Journal of Chromatography, 123 (1976) 419–428

CHROM. 9114

Note

Chromatographic separation studies of solvent refined coal

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(Received February 16th, 1976)

One of the processes currently under development for coal desulfurization is the solvent refining or dissolution process. A solution that contains approximately 90% of the carbon in the original coal is suspended in a high-boiling solvent, raised to a temperature between 300–400°F and exposed to an atmosphere of hydrogen. After exposure the solution is filtered and cooled. The cooling step causes the solution to precipitate a black material. Separation and chemical characterization of the components in this black material, solvent refined coal (SRC), is currently being studied by several investigators[1–3].

A recent nuclear magnetic resonance (NMR) study[4] has shown that hexamethylphosphoramide-soluble SRC solid surprisingly contains approximately 95% aromatic material. A more definitive characterization of SRC in this investigation was precluded, however, because of the varied chemical components in the coal. In order to identify some of the chemical constituents of SRC, an initial separation of SRC into a small number of fractions seemed desireable. With this in mind a study was begun which was designed to separate quickly and economically SRC solids into preparative-size fractions for subsequent characterization via various analytical techniques. The initial results of our study which concerns the separation of the tetrahydrofuran (THF) soluble portion of SRC (0.190 g/ml) according to effective molecular size are reported herein. In addition, we wish to discuss the further separation of the "sized" components by a reversed-phase technique.

EXPERIMENTAL

The SRC sample on which all of the separations have been accomplished was obtained from a Catalytic Inc. pilot plant (Wilsonville, Ala., U.S.A.).

The liquid chromatograph used was a Model 3500B (Spectra Physics, Santa Clara, Calif., U.S.A.) equipped with a mixed-wavelength absorbance detector and a thermostated refractive index detector. The Styragel columns were obtained from Waters Assoc. (Milford, Mass., U.S.A.). The Licrosphere column was obtained from Spectra Physics. The Spherisorb ODS and Spherisorb 5 μ silica were also obtained from Spectra Physics.

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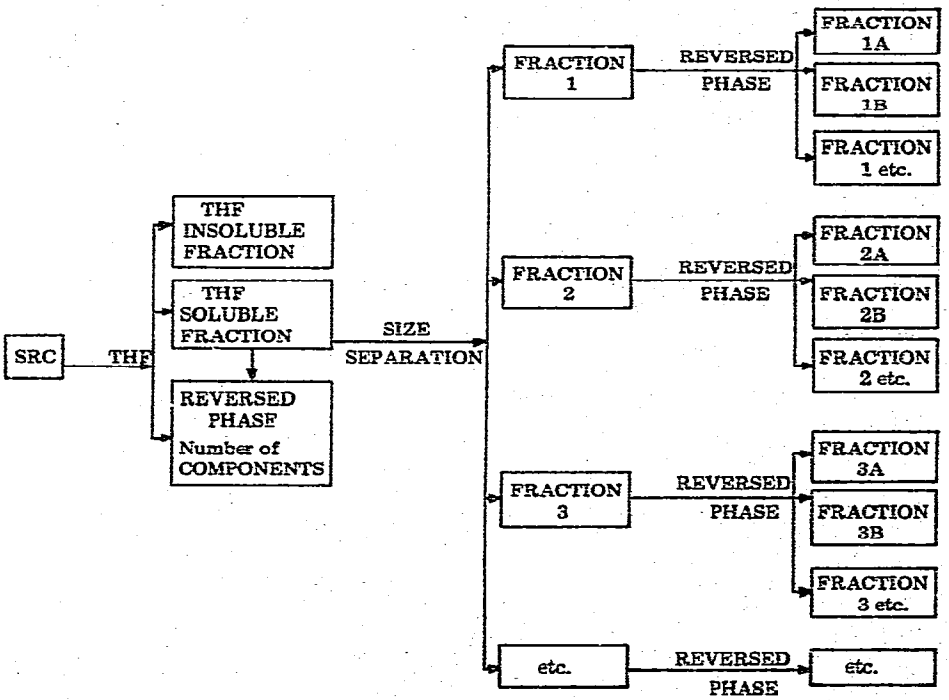
Bio-Beads S-X12 and S-X4 were obtained from Bio-Rad Labs. (Rockville Centre, N.Y., U.S.A.). The Bio-Bead columns were packed with a THF slurry of the beads (swelled for 1 h in THF) using occasional nitrogen (8 p.s.i.) to facilitate packing. The glass column(s) (8 mm × 120 cm) was attached to the chromatograph employing a packed column extension and allowed to pack under normal operating conditions for 2 h. The extension was removed leaving a clean-cut top surface of packing to which the fitting was immediately attached and the flow initiated. Failure to keep the beads moist with THF resulted in channeling within the column. Tetrahydrofuran was obtained from Aldrich (Milwaukee, Wisc., U.S.A.) and was freshly distilled from Na and NaI before use. Methanol was obtained from Burdick & Jackson Labs. (Muskegon, Mich., U.S.A.).

