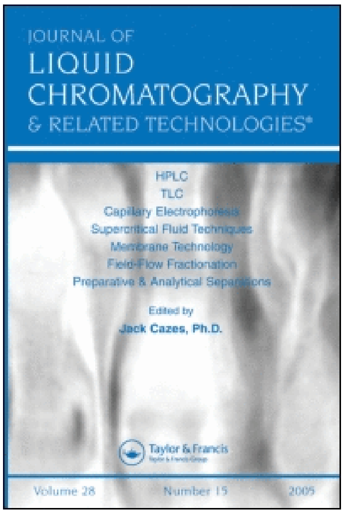

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Characterization of High-Ash Brazilian (Mina Do Leão) Coal-Derived Liquids by High Performance Liquid Chromatography Group Type Separation

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CHARACTERIZATION OF HIGH-ASH BRAZILIAN (Mina do Leão) COAL-DERIVED LIQUIDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY GROUP TYPE SEPARATION

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ABSTRACT

A comparative study was carried out on two high-ash coals, Wyodak III (American) and Mina do Leão(Brazilian), with respect to their content of saturates, olefins, aromatic hydrocarbons and polar compounds. A pyridine extract of each coal was fractionated by a silica gel preparative scale column generating four fractions of increasing polarity. Each fraction was colleted and examined by normal phase HPLC using "on-line" coupled silica and cyano-bonded columns. The results show that preparative scale fractionation alone is not enough to characterize coal-derived liquids, but it will be useful as a first step to generate fractions for HPLC characterization.

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INTRODUCTION

Fossil fuels, which are used as an energy resource, are produced by the gradual slow decomposition of organic materials and residues over millions of years (1). For many years, petroleum was the major energy and feedstock resource. However, after the "70's world energy crisis", the concern of researches was to find alternative resources to replace petroleum and its derivatives. Among these resources, coal has received considerable attention since it was believed that most of the existing petrochemical facilities could be easily adapted to coal processing (2).

The fact that liquid fuels can be more easily stored, handled, transported and processed than other fuels (6) such as solar, nuclear and hydrogen, makes coal-derived liquids a natural substitute for the liquid fuels and feedstocks generated by the petrochemical industry (7,8). It is now established that the highly variable nature of coal and the high-ash, high-sulfur and high-nitrogen content of coal-derived liquids makes them much more complex than petrochemicals and that more time will have to elapse before the actual chemical constitution of coal and its derivatives can be well-understood (3-5).

In spite of the tremendous efforts allocated to the analysis of coal-derived liquids, little is known about their chemical composition (1,3). This is due in part to the complexity of the sample but also to the inadequacy of present analytical methods and separation procedures (9,10), which are often direct applications of the methodology used with petrochemicals derivatives to the coal-derived liquids.

In order to fractionate these mixtures, two approaches are utilized: solvent extraction and liquid column chromatography. Although solvent extraction has long been used as a method of process monitoring (11,12) it does not procedure chemically meaningful fractions (13) according to solubility. The solvent extracted fractions are *oils* (pentane solubles), *asphaltenes* (benzene soluble-pentane insoluble) and *asphaltols* or *pre-asphaltenes* (pyridine soluble-benzene insoluble) (14), although no chemical identification has been established. The solvent extraction methods currently used, though simple and inexpensive are time consuming and present problems with reproducibility, solvent evaporation, co-extraction and loss of volatiles (13,15). In addition, possible interconversions during the processing makes it difficult to redissolve the solvent--derived fractions which usually contain some insoluble material.

In order to avoid these problems and to obtain chemically discrete fractions to be further characterized, the liquid fuel mixtures have been fractionated by liquid column chromatography. The first successful separation of residual oils into discrete chemical classes was obtained by Jewell et al (16) who separated the petroleum residuals into four fractions which they classified as saturates, aromatics, resins and asphaltenes ("SARA"). This method, as well as some of its modifications, has been extensivelly utilized in the characterization of a large variety of liquid fuels, among which are petroleum crudes, shale oils, coal oils and similar materials (17-28). In most of the liquid chromatographic methods used, the fossil fuel extract is first treated with a non-polar hydrocarbon (such as n-pentane) to precipitate the asphaltenes and the remaining solution is applied to an Attapulgus clay column to separate resins from oils. Finally, the oils are fractionated to saturates and aromatics on alumina and/or silica columns (22). All these steps, in addition to being unnecessary and inconvenient, do not provide actual group-type distribution in the extract, since part of the resins could be co-precipitated with asphaltenes (29). Recently Johanse, Ettre and Miller have applied Gas Chromatography (30), Liquid Chromatography (31) and a combination of Liquid and Gas Chromatography (32) to the analysis of hydrocarbons in gasolines and distillates. They separated 268 peaks from gasoline (32) and identified 120. These results, with sample much less complex than coal-derived liquids, suggest that a pre-fractionation of the sample is mandatory in order to obtain more discrete fractions to be analysed.

