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Note

Rapid method for characterization of heavy petroleum fractions

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Gel permeation chromatography (GPC) has often been utilized for "fingerprinting" of petroleum products and for the preparation of molecular-weight fractions for subsequent analysis¹. Altgelt and Hirsch² used a 70-l polystyrene gel preparative column to separate a Venezuelan asphalt into seven fractions for additional analysis. Elution was complete within 3 h. Albaugh and Talarico³ used multiple detectors and a Styragel® column for the analysis of several petroleum products. Samples (5 mg) of crude oils were separated within 2 h. Done and Reid⁴ produced GPC "fingerprints" on 60-Å Styragel for 50 crude oils and found that most could be classified by five distinct profiles. Analysis time for each was less than 1 h. Suatoni and Garber⁵ used 10- μ m LiChrosorb® (adsorption high-performance liquid chromatography) for group type analysis of petroleum fractions in the boiling point range of 190-360°.

In this paper, the use of LiChrospher® and LiChrosorb to obtain profiles of molecular-weight distributions is shown for some petroleum crudes, pitches, and asphaltenes. The elution time was less than 30 min, and data were obtained on less than 16 μ g of sample.

EXPERIMENTAL

Apparatus

All plumbing was performed with 3.18 mm O.D. (2.16 mm I.D.) and 1.59 mm O.D. (0.51 mm I.D.) stainless-steel tubing (Alltech Associates, Arlington Heights, Ill., U.S.A.). The columns were fitted with zero-dead-volume unions having 0.5- μ m filtering disks and were connected by 2 cm of 0.25 mm I.D. stainless steel tubing. Two in-line filters, 7 μ m (Nypro Co., Willoughby, Ohio, U.S.A.) were used to filter the mobile phase both before it entered the Milton Roy pump (Model 196-31, Riviera Beach, Fla., U.S.A.) and after it passed through the pulse-damping system.

The pulse-damping system consisted of a 25 cm \times 4.7 cm O.D. stainless-steel cylinder which held approximately 250 cm³ of solvent, followed by 3.05 m of 0.25 mm

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I.D. tubing which was coiled in 2-cm loops. This made the system virtually pulseless. A 3000 p.s.i.g. pressure gauge (Matheson Co., East Rutherford, N.J., U.S.A.) was used to monitor pressure.

A sampling valve (Valco Instruments, Houston, Texas, U.S.A.) fitted with a 10- μ l sample loop and operated by an air-actuated solenoid (Humphrey Products, Kalamazoo, Mich., U.S.A.) was used to inject samples. Absorbance was monitored at 254 nm with a DuoMonitor[®] detector (Model 1222, Laboratory Data Control, Riviera Beach, Fla., U.S.A.) which was fitted with a 25- μ l cell. Chromatograms were recorded on a strip chart recorder (Model 385, Linear Instruments, Irvine, Calif., U.S.A.).

Chemicals

Polystyrene standards (Pressure Chemical Co., Pittsburgh, Pa., U.S.A.) and *o*-xylene (Matheson, Coleman & Bell, East Rutherford, N.J., U.S.A.) were used to construct the calibration curves. (Using such standards does not give exact molecular-weight distributions due to intrinsic differences in hydrodynamic volume between the compounds found in petroleum samples and the polystyrenes, but it does permit a rough estimate of molecular weights to be made⁶.) The Witco petroleum pitch and the Ashland petroleum pitch were obtained from Airco-Speer (Niagara Falls, N.Y., U.S.A.). The Boscan petroleum crude, Boscan asphaltene, and Morichal petroleum crude were obtained from Petroven (Caracas, Venezuela).

The petroleum samples were dissolved in chloroform. The petroleum pitches were filtered through a 0.45- μ m mixed cellulose acetate and nitrate filter (Millipore Corp., Bedford, Mass., U.S.A.). Water droplets were skimmed from the surface of the Morichal crude before the sample was diluted to volume with the remaining chloroform.

Polystyrene standards were dissolved in chloroform. Each sample solution contained only one component so that peak maximum could be unambiguously determined. The concentration of each polystyrene standard was approximately 5 mg/cm³.

The 25-cm stainless-steel columns (6.35 mm O.D., 5.33 mm I.D.) were packed with 500 Å pore size and 100 Å pore size LiChrospher and 60 Å pore size LiChrosorb (EM Laboratories, Elmsford, N.Y., U.S.A.). The surfaces were modified using trimethylchlorosilane (Pierce, Rockford, Ill., U.S.A.). Thus, the LiChrosorb column was used primarily in the exclusion mode rather than the adsorption mode in this application. The mobile phase consisted of chloroform-2-propanol (90:10) (J. T. Baker, Phillipsburg, N.J., U.S.A.).