RESULTS AND DISCUSSION

The schematic overall plan of attack devised for the separation and analysis of the components of SRC is shown below.



Prior to the achievement of the desired size separation using Bio-Beads S-X4 numerous molecular-size separators were investigated. Those studied were μStryragel, Styragel (60 Å), Licrosphere (100 Å), and Bio-Beads S-X12. The chromatograms obtained on each packing material with experimental conditions for each are shown in Figs. 1–4.

Although the Bio-Beads S-X12 columns allowed a limited separation of the SRC sample, the Styragel and Licrosphere columns were much less effective with no

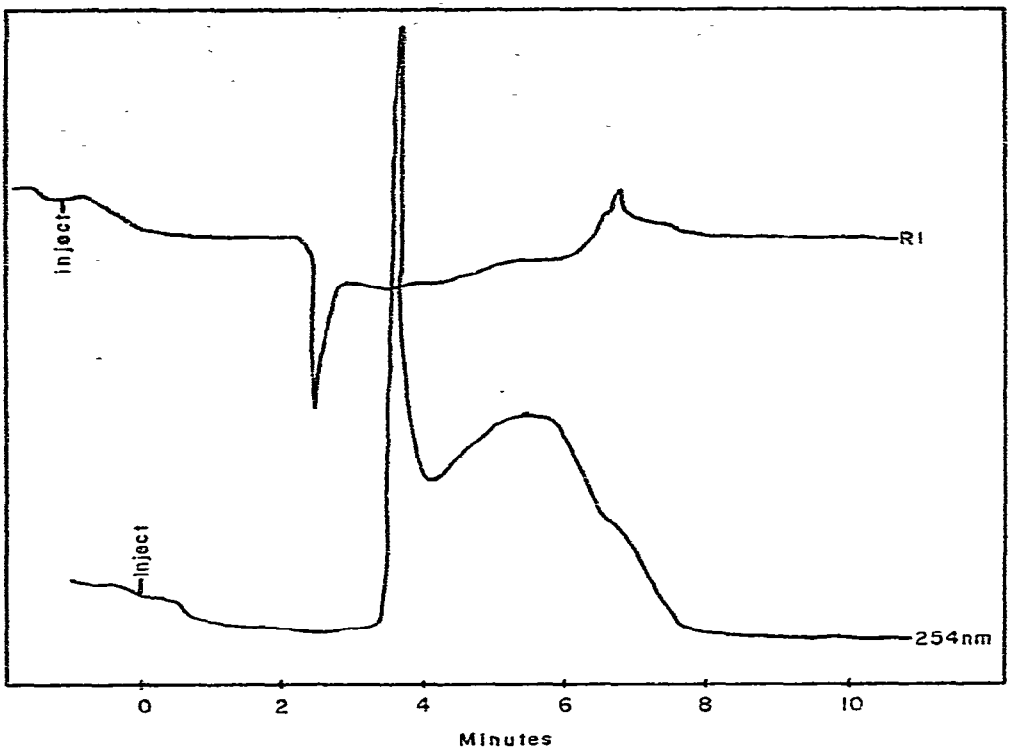


Fig. 1. Stainless-steel column (8 mm × 180 cm) packed with 60 Å μStyragel; THF flow-rate, 2.5 ml/min; pressure, 2100 p.s.i.; detection, refractive index; sample, 2 ml THF-soluble SRC solid.