With these problems in mind, we have developed a multidimensional off-line chromatographic scheme to generate discrete coal-derived fractions which can be directly and easily characterized using readly available analytical tools such a High Performance Liquid Chromatography (HPLC) (26) alone or in combination with other techniques such as Fourier Transform Infra--Red (HPLC/FT-ir) (33). Nuclear Magnetic Resonance (HPLC/n.m.r.) (34), High Resolution Gas Chromatography (HPLC/HRGC) (35) and Mass Spectrometry (HPLC/MS) (36). The method developed includes a pre-fractionation of the whole coal-derived liquid into discrete fractions according to polarity. Each of these fractions is further characterized by HPLC with dual detection. For the purpose of this work, a comparison is made between a widely-used American coal (Wyodak III) and a typical Brazilian Coal (Mina do Leão I).

EXPERIMENTAL

Samples - Two different coal samples were used: Mina do Leão I (an Brazilian coal) and Wyodak III (an American coal). Elemental analysis for both coals was performed by Galbraith Laboratoires, Inc. (Knoxville, Tennessee) and the results are shown in Table 1.

TABLE 1

Elemental Analysis

	%C	%H	%N	%S	%O
Wyodak III Coal (USA)	48.27	4.49	0.73	6.50	24.49
Mina do Leão I Coal (Brazilian)	33.65	3.09	0.65	12.57	14.84

TABLE 2

Thermogravimetric Analysis*

	Wyodak III	**Leão I**
Fixed Carbon (%)	41.4	40.2
Volatiles (%)	36.9	22.5
Ash (%)	21.6	37.2

*** Moisture free basis**

Table 2 shows the results of thermogravimetric analysis for both coals, determined with a Du Pont 950 Thermogravimetric Analyzer coupled to a Du Pont 900 Differential Thermal Analyzer (Du Pont, Wilmington, DE 19898). The volatile material was determined in a nitrogen environment while fixed carbon and ash were determined in an oxygen one.

Sample Preparation - A schematic of the steps involved in the sample preparation is shown in Figure 1. The solid coal was finely ground and sieved through a 60 mesh screen (A.S.T.M. E-11 Specification). Fifty grams of powdered coal was then extracted in an inert atmosphere using a Soxhlet system, until the refluxing pyridine (ratio 1:14 w/v) was clear and colorless. This procedure, which has been extensively used in the preparation of coal-derived liquids (14), gave approximatly 600 mg of liquid product from the Wyodak III and 1500 mg from the Mina do Leão I coals.

Preparative Scale Liquid Chromatography - Two identical glass columns (1 m x 2.5 cm I.D.) were dry-packed with 70-230 mesh silica gel 60 (E.M. Science, Gibbstown, NJ), previously washed with methanol, filtered and dried by rotary evaporation. The extracted coal liquids were redissolved in pyridine and mixed with part of the silica gel under continuous agitation. The solvent was removed