Procedure

All samples and standards were injected at a flow-rate of 0.5 cm³/min. Three different systems of columns were examined, LiChrosorb SI 60 alone, LiChrospher SI 500 and SI 100 in series, and LiChrospher SI 500, LiChrospher SI 100, and LiChrospher SI 60 in series.

RESULTS

Calibration curves for the three systems are given in Figs. 1-3. The calibration

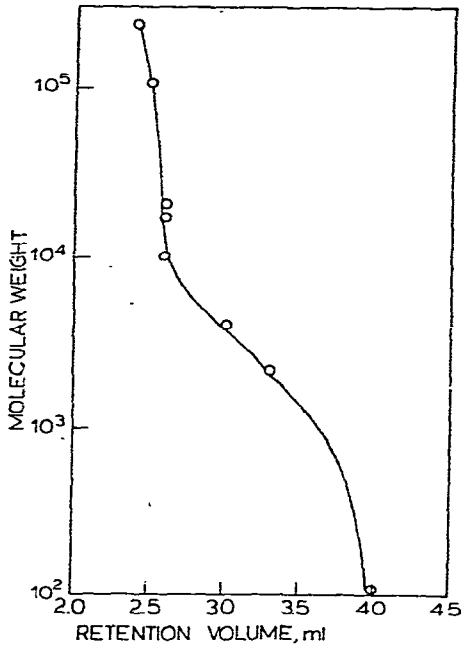


Fig. 1. Calibration curve for the LiChrosorb SI 60 column.

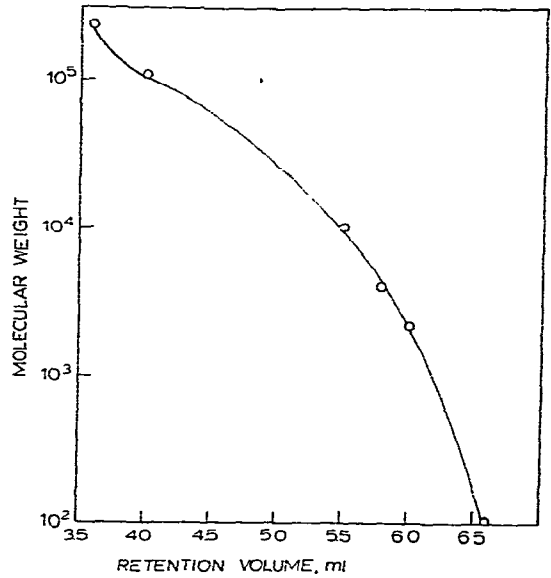


Fig. 2. Calibration curve for the LiChrospher SI 500 and SI 100 columns in series.

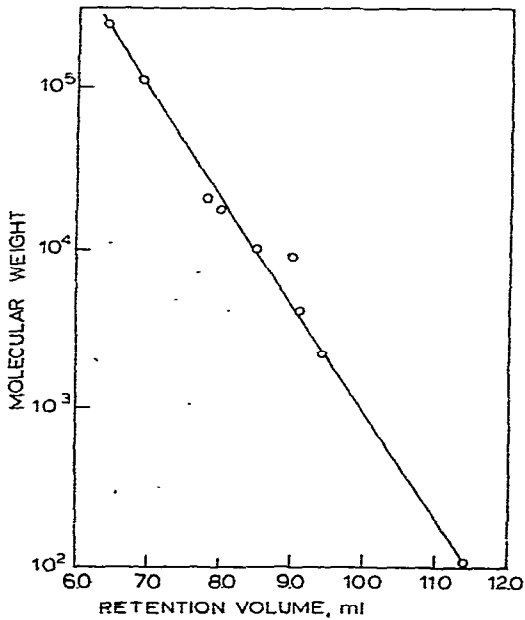


Fig. 3. Calibration curve for the LiChrospher SI 500, SI 100, and LiChrosorb SI 60 columns in series.