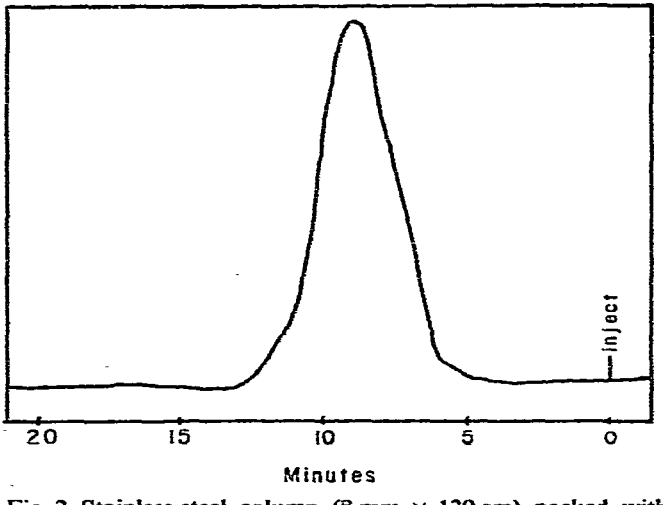


Fig. 2. Stainless-steel column (8 mm × 120 cm) packed with 60 Å Styragel; THF flow-rate, 1.0 ml/min; pressure, 60 p.s.i.; detection, UV at 254 and 280 nm; sample, 10 μl THF-soluble SRC solid.

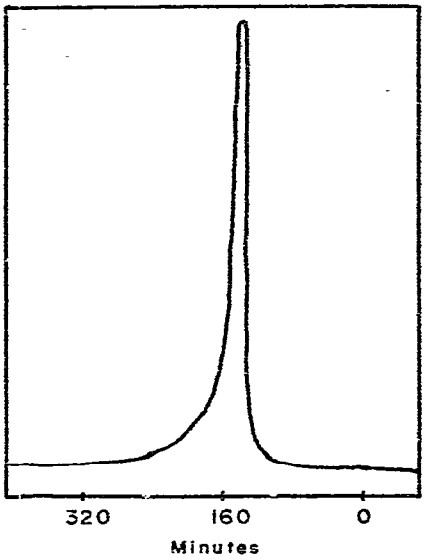


Fig. 3. Stainless-steel column (3 mm × 250 cm) packed with 100 Å Licrosphere; THF flow-rate, 0.4 ml/min; pressure, 310 p.s.i.; detection, UV at 254; sample, 10 μl THF-soluble SRC solid.

detectable separation. In a limited study, μStyragel separated THF-soluble SRC into at least three components, but since preparative size fractions were desired further work with μStyragel was discontinued because of its high cost. Using Bio-Beads S-X4 we have separated the SRC material into four components (Fig. 5). Several factors were instrumental in the selection of Bio-Beads for this study. The first was cost, Bio-Beads are relatively inexpensive when compared to other packing materials. Secondly, Bio-Beads are easily packed at low pressure and finally the use of glass afforded the opportunity to view the separation and thus, allow easy monitoring of the separation in progress.

Bio-Beads Series S is a series of neutral, porous styrene–divinyl benzene copolymer beads intended for the gel permeation separation of lipophilic polymers and other solutes using organic solvents[5]. Mulder and Buytenhuys[6] have illustrated

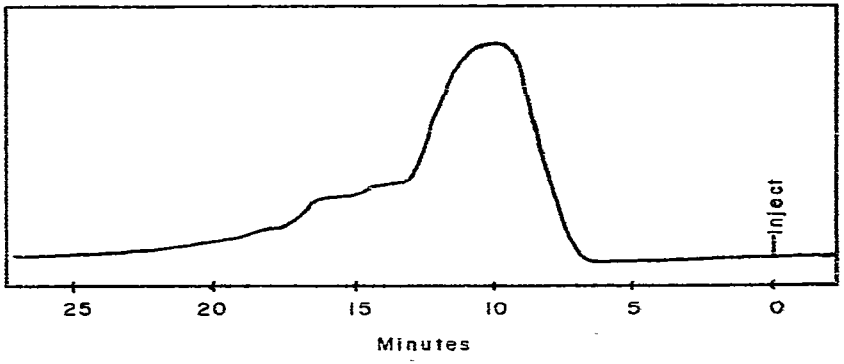


Fig. 4. Glass column (5.5 mm × 240 cm) packed with Bio-Beads S-X12; THF flow-rate, 0.8 ml/min; pressure, 40 p.s.i.; detection, UV at 254; sample, 2 ml THF-soluble SRC solid.