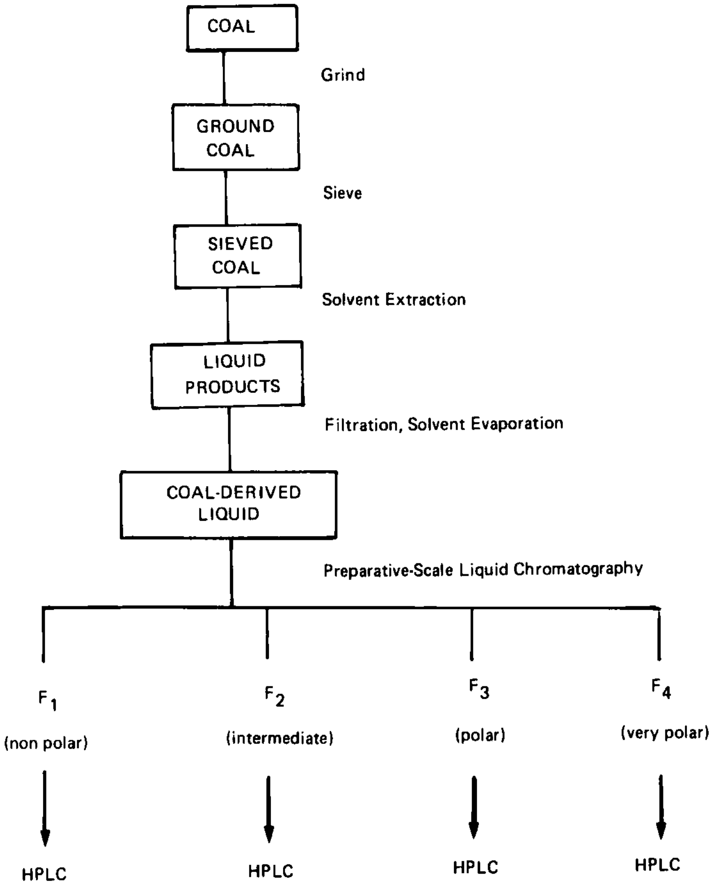

Figure 1 - Schematics of the Analytical Method

by rotary evaporation and the solid oven-dried to constant weight under a controlled nitrogen flow at 125^{0}C before the chromatographic analysis. This mixture (coal-liquid-coated silica gel) was then added to the top of the column. The choice of eluents was based on Hildebrand solubility parameters (37) and supported by Thin-Layer Chromatography (TLC), using silica gel plates (Eastman, Rochester, NJ). These eluents, listed in Table 3, were applied sequentially to the preparative scale columns. Following elution of the fractions, the solvents were removed by rotary evaporation and the remaining solids weighed.

TABLE 3

Elution System Used for the Pyridine Extracts of Coal on Preparative Scale Silica Column

FRACTION	**ELUENT**	**SOLVENT POLARITY(δ)**[a]	**CLASSICAL FRACTIONATION CORRESPONDENCE**[b]	**POSSIBLE COMPOSITION OF THE ELUTED FRACTION**[c]
F_1	Toluene: Heptane (35/65)	7,9	Oils	Saturated,olefinic and Aromatic Hydrocarbons
F_2	$CH C\ell_3$: Toluene (75/25)	9,0	Asphaltenes	Monofunctional O, N, S compounds
F_3	$CH C\ell_3$: Acetonitrile (90/10)	9,4	Asphaltenes	Phenols, N-Aromatics and Poly functional compounds
F_4	Pyridine	10,4	Asphaltols	Polyphenol and Highly Functional Compounds

a - δ, Hildebrand Solubility Parameter (37).

b - References 13, 28, 38.

c - References 1, 2, 38, 39.

High Performance Liquid Chromatographic Separation - The analytical instrument used was a Varian 5020 High Performance Liquid Chromatograph (Varian Associates, Walnut Creek, CA), with a fixed wavelength (254 nm) U.V. detector in series with a differential refractometer. The peaks were recorded on a dual pen recorder, Varian model 5176, while the retention times and areas were calculated by a Varian CDS 111 System. Two high pressure six-port Valco valves (Model N 60) were utilized, one for injection and the other for backflush. The optimum conditions were obtained using two colunms connected in series, a 5 μm chemically-bonded cyanopropyl column (250 mm x 4.0 mm I.D., Micropak-CN, Varian) coupled to a 5 μm silica column (300 mm x 4.6 mm I.D., Micropak-Si 5, Varian).

Each fraction from the preparative scale separation was dissolved in an appropriate solvent. Samples of the same fraction from the American and Brazilian coals were prepared so as to contain equal amounts of extracted material per milliliter although solubility limitations between fractions prevented use of equal concentrations throughout. 10 μℓ of each of these solutions were injected into the HPLC system for elution with n-hexane previously dried with activated 5 A molecular sieve and then filtered through a 2 μm filter (Millipore, Milford, Massachusetts).

The cyanopropyl column retained the polar compounds while group type separation of paraffins and naphthenes (S), olefins (O), and aromatics (A) occurred on the silica column. When this separation was complete (ca. 18 minutes) the cyanopropyl column was backflushed to remove the polar compounds (P). The change in flow rate from 1.0 mℓ/min to 3.0 mℓ/min for the backflush prevented use of the refractive index (R.I.) detector in this part of the analysis.

RESULTS AND DISCUSSION

Until the present study no chemical characterization of Brazilian coal-derived liquids has been reported using chromatographic techniques, although some studies have been carried out on coal conversion (40). Our efforts were directed towards characterizing coal-derived liquids from Mina do Leão I coal, a sub-bituminous, high-ash coal (41), using preparative scale choromatography in conjunction with HPLC.

Preparative Scale Separation - The preparative scale liquid chromatographic separation of compounds by group-type has been widely used for characterization of fuels such as crude oil (42), shale oil (43), coal (44) and solvent refined coal, SRC (45). In some cases this is the only characterization, using silica, alumina or both as stationary phases. In this work, four fractions of increasing polarity were collected from the preparative scale column fractionation and roughly related (Table 3) to the classical fractionation: oils (F_1), asphaltenes (F_2 and F_3) and asphaltols (F_4). It should be noted (Table 4) that the preparative scale fractionation generates a more "balanced" distribution of the fractions for the Brazilian coal (BF) than for the American coal (AF). The relative amount of polar compounds extracted from the Wyodak III coal (AF_4. Table 4) is about double that for the Brazilian coal (BF_4).

Meanwhile, the fraction F_1 eluted with heptane/toluene is three times more abundant in the Brazilian coal. Based on these data, it is expected that a more refined analysis of both coals should reflect the same tendency: the amounts of hydrocarbons relative to polar compounds would be larger in the Brazilian coal than in the American coal. For this purpose, all the experiments were conducted under strictly controlled conditions to insure reproducibility and permit this kind of comparison.

