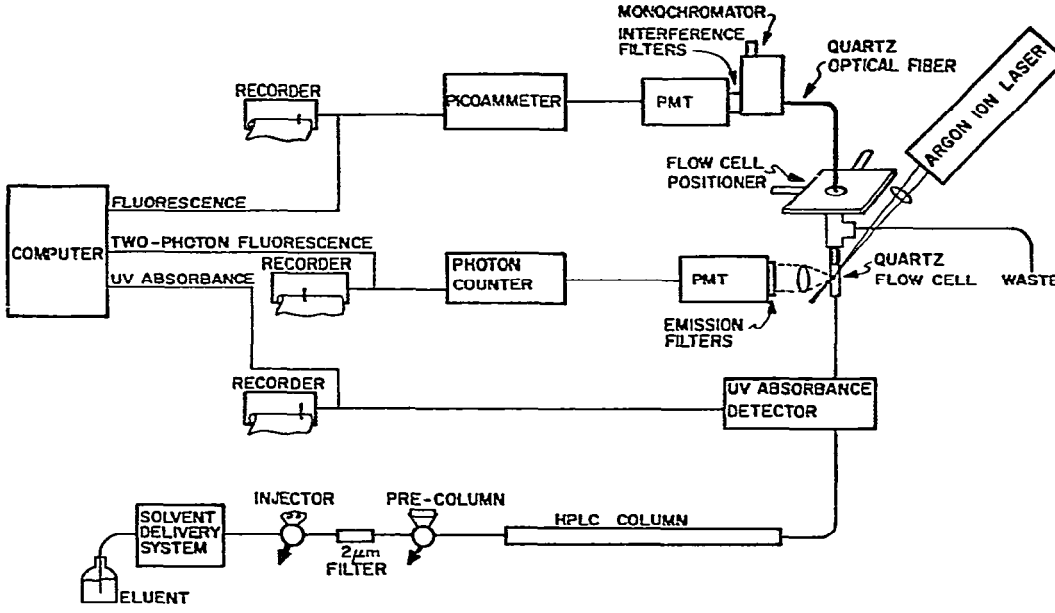


Fig. 1. Experimental arrangement for HPLC with laser-based detectors.

samples was collected by the optical fiber and isolated at 540 nm with a f/3.9 monochromator (Minochrom 1 from PTR Optics, Waltham, MA, U.S.A.) at a bandpass of 6 nm, plus two interference filters (Corion, Holliston, MA, U.S.A.; SS-5400). The excitation and emission wavelengths matched closely the corresponding peaks in the visible excitation and emission spectra of the bulk asphaltene. A photomultiplier tube (Amperex, North American Philips, Hicksville, NY, U.S.A.; 56 TVP) operating at 2000 V from a power supply (Hammer, Princeton, NJ, U.S.A.; Model NV-13-P) provided an output through a picoammeter (Keithley, Cleveland, OH, U.S.A.; Model 417). TPF was collected at 90° to the laser beam by a 38-mm diameter f/1.0 quartz lens through a 1-cm cell filled with saturated $CuSO_4$ solution and three filters (Corning, Corning, NY, U.S.A.; 7-54). This resulted in a transmission bandwidth of about 50 nm centered at 375 nm. TPF was recorded using a photomultiplier tube (Amperex, North American Philips, Hicksville, NY, U.S.A.; 56 DVP) operated by a 2000 V power supply (Keithley, Cleveland, OH, U.S.A.; Model 242) and a photon-counting system (Ortec, Oakridge, TN, U.S.A.; Model 9300). The analog output from each of the three detectors was displayed on separate chart recorders (Houston Instruments, Austin, TX, U.S.A.; Model 5000) and simultaneously fed into a PDP 11/10 computer (Digital Equipment, Maynard, MA, U.S.A.) with a LPS-11 laboratory interface, to provide a permanent record.

Data treatment

Background levels in the presence of pure eluent were subtracted from the chromatograms. The LF and TPF intensities were then normalized to the internal standard peaks to account for variations in alignment and focusing. The retention times were normalized to that of the major peak in the TPF chromatogram.

RESULTS AND DISCUSSION

Reproducibility

Even though the injection quantities were kept to 40 μg, contamination still prevented the use of a single column for all the work, and six different columns (from the same production batch) were used. Yet smaller injection quantities can be used if only the LF detector is of interest because of its higher sensitivity, but signal degradation will occur for the other two detectors. As expected, injections using the same column are more reproducible than injections using different columns. This can be seen from Fig. 2, which shows a reproducibility study using the TPF detector. It is also evident that information towards the end of the chromatograms shows more variation. This is a direct result of the pre-column switching procedure. It was found that about 80–90% of the asphaltene components (as measured by these detectors) which are eluted from the pre-column with 15 ml of 50% acetonitrile in water are eluted with the first 4-ml portion in these runs. The integrity of the asphaltene sample is therefore sufficiently preserved in spite of the pre-column switching procedure. We found that the normalized retention times and signal magnitudes for all peaks in the order of ten replicates of a given SRC had relative standard deviations of 2% and 9% respectively. Considering the complexity of these samples, the reproducibility is good.