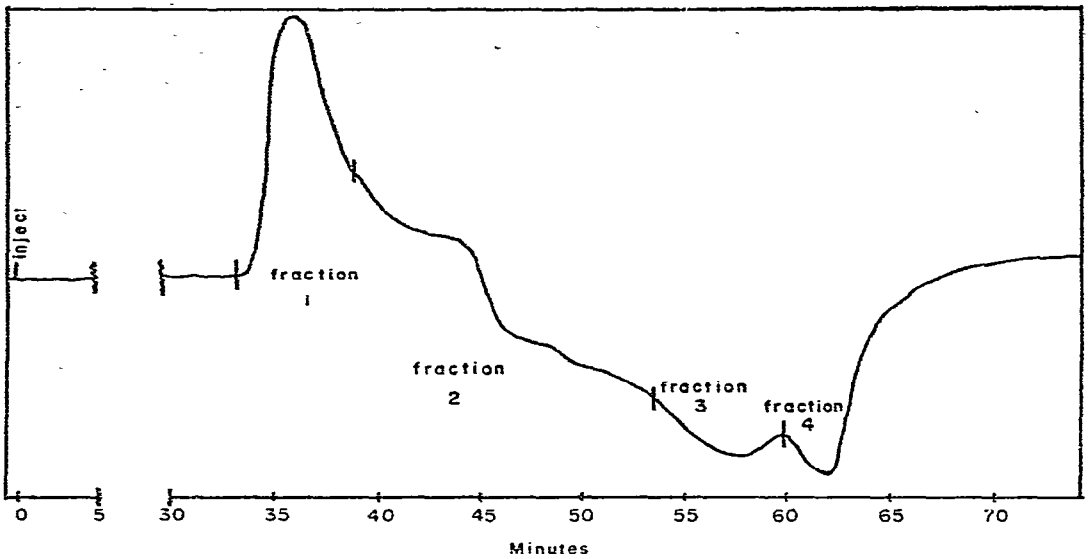


Fig. 5. Glass column (5.5 mm × 240 cm) packed with Bio-Beads S-X4; THF flow-rate, 0.8 ml/min; pressure, 40 p.s.i.; detection, refraction index; sample, 2 ml THF-soluble SRC solid.

TABLE I

SEPARATION OF THF-SOLUBLE SRC ON BIO-BEADS S-X4 COLUMN

Fraction no.	*Collection time start–stop (min)*	*Approx. percentage of sample injected*
1	35–40	20
2	40–55	70
3	55–60	5
4	60–70	5

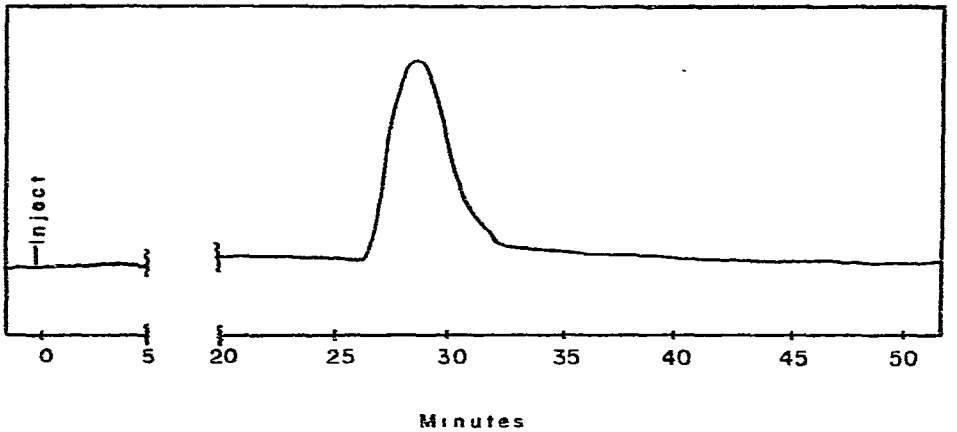


Fig. 6. Fraction 1 reinjected to get fraction 1A. Conditions: see Fig. 5.