High Performance Liquid Chromatography - HPLC has already been used for the characterization of coal-derived liquids (20-22,46-49). In most cases, the whole coal extract was applied to the HPLC system, resulting a very complex chromatogram, difficult to interpret. In this work, each of the four fractions collected from preparative

TABLE 4

Yields from Wyodak III and Mina do Leão I Coals Fractionated on Preparative Scale Silica

Wyodak III (American)

COAL FRACTION	COLOR OF ELUTED FRACTION	ELUTED AMOUNT (g)*	% OF TOTAL ELUTED
AF_1	light yellow	0.054	6.7
AF_2	yellow	0.020	2.4
AF_3	orange	0.080	9.8
AF_4	dark brown	0.657	81.0
		0.811	99.9

Mina do Leão I (Brazilian)

COAL FRACTION	COLOR OF ELUTED FRACTION	ELUTED AMOUNT (g)*	% OF TOTAL ELUTED
BF_1	light yellow	0.319	19.8
BF_2	yellow	0.278	17.3
BF_3	orange	0.350	21.7
BF_4	dark brown	0.661	41.1
		1.608	99.9

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* After drying

TABLE 5

Standard Mixture for the Group-Type Separation

PARAFFINS	NAPHTHENES	OLEFINS	AROMATICS	POLARS
Heptane	Cyclobutane	Hexene	Benzene	Phenol
Octane	Methylcyclobutane	Heptene	Toluene	o-Chlorophenol
Nonane	Dimethylcyclobutane	Octene	o-Xylene	
Decane	Methylcyclopentane	Nonene	m-Xylene	
Undecane	Cyclopentane	Decene	p-Xylene	
Dodecane	Dimethylcyclopentane	Undecene	Ethylbenzene	
Tridecane	Cyclohexane	Dodecene	Naphtalene	
Tetradecane	Cycloheptane	Tridecene		
Pentadecane	Cyclooctane	Tetradecene		
Hexadecane	Methylcyclooctane	Heptadecene		

scale fractionatio was injected. The chromatograms for the different fractions are displayed in Figures 2 through 9. Figure 10 shows the chromatogram of a standard mixture utilized for the development of the experimental conditions. The components of this mixture, listed in Table 5, were selected from those already indentified in liquid fuels (1,22,36,38). However, comparison of Figure 10 with Figures 2 to 9 immediatly suggests that the separated fractions are significantly more complex than the standard mixture.

HPLC Group-Type Separation of Fraction F_1 - By comparing fraction BF_1 (Figure 2) with AF_1 (Figure 6) one can notice that the amount of polar compounds is higher than expected, since, according to the literature (1,2,38) fractions eluted with a mixture of heptane and toluene should be predominantly hydrocarbons. It is possible that some heterocyclic compounds of intermediate polarity are

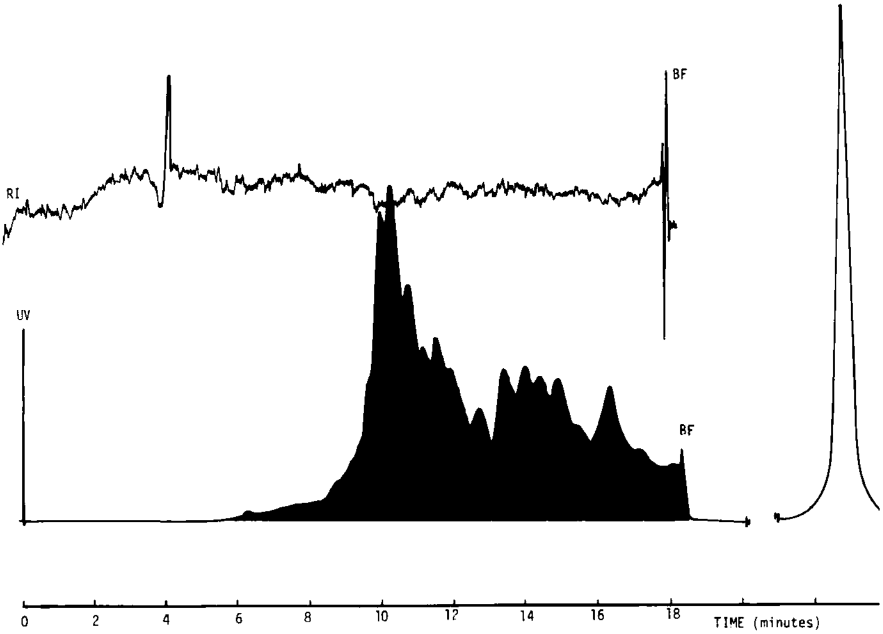

Figure 2 - High Performance Liquid Chromatogram of Fraction BF_1 colleted from Preparative Scale Fractionation. Solvent: Hexane. Columns: Cyano Bonded Silica and Silica in Series. Eluent: Dry Hexane; Flow Rate 1.0 ml/min. Detection: Refractive Index Detector (R.I.) and Ultra-Violet Detector (U.V.) fixed at 254 nm. Injection: 10 µl. BF = Backflush Point, flow rate 3.0 ml/min. Shaded area = = Aromatics.