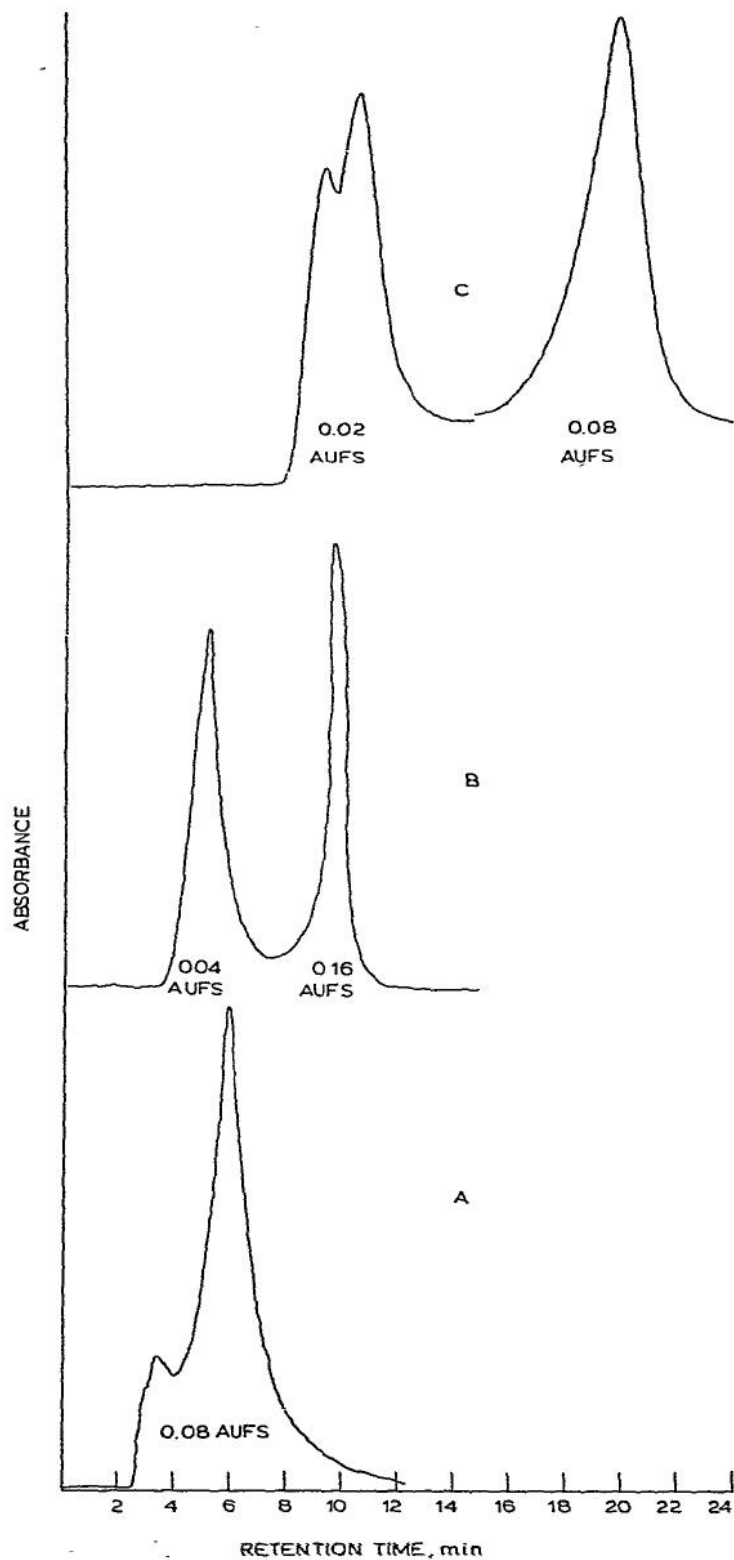


Fig. 4. Chromatograms of Boscan crude. (A) LiChrosorb SI 60 column; (B) LiChrospher SI 500 and SI 100 columns in series; (C) LiChrospher SI 500, SI 100, and LiChrosorb SI 60 columns in series.

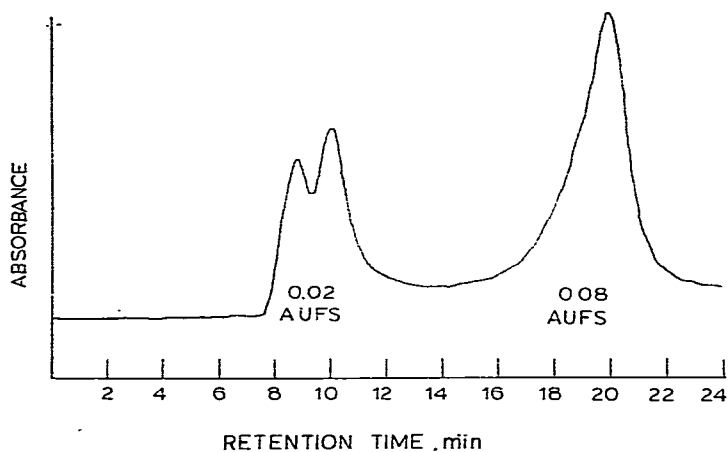


Fig. 5. Chromatogram of Morichal crude on the three-column system.

curve for the three-column system was linear for the molecular-weight range 100 to 233,000 molecular-weight units. The calibration curve for the other two systems followed the usual S-shaped pattern⁷. Resolution increased with the addition of each column (Fig. 4).