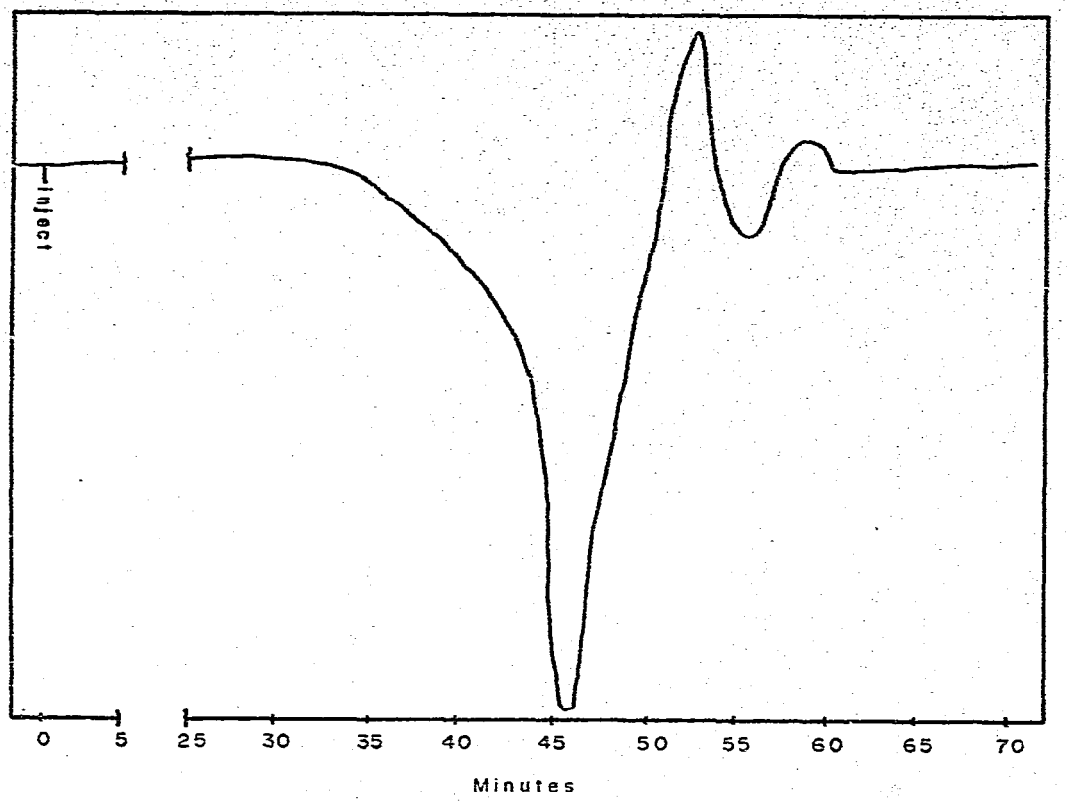


Fig. 7. Fraction 2 reinjected to get fraction 2A. Conditions: see Fig. 5.

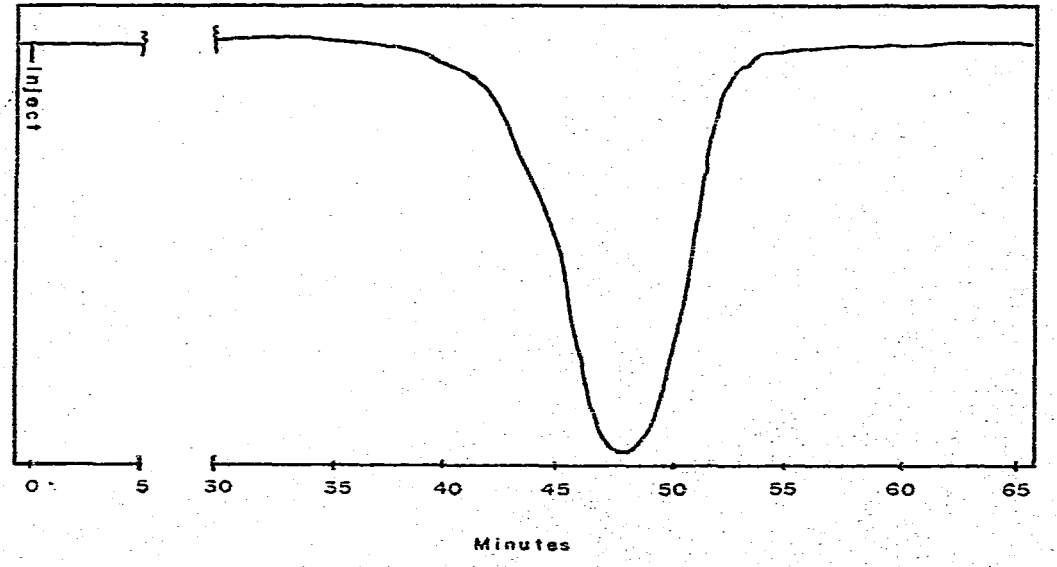


Fig. 8. Fraction 3 reinjected to get fraction 3A. Conditions: see Fig. 5.

