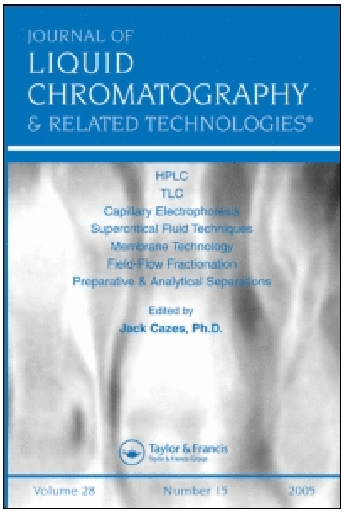

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SEPARATION OF FULLERENES C_{60}, C_{70}, AND C_{76-84} ON POLYSTYRENE DIVINYLBENZENE COLUMNS

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ABSTRACT

New HPLC methods have been developed to effectively separate and recover essentially pure amounts of C_{60} and C_{70} fullerenes from the lower MW contaminants and higher MW fullerenes co-extracted from carbon soot. Separation with toluene/methylene chloride mobile phase results from different degrees of interaction of conjugated π-electrons of the fullerenes and the polystyrene divinylbenzene (PSDVB) resin stationary phase. The presence of either toluene or CS_2 in the mobile phase attenuates π-electron interactions. The separation mechanism becomes predominantly size exclusion chromatography for a CS_2 concentration in the mobile phase $\geq$ 60%.

Excellent separation of C_{60}, C_{70} and C_{76-84} is obtained with the analytical Envirosep-ABC™ columns in less than 15 minutes. Substituted fullerene reaction products are also well separated from their parent compounds. The effects of column size and PSDVB pore size on analytical separation, along with the effects of pore size, mobile phase, and sample size on semi-preparative separation of C_{60} and C_{70} are reported. Semi-preparative columns can

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process with satisfactory resolution more than 14.5 mg of fullerenes per run using methylene chloride:toluene as mobile phase. These studies led to the development of an optimized set of columns consisting of a guard column (60x21.2 mm) and a modified preparative column (350x21.2 mm) with improved flow design and separation efficiency.

INTRODUCTION

The existence of a round, hollow, geodesic-sphere shaped molecule consisting of 60 carbon atoms was first proposed in 1985 by Kroto et al. (1). In 1990, Krätschmer et al. (2) reported a process based on resistive heating of carbon rods in an inert helium atmosphere, by which measurable amounts of C_{60} and other less round molecules of similar structure, such as C_{70}, were prepared. This new form of carbon complements the well known pyramidal shape of diamond carbon, and the hexagonal shape of graphite sheets. These molecules are referred to as buckminsterfullerenes or fullerenes in honor of Buckminster Fuller, the inventor of the geodesic dome.

Besides the normally occurring carbon soot contaminants such as benzene, anthracene and other polynuclear aromatics, and the well defined C_{60} and C_{70}, a variety of fullerenes of more complex form are also produced, including C_{32}, C_{50}, C_{84}, and other fullerenes even larger than C_{960} (3). By far the most abundant of all fullerenes in the raw soot are C_{60} and C_{70}, with a ratio C_{60}/C_{70} of about 7/1. The high resonance energy of C_{60} and C_{70} brought about by their conjugated double bonds enhances their molecular stability and strength. C_{60} is reported to be stable to pressures up to 2.6 x 10^6 psi (4) and, like carbon graphite, is stable in many organic solvents for several weeks.

Simple resistive heating yields less fullerenes than vaporization by plasma arc or Nd:YAG laser vaporization.

In the plasma arc method, the two rods are brought to touch each other to strike an arc and then are separated to a distance where maximum plasma brightness occurs. Using this method, yields of soluble material, mainly fullerenes C_{60} - C_{266}, of up to 44% are obtainable (5). Thomas (6) provides a detailed review of the analytical chemistry of buckminsterfullerene C_{60}.