coeluted in these fractions. The HPLC analysis shows relatively higher amounts of these polar compounds in the Brazilian coal. Moreover, no saturates (S) or olefins (O) appeared in the BF_1 fraction while the AF_1 showed the presence of both classes (Figure 6). On the other hand, both AF_1 and BF_1 show significant quantities of aromatics (shaded area) which, due to the long elution time, must included various polyaromatic species (39) compared to the simple aromatics in the standard mixture, Figure 10.

HPLC Group-Type Separation of Fraction F_2 - In spite of the mild elution strength of the eluent utilized for the F_2 fractions in

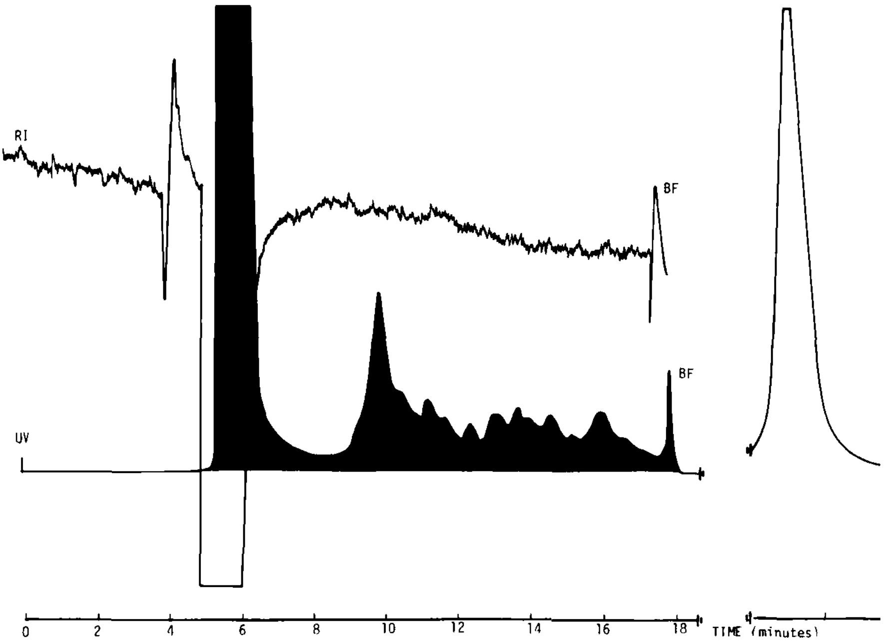

Figure 3 - HPLC Chromatogram of Preparative Scale Fraction BF_2. Solvent: Benzene. Conditions same as Figure 2.

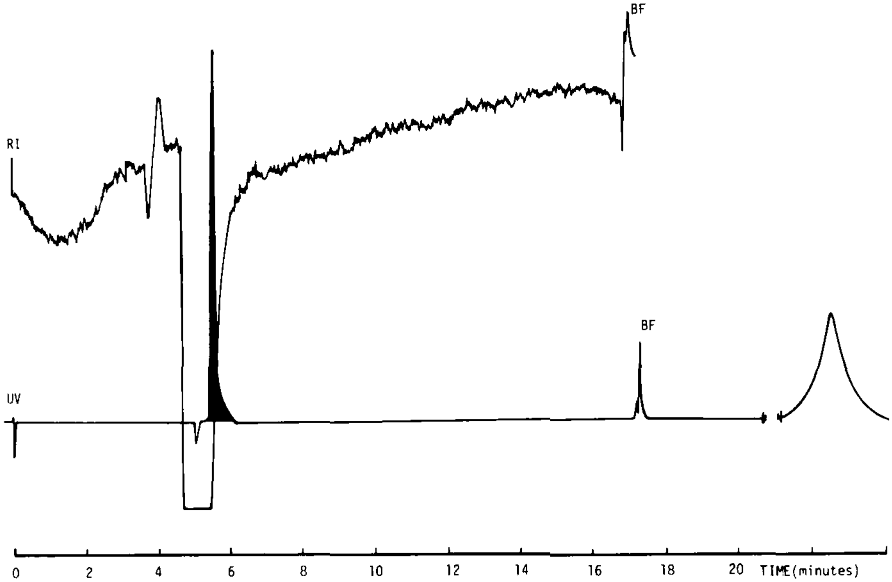

Figure 4 - HPLC Chromatogram of Preparative Scale Fraction BF_3. Solvent: THF. Conditions same as Figure 2.