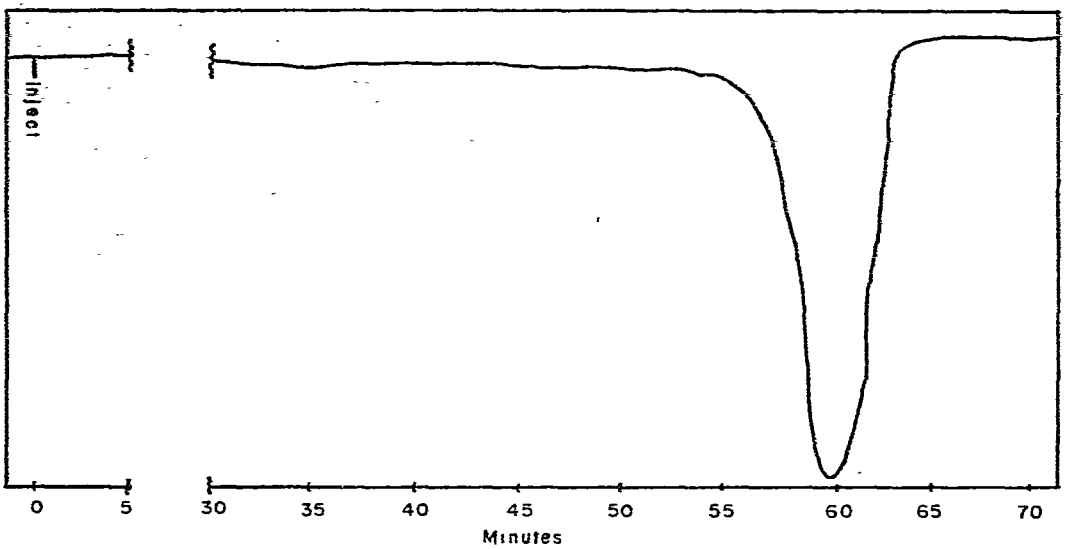


Fig. 9. Fraction 4 reinjected to get fraction 4A. Conditions: see Fig. 5.

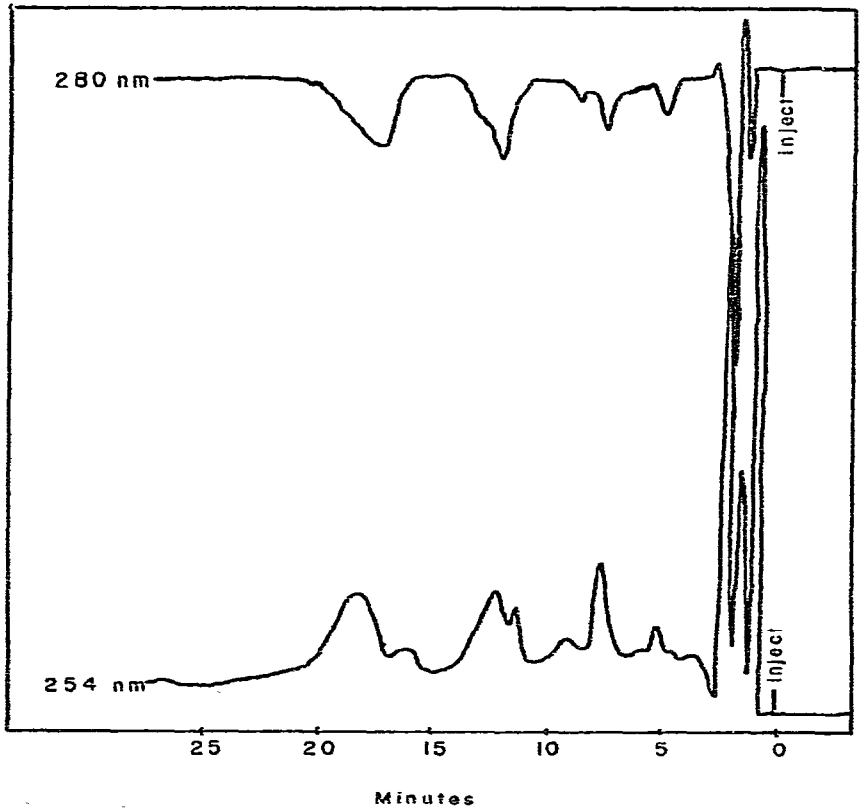


Fig. 10. Stainless-steel column (3 mm × 250 mm) packed with 5 μ-Spherisorb ODS; mobile phase, methanol–water (60:40); flow-rate, 0.8 ml/min; pressure, 1500 p.s.i.; detection, UV at 254 and 280 nm; sample, 10-μl fraction 2A.