Mixtures of fullerene complexes in carbon soot as prepared by a contact arc method are available from MER Corporation of Tucson, Arizona. Fractional content of C_{60} and C_{70} in the carbon soot obtained by this method can vary widely, between approximately three (3) and 33 percent by weight. The fullerenes are recovered from the carbon soot by either liquid extraction with hexane, benzene, toluene, pyridine, or tetramethylbenzene (5), sublimation under vacuum in inert helium atmosphere (7) or supercritical fluid extraction (8,9). Smart et al. (10) report that extraction with aromatic solvents is an activated process, and recoveries increase rapidly with increasing extraction temperature. The difficulty in desorbing the fullerenes from the carbon soot matrix appears to be the limiting factor in achieving quantitative recoveries.

Regardless of the extraction method employed, further separation is needed to obtain substantially pure fractions of C_{60} and C_{70}. Separation of C_{60} from low molecular weight compounds and higher fullerene extracts on an alumina column was reported by Diederich et al. (11). In this method, the carbon soot extract is first adsorbed on neutral alumina, and is then chromatographed on the same alumina column with a mixture of 5% hexane in toluene to elute C_{60}, and 10-50% hexane in toluene to elute C_{70}. However, because of the low solubility of fullerenes in hexane, large volumes of solvent are needed to elute C_{60}. In the same manner, C_{60} is separated from a fullerene mixture on a graphite column, and C_{70} and higher fullerenes are subsequently recovered by soxhlet extraction (12).

Good separation of C_{60} and C_{70} is achieved with Pirkle's phenylglycine-based HPLC column packing using hexane as mobile phase. The separation is based on π-π interactions between the fullerenes and the dinitrobenzamide groups on the support (13). The separations are, however, limited to very low sample sizes due to the low solubility of fullerenes in the mobile phase. Kikushi et al. (14) report an HPLC separation method for fullerenes using carbon disulfide (CS_2) as mobile phase, wherein partial separation of C_{60}, C_{70} and higher molecular weight (MW) fullerenes was achieved by recycling column effluent. Although resolution is low, the high solubility of fullerenes in CS_2 ($\approx$30-40 mg/mL) allows processing of larger sample sizes, and converts the separation mechanism to predominantly size exclusion chromatography.

In this paper, methods for separation of C_{60} and C_{70} on a PSDVB resin stationary phase with Envirosep-ABC™ (Phenomenex Inc., Torrance, CA) columns are reported. Conventionally, these columns are used for size exclusion chromatography. These columns find application in the enrichment of lower MW contaminants from high MW biogenic materials and sediment extracts (15,16).

In separation of fullerenes, an additional interaction force results from the π-π electron interactions between the aromatic fullerenes and the stationary phase. Separation of species of both fullerenes is thus achieved mainly by a combination of adsorption chromatography and size exclusion chromatography, and is accomplished in less than 12 minutes on a 7.8 x 300 mm column. An optimized column set for semi-preparative separation consists of a 60x21.2

mm guard column in series with a 350x21.2 mm column. Note that after this work was completed, we learned of similar work by Meir and Selegue (17) who used Waters (Milford, MA) Ultrastyragel columns and toluene mobile phase to separate C_{60} and C_{70}. The toluene:methylene chloride mobile phase employed in this work provides better separation.

EXPERIMENTAL RESULTS

The UV spectra of C_{60} and C_{70}, and the separation of fullerenes and substituted fullerene reaction products are now reported. The effects of column size and PSDVB pore size on analytical separation, along with the effects of pore size, mobile phase, and sample size on semi-preparative separation of C_{60} and C_{70} are used to determine optimum separation conditions.