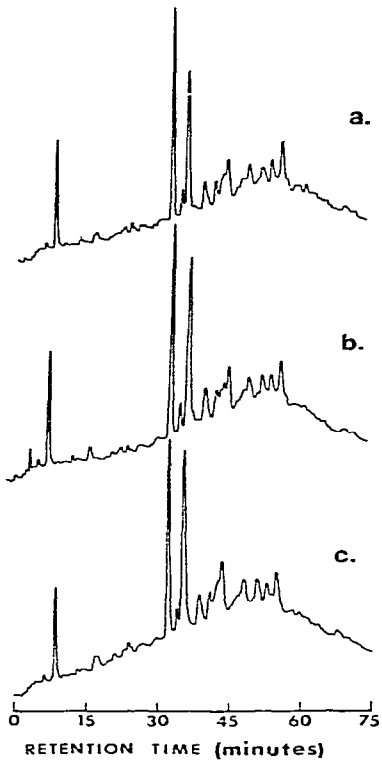
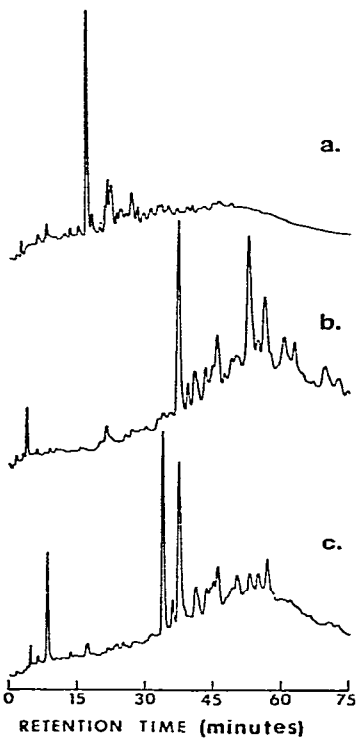


Fig. 2. Reproducibility study for triplicate injections for the TPF detector. Chromatograms a and b were obtained using the same column while chromatogram c was obtained using a different column from the same batch.

Detector comparison

Chromatograms from each of the three detectors for a particular run are shown in Fig. 3, indicating that information obtained from each is quite independent and the three complement one another. It should be noted that even if peaks occur at the same retention time, they need not correspond to the same component. The ratio of the peak heights of the two largest peaks in the TPF chromatogram is 1.2 while peaks appearing at the same retention times in the LF chromatogram have a ratio of 0.05, underscoring the differences in the two detectors. The asymmetry of the peaks appearing at 43 min in the two fluorescence detectors indicates the possible contributions from two peaks, the later eluting one giving a smaller response in both cases. This is more evident from the corresponding portion of the UV chromatogram, where two nearly resolved peaks appear due to a different set of response factors.



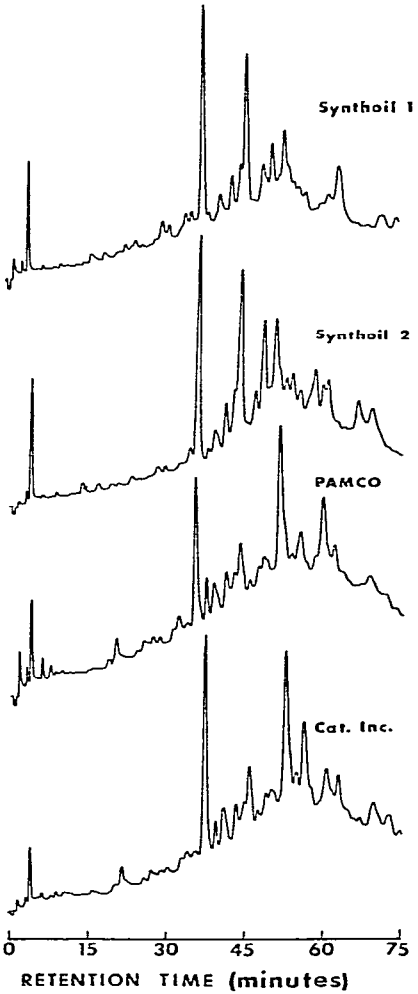


Fig. 3. Information from the three detectors for the same injection. a, UV detector; b, LF detector; c, TPF detector.

Fig. 4. Sample comparison using the LF detector. The labels refer to the four solvent-refined coals specified in the text.