the operating ranges of Bio-Beads S products by separating mixtures of components of known molecular weights with several different Bio-Beads products. Other applications of Bio-Beads include separation of lipids, alkanes, fatty acids, polystyrenes, and vitamins. They have also been used to determine molecular weights and molecular weight distributions[7]. The employment of this gel permeation material for the separation of fossil fuel, however, has apparently not been reported.

Sample injections up to 2 ml of a saturated THF solution of SRC were routinely placed on the column and eluted with THF. Sample collection was begun as soon as numerous repetitions could be obtained on the chromatogram seen in Fig. 5. Table I shows the fraction number, the approximate percentage of the sample injection, and the length of time over which the fraction was collected at a flow-rate of 0.8 ml/min with a 8 mm × 240 cm column.

After sufficient quantities of fractions 1, 2, 3, and 4 were obtained, the Bio-Beads S-X4 column was removed, and a Spherisorb ODS column (250 × 3 mm I.D., stainless steel) was installed. Fractions 1, 2, 3, and 4 were injected onto the Spherisorb column and the chromatograms obtained. It was seen that there was a tremendous difference between fractions 1 and 2 when compared to 3 and 4. However, 3 and 4

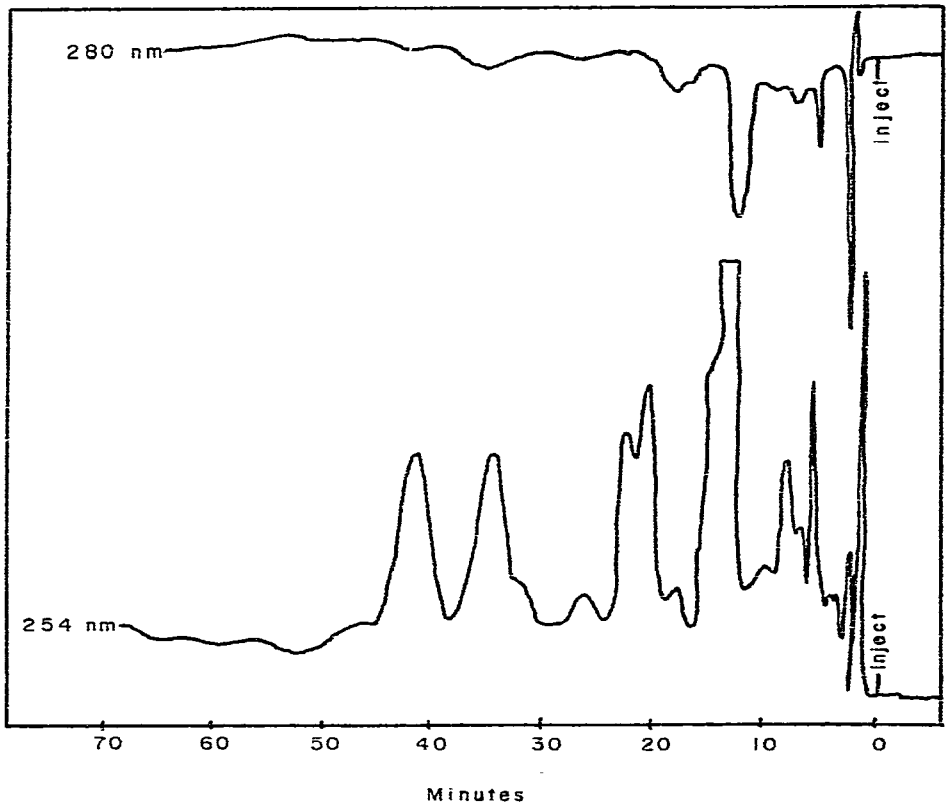


Fig. 11. Stainless-steel column (3 mm × 250 mm) packed with 5 μ-Spherisorb ODS; mobile phase, methanol–water (60:40); flow-rate, 0.8 ml/min; pressure, 1500 p.s.i.; detection, UV at 254 and 280 nm; sample, 10-μl fraction 3A.