Two Envirosep-ABC PSDVB columns, available from ABC Laboratories, Inc., 300 mm long, and having column I.D. of 7.8 mm and 22.5 mm respectively, were equilibrated with methylene chloride, and eluted with methylene chloride at 2 and 5 mL/min respectively. A sample mixture was prepared by thorough mixing of 3 mg of a mixture of C_{60} and C_{70} fullerene compounds in 7 mL of methylene chloride. The sample was then allowed to equilibrate. 5 μl and 50 μl samples of this solution were injected into the 7.8 mm and the 22.5 mm column respectively. Column oven temperature was set to 40 °C. Each column was evaluated individually for detection and separation of the C_{60} and C_{70} mixture by monitoring the UV absorption at 240 nm as this wavelength provided maximum sensitivity for the C_{70} compound. A Hewlett Packard 1090 series HPLC system equipped with a photodiode array detector was used for mobile phase delivery and detection. Two peaks were observed on each column and each peak was collected individually.

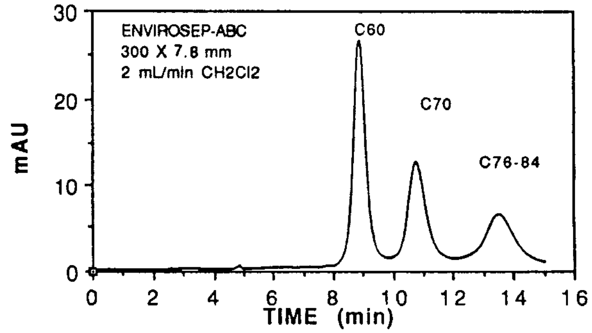

FIGURE 1. Separation of Fullerenes C_{60}, C_{70} and C_{82} on a 7.8 mm I.D., 300 mm Long Envirosep-ABC Column.

The elution time for C_{60} and C_{70} from the 7.8 mm I.D. column are 8.9 minutes and 11.3 minutes respectively (Figure 1). This reversed size exclusion elution order indicates that the dominant retention mechanism of C_{60} and C_{70} is not size exclusion since C_{70} has a larger molecular volume than C_{60}, about 7x7x9 Å ellipsoid vs 7 Å sphere (17). Given the aromaticity of both the analytes as well as the stationary phase, it appears that the most plausible mechanism for the separation of C_{60} and C_{70} is an instantaneous dipole-induced dipole interaction. The high polarizability of π electrons of the fullerenes, from the continuous electron density fluctuation, results in especially strong dispersion forces among molecules with conjugated π electrons (i.e., the aromatic π electrons of C_{60} and C_{70} molecules interact with the π electrons of the PSDVB stationary phase in a manner analogous to large polynuclear aromatic hydrocarbons). Thus, this elution order indicates that adsorption chromatography dominates exclusion chromatography, and that the greater number of unsaturated bonds in C_{70} with respect to C_{60} induces adsorption forces that are significant enough to overcome steric effects and alter the expected elution profile from a conventional size exclusion column. The UV spectrum for recovered C_{60} and C_{70} are shown in Figures 2 and 3 respectively.

The eluate containing the first peak (C_{60}) bore a purple color and had a UV spectrum similar to that of a reference spectrum for C_{60}. The eluate containing the second peak (C_{70}) bore a rose-violet color, and exhibited a similar spectrum as a reference spectrum of C_{70} in the region of 220 - 400 nm.

A typical chromatogram obtained with the 22.5 mm I.D. column is shown in Figure 4. This column has a larger loading capacity than the 7.8 mm I.D. column. Typically, 2-3 mL of saturated solutions of C_{60} and C_{70}, corresponding to roughly 10 mg of fullerenes, are well separated with this column.