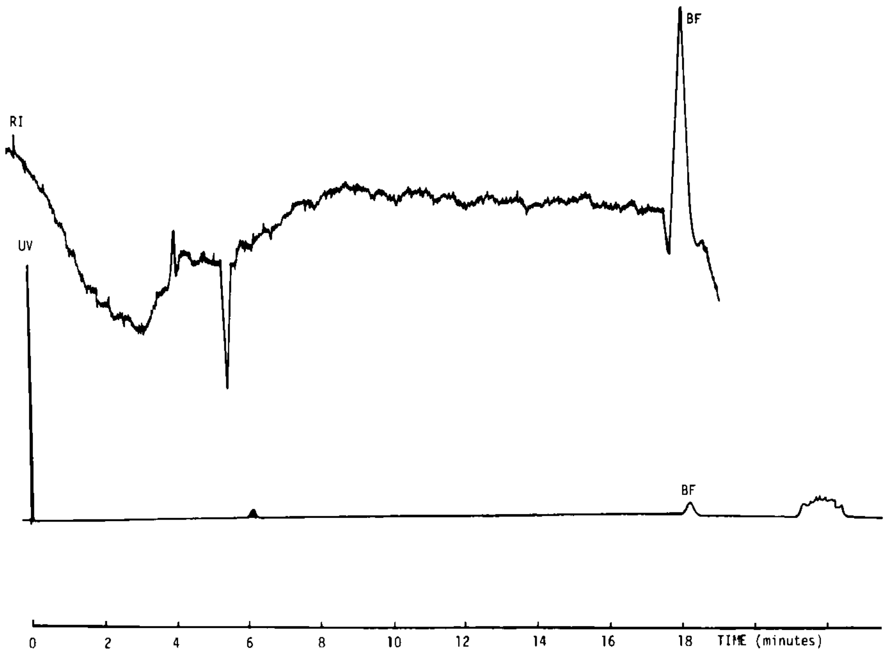

Figure 5 - HPLC Chromatogram of Preparative Scale Fraction BF_4. Solvent: Methanol. Conditions same as Figure 2.

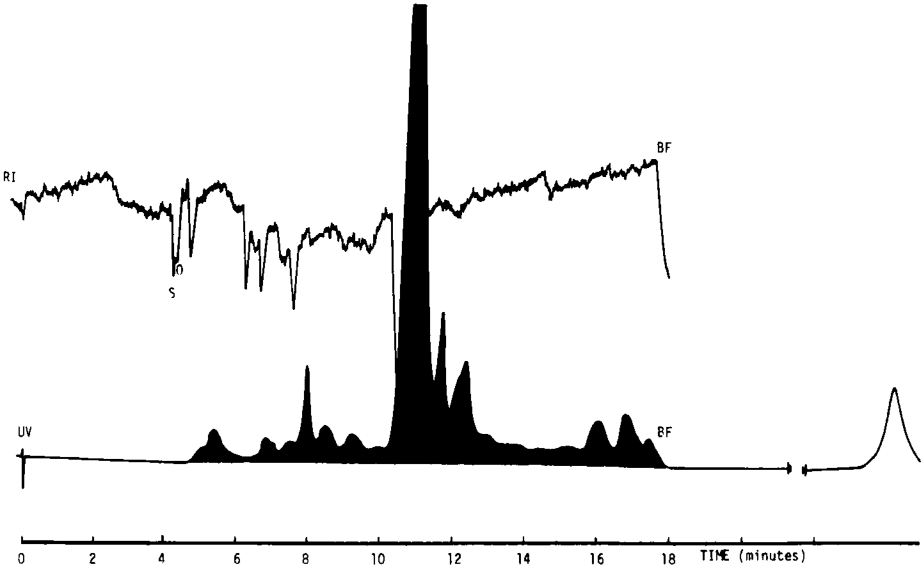

Figure 6 - HPLC Chromatogram of Preparative Scale Fraction AF_1. Solvent: Hexane. Conditions same as Figure 2.