A distinctive feature in Fig. 3 is the positions of the different "center-of-mass", *i.e.*, when about 50% of the weighted response has passed the detector in question. These are in the order UV, TPF and LF. The nature of reversed-phase separation using this gradient generally makes the smaller components elute early and the larger components elute late. Since the LF detector requires electronic conjugation for the necessary spectral red-shift, very little response shows up early in the chromatogram. Even when the individual concentrations of the components decrease towards the end of the chromatogram, as a result of our pre-column switching and as evidenced by the falling response in the UV detector, the LF response remains high. Chromatograms from the TPF detector present an interesting case. Presumably the abundance of two-photon states around 244 nm (twice the photon energy) is not too different from one-photon states at 254 nm (UV detector). The smaller response of TPF early in the chromatogram is an indication of the lower overall sensitivity of the process. The components towards the later part of the chromatograms are rich in electronic states in the 488 nm region, as seen from the LF chromatogram. These same electronic states serve to resonantly enhance the TPF process, thus providing a larger signal. The TPF still falls off a bit earlier than the LF signal, probably because of gradually decreasing concentrations and the lower overall sensitivity of the former process. Our choice of visible wavelengths in excitation and emission is thus justified, since the UV detector is not suitable for these components. Even if a UV fluorometric detector is used, one still favors the smaller, less conjugated components. The use of laser excitation in this work allowed us to detect fluorescence in the heart of the Raman scattering region of the eluents, without suffering from decreased sensitivity. The multi-detector approach described here therefore provides a wealth of information, even though baseline chromatographic resolution is generally not achieved for these complex samples.

Sample comparison

Fig. 4 shows chromatograms for the four different samples studied, all from the LF detector. Some consistent, distinctive features can be identified even without statistical analysis. The locations and the relative heights of the two major peaks in each chromatogram are sufficient to distinguish the PAMCO and the Catalytic Inc. samples from the two Synthoil samples, and from each other. As expected, the two Synthoil samples are more difficult to distinguish. Minor features around 33 min and 37 min are useful for visual comparison in that case. At first sight it may seem that features after 50 min are distinctive for each sample. However, intrasample correlation of those features is not good due to the pre-column switching procedure, and those features cannot be used.

The chromatograms shown in Fig. 4 are scaled relative to the major peaks for display purposes. In actual fact, the signal-to-noise ratio is much better than that indicated by the thickness of the lines. Typically there are a total of about 60 chromatographic peaks (per injection) with signal-to-noise ratios better than 30. We found that many of these peaks are in fact good discriminants for the four SRCs. Naturally, many more samples of the SRCs are needed to apply standard pattern recognition techniques to classify these samples and to extract features that are characteristic of the SRCs. A preliminary study on the intersample *versus* intrasample variations of these peaks however shows that the scheme presented here is reproducible enough for

classification studies. Such studies can then help to identify portions of the chromatograms that are characteristic of the SRCs, to provide insight into the coal-refining processes.

ACKNOWLEDGEMENTS

We thank Dr. T. F. Yen and Dr. S. Gasior for providing us with samples of the solvent-refined coals used in this work. We also thank R. Healy for helping in the extraction steps, and A. Brearley for helping in the data analysis.

Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Director for Energy Research, Office of Basic Energy Science, WPAS-KC-03-02-03.

REFERENCES

1 *Battelle Energy Program Report, Liquefaction and Chemical Refining of Coal*, Battelle Institute, Columbus, OH, 1974.
2 R. Yoshida, Y. Maekawa, T. Ishii and G. Takeya, *Fuel*, 55 (1976) 337.
3 N. P. Cochran, *Sci. Amer.*, 234 (1976) 24.
4 F. K. Schweighardt, H. L. Retcofsky, S. Friedman and M. Hough, *Anal. Chem.*, 50 (1978) 368.
5 T. Yoshida, Y. Maekawa, H. Uchino and S. Yokoyama, *Anal. Chem.*, 52 (1980) 817.
6 I. Schwager and T. F. Yen, *Anal. Chem.*, 51 (1979) 569.
7 R. S. Brown, D. W. Hausler and L. T. Taylor, *Anal. Chem.*, 52 (1980) 1511.
8 B. C. Bockreth, K. T. Schroeder and F. W. Steffgen, *Anal. Chem.*, 51 (1979) 1168.
9 M. Anbar and G. A. St. John, *Fuel*, 57 (1978) 105.
10 J. E. Dooley, C. J. Thompson and S. E. Scheppele, in C. Karr (Editor), *Analytical Methods for Coal and Coal Products*, Academic Press, New York, 1978, Ch. 16.
11 I. Schwager and T. F. Yen, *Fuel*, 58 (1979) 219.
12 W. A. Dark, W. H. McFadden and D. L. Bradford, *J. Chromatogr. Sci.*, 15 (1977) 454.
13 R. P. W. Scott, *J. Chromatogr. Sci.*, 18 (1980) 49.
14 Y. Hirata and M. Novotný, *J. Chromatogr.*, 186 (1979) 521.
15 M. J. Sepaniak and E. S. Yeung, *J. Chromatogr.*, 190 (1980) 377.
16 E. S. Yeung and M. J. Sepaniak, *Anal. Chem.*, 52 (1980) 1465A.
17 M. J. Sepaniak and E. S. Yeung, *Anal. Chem.*, 49 (1977) 1554.
18 F. K. Schweighardt and B. M. Thames, *Anal. Chem.*, 50 (1978) 1381.
19 G. J. Diebold and R. N. Zare, *Science*, 196 (1977) 1439.