Separation of Fullerenes C_{60} and C_{70} from their Reaction Products

Substituted fullerene products obtained by bromination and oxidation of C_{60} and C_{70} are also well separated from their parent compounds. Figure 5 shows the UV HPLC chromatogram of the product of oxidation of a C_{60}/C_{70} mixture in a methylene chloride/toluene solution (18). The sample was eluted with methylene chloride mobile phase through a 50 x 7.8 mm guard column and a 300 x 7.8 mm column disposed in series. The first peak at 5.04 minutes corresponds to toluene, while reaction products include the 6.62 and the 7.45 minute peaks. Based on structure elucidation studies by UV, negative ion mass spectrometry, and ^{13}C NMR, the 6.62 minute product is proposed to be $C_{60}NO_6$. The reaction products are thus well separated from the reactants C_{60} and C_{70} which elute at 10.49 and 13.14 minutes respectively. The shorter retention times of reaction products as compared

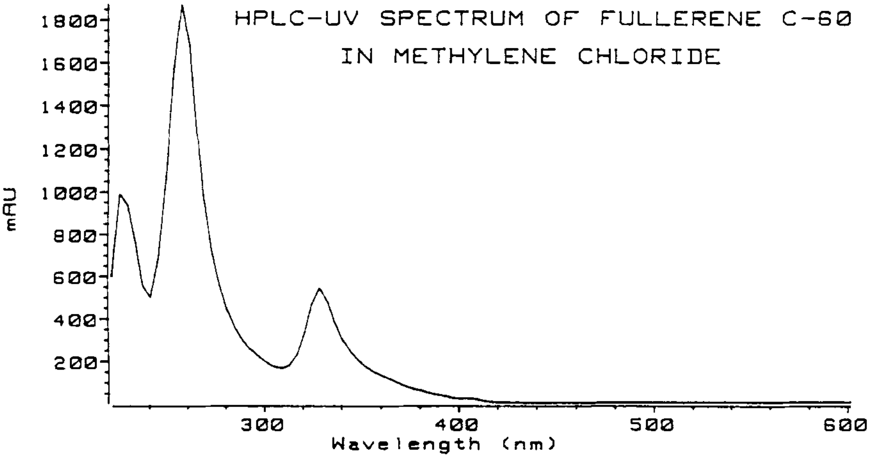

FIGURE 2. UV Spectrum of Fullerene C_{60}.

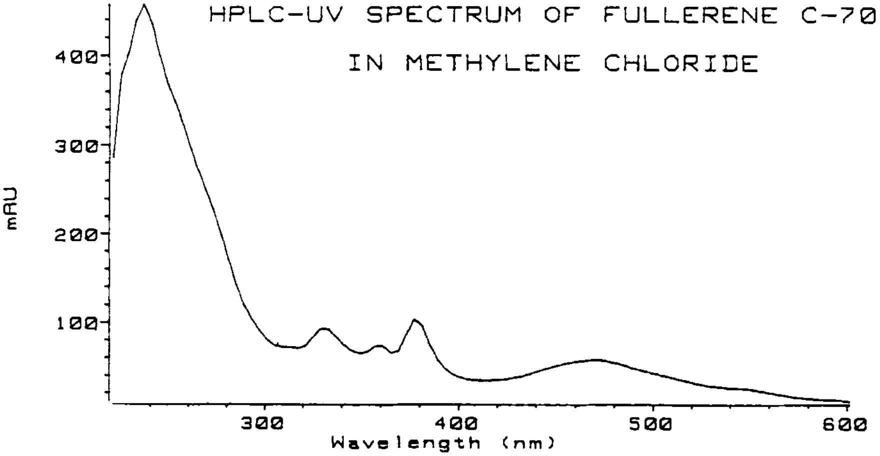

FIGURE 3. UV Spectrum of Fullerene C_{70}.