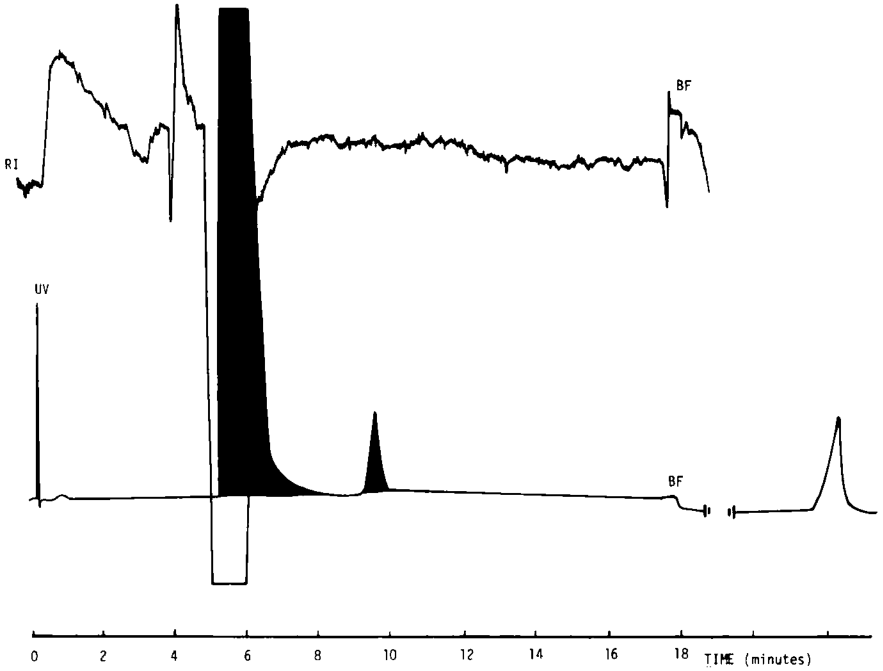

Figure 7 - HPLC Chromatogram of Preparative Scale Fraction AF_2. Solvent: Benzene. Conditions same as Figure 2.

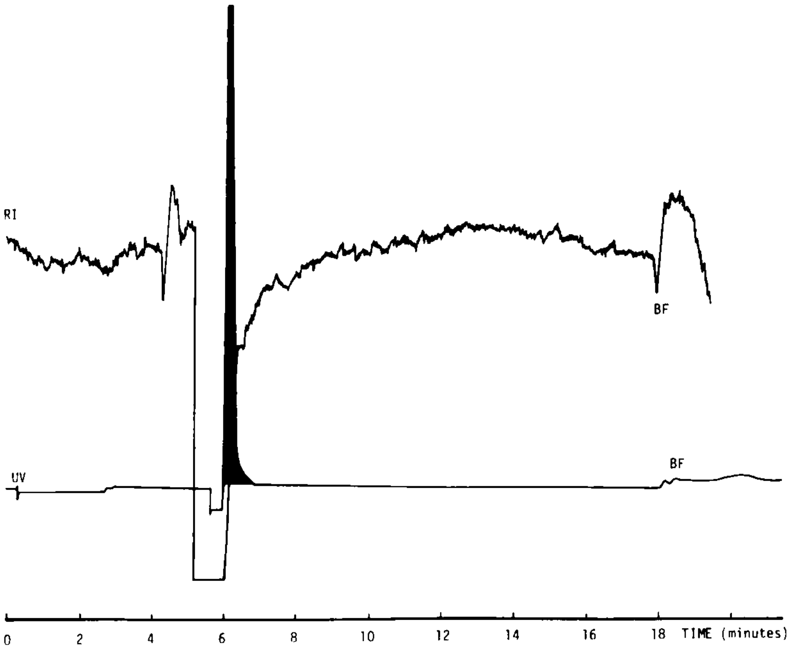

Figure 8 - HPLC Chromatogram of Preparative Scale Fraction AF_3. Solvent: THF. Conditions same as Figure 2.

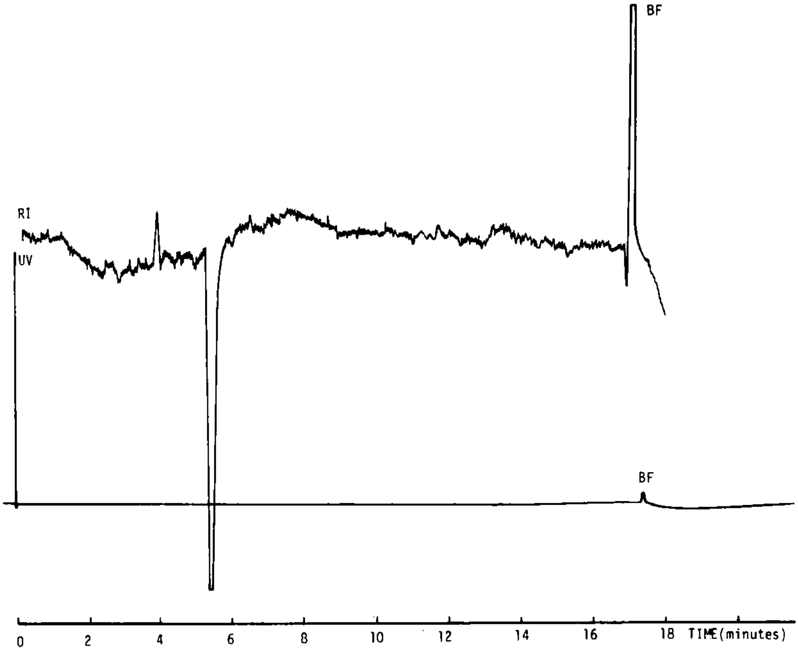

Figure 9 - HPLC Chromatogram of Preparative Scale Fraction Af_4. Solvent: Methanol. Conditions same as Figure 2.