The first group of samples were the petroleum crudes. Chromatograms of the Boscan and Morichal crudes (Figs. 4 and 5) showed no major differences in the high-molecular-weight distribution of the UV-absorbing components. Both samples showed higher concentrations of the UV-absorbing species in the <1100 than in the >200,000 molecular-weight range. These Venezuelan crude oils were taken from wells 800 miles apart and have been shown to differ significantly in the quantities of some elements such as metals and sulfur⁸. (For example, Boscan crude contains approxi-

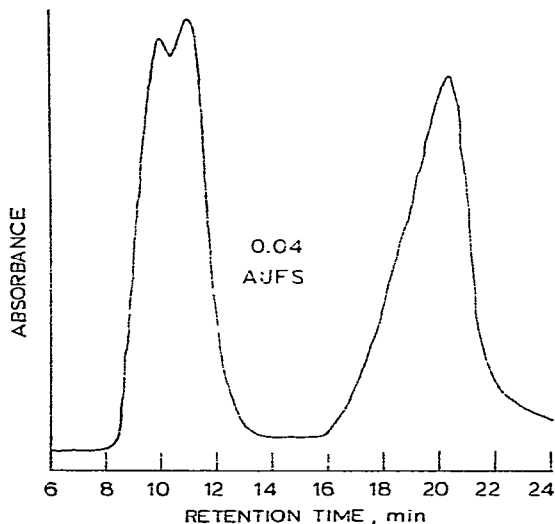


Fig. 6. Chromatogram of Boscan asphaltene on the three-column system.

mately 1200 ppm vanadium and 115 ppm nickel; Morichal crude contains approximately 100 ppm vanadium and 45 ppm nickel.)

The pentane-insoluble fraction (asphaltene) of the Boscan crude was also examined (Fig. 6). The chromatogram of the asphaltene differed from that of the crude in that a loss of some of the lower-molecular-weight species is evident in the asphaltene fraction.

Chromatograms of the two petroleum pitches (Figs. 7 and 8) showed only low-molecular-weight species. These pitches, obtained from commercial sources, are the solid residues obtained from petroleum crudes after refinement. The chromatograms of the pitches showed only one peak in all three column systems.

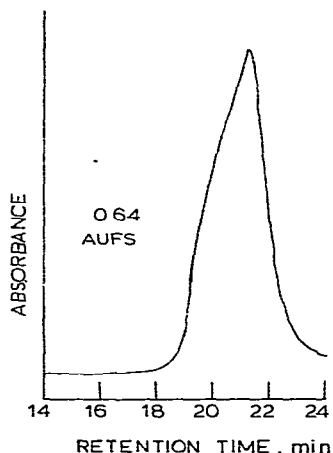


Fig. 7. Chromatogram of Witco petroleum pitch on the three-column system.

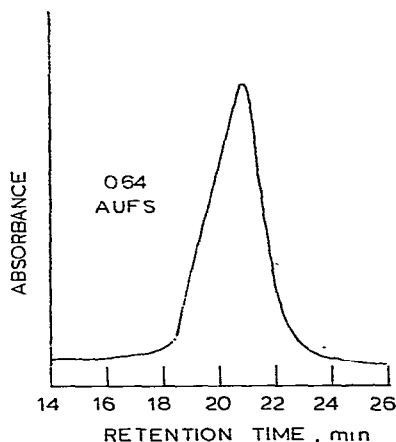


Fig. 8. Chromatogram of Ashland petroleum pitch on the three-column system.

DISCUSSION

This study has shown the feasibility of obtaining rapid "fingerprints" of small quantities of petroleum products. Elution times were less than 30 min for less than 16 μg of sample.

Resolution was shown to be improved by using silanized LiChrospher SI 500, LiChrospher SI 100, and LiChrosorb SI 60 in series, although analysis time increased. The calibration curve for the three-column system was linear from 100 to 233,000 molecular-weight units.

Silanized LiChrosorb SI 60 was shown to be a useful packing material in primarily the exclusion chromatographic mode. Previously, this material has been used mostly in the adsorption mode⁵.

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