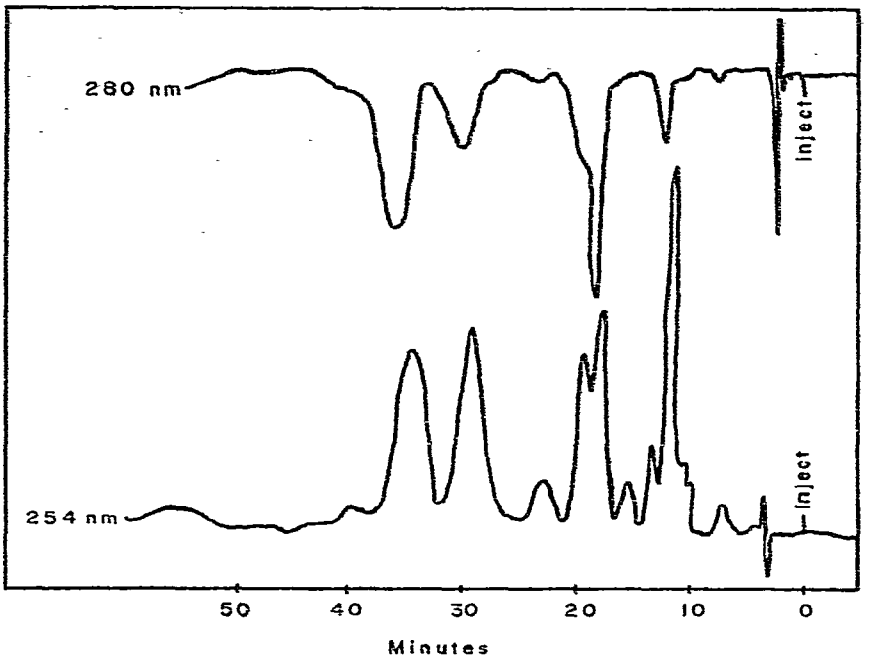


Fig. 12. Stainless-steel column (3 mm × 250 mm) packed with 5 μ-Spherisorb ODS; mobile phase, methanol–water (60:40); flow-rate, 0.8 ml/min; pressure, 1500 p.s.i.; detection, UV at 254 and 280 nm; sample, 10-μl fraction 4A.

seem surprisingly similar with only small differences in retention times. The conclusion reached at this point is that there is a size separation occurring on the Bio-Beads S-X4 but components 3 and 4 are not resolved to any great extent. With this in mind, all fractions were separately reinjected onto the Bio-Beads S-X4 column. The chromatograms of these reinjected materials are shown as Figs. 6–9. It can be seen that all four components have different retention times and are surprisingly "pure". The components now termed 1A, 2A, 3A, and 4A were isolated and reinjected onto the Spherisorb column. No appreciable difference was noted between the chromatograms of fractions 2, 3, 4, and their counterparts 2A, 3A, and 4A (Figs. 10–12). However, there was a large difference in component 1A when compared to 1. Component 1A showed no absorbance at either 254 or 280 nm when injected onto the Spherisorb ODS column. An investigation was undertaken to determine the cause of this. It was found that components 2A, 3A, and 4A are all soluble in the mobile phase, methanol–water (60:40), whereas component 1A has no solubility in the mobile phase. In fact it is not even soluble in pure methanol. Therefore, it was concluded that the possibility for chromatography using methanol–water on a Spherisorb ODS column did not exist for component 1A. Current investigations are underway to establish conditions for reversed-phase chromatographic analysis of component 1A.

In conclusion Bio-Beads S-X4 has separated the THF-soluble portion of SRC into four molecular sizes. Reinjection of each of these fractions on to an S-X4 column reveals very little contamination of one fraction by another. Analytical separation on a Spherisorb ODS column suggests fractions 3 and 4 are chemically similar.

Fraction 2 while being soluble in methanol–water and in largest quantity is unique and probably less complex. Alternatively, fraction 2 may be just as complex as fractions 3 and 4 but it contains few components which absorb at 254 and 280 nm. Fraction 1, on the other hand, is insoluble in methanol and does not lend itself to separation via the techniques used for the other fractions. Chemical characterization of the separated fractions is now in progress using analytical approaches previously employed on the original SRC sample[4].

ACKNOWLEDGEMENT

The financial support of the VPI and SU Research Division is gratefully appreciated.

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