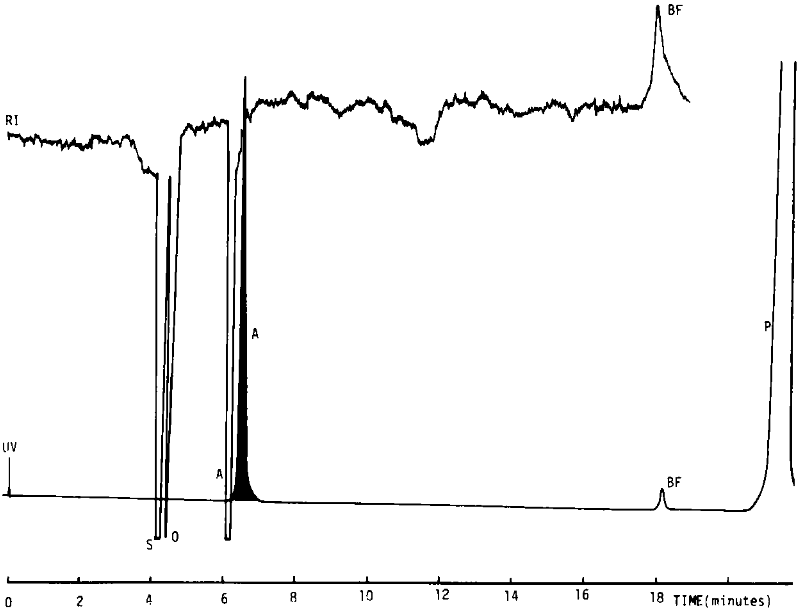

Figure 10 - HPLC Chromatogram of a Standard Mixture. Conditions same as Figure 2. For the identity of the individual components in each group refer to Table 5.

the preparative scale separation (chloroform/toluene), the amount of polar compounds found in the Brazilian coal is very high. The major difference observed between the coals in F_2 fractions is that the aromatics content of BF_2 (Figure 3) is by far more complex than that of AF_2 (Figure 7). Neither fraction contains saturates or olefinic hydrocarbons.

HPLC Group-Type Separation of Fraction F_3 - Even though the predicted content of fraction F_3 is the asphaltenes, HPLC analysis of the fractions AF_3 and BF_3 (Figures 4 and 8) are much simpler than the preceeding ones; AF_3 contains only simple aromatics while BF_3 shows both aromatics and a small peak attributed to polar compounds.

HPLC Group-Type Separation of Fraction F_4 - This fraction contains essentially a discrete class of aromatics and a small polar mixture. (Figure 5 and 9). In this case, the relative amounts and identity of the fractions seem to be similar in both coals. However, these fractions (AF_4 and BF_4) were of low solubility which may have prevented detection of minor components.

Aromatics Fraction - The aromatics fraction is by far the major class extracted from coal using polar extracting agents, which is in accordance with the literature (50). Since aromatic compounds are separated on silica gel principally by ring size (51), a qualitative comparison can be made between liquids derived from different coal samples as well as between fractions of the same coal sample. There is no adequate quantitative method for HPLC group-type separation of coal-derived liquids, since the compounds present in the sample have widely different response factors in all detectors. However, it is expected that the success obtained with other fuels (31) will also be obtained with coal-derived liquids. It can be seen by examining the chromatograms (Figures 2 - 9) that the complexity of the aromatic fraction observed decreases in going from the less polar to the more polar eluents of the preparative-scale separation. Thus, the F_1 fractions (eluted with heptane/toluene) show a very complex aromatic mixture while the F_3 and F_4 fractions show a simpler aromatic content. There is also a large difference in aromatic composition between the corresponding fractions of the American and Brazilian coals (compare, for example, fractions BF_2 and AF_2). Moreover, it is noted that the U.V. response of the aromatic fractions decreases relative to the refractive index response upon going from less polar fractions to more polar ones. This type of behavior is the same for both coals and reflects the differences in chemical composition among the different fractions.

In this work the major effort was directed towards a comparative analysis of a typical Brazilian coal (Mina do Leão I) and a high-ash American coal (Wyodak III), since the composition of Brazilian coal extracts is unknown. Both, the preparative scale chromatography and the HPLC analysis indicate that the Brazilian coal is considerably more reactive, extractable and complex than the American one, with the Brazilian also having a higher polynuclear aromatic content.

The results of this study show that while preparative scale fractionation alone is not sufficient to characterize coal-derived liquids, it allows the preparation of more discrete fractions, cleared of ash and high polymers, which can be further characterized by normal phase HPLC. The collected fractions from normal phase HPLC can then be further characterized and perhaps, quantified by other chromatographic techniques, work which is now in progress.

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