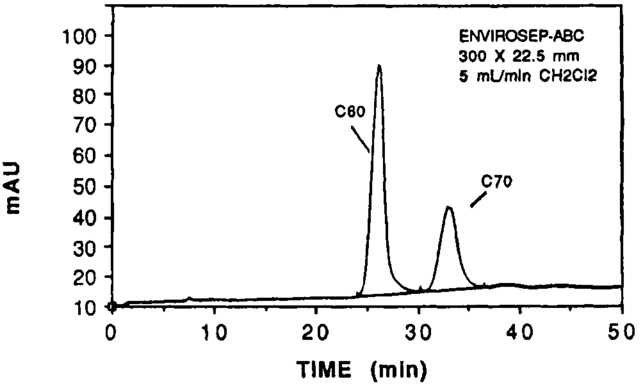

FIGURE 4. Separation of Fullerenes C_{60} and C_{70} on a 22.5 mm I.D., 300 mm Long Envirosep-ABC Semi-Preparative Column.

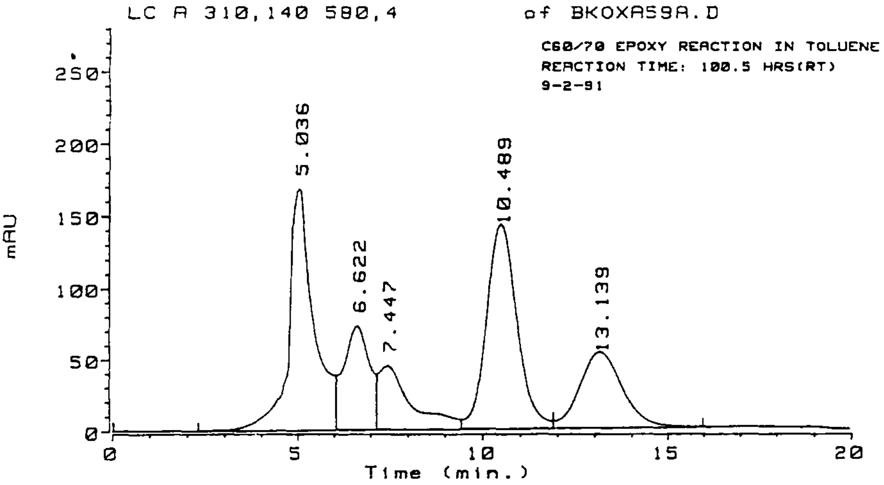

FIGURE 5. Separation of Fullerenes C_{60} and C_{70} from their Oxidation Reaction Products.

to the parent compounds is due to their lower aromaticity. This is a consequence of breakup of π-π bonds by addition reactions. This separation method is thus powerful enough to separate fullerenes from their corresponding substituted forms. The reaction mixture was sampled at different reaction times. Determination of the composition of the reaction mixture at different reaction times is used to study the reaction kinetics.

Characterization of Chromatographic Separations

Results on the effects of column packing pore size, mobile phase, and sample size on the chromatographic separation of C_{60} and C_{70} are now reported.

Effect of Column Packing Pore Size

Three Envirosep columns, 300 X 7.8 mm, containing 10 μm average O.D. resin beads having average pore sizes of 50, 100, and 500 Å, were used under identical chromatographic conditions (see footnote in Table 1) to study the effect of column packing pore size on resolution (R), selectivity (α), capacity factor (k'), and column efficiency (HEIGHT/AREA). The amount of divinylbenzene (the % crosslinkage of polystyrene) is the main difference among these three packings.

Table 1 shows that chromatographic selectivity decreases with increasing pore size. Thus, the amount of crosslinking agent divinylbenzene in the column packing affects selectivity positively. Capacity factors for C_{60} and C_{70} are inversely proportional to the pore size of the packing. The higher k' are due to the larger surface area of the smaller pore size packing. The 100 Å pore size column packing yields optimum results for combined resolution and elution time.

TABLE 1. Effect of Resin Pore Size on the Separation of C_{60} and C_{70}.

Pore Size (Å)	R	α	k'		HEIGHT/AREA	
			C_{60}	C_{70}	C_{60}	C_{70}
50	1.84	1.34	3.58	4.79	0.024	0.018
100	2.19	1.29	2.80	3.61	0.034	0.025
500	2.04	1.25	2.41	3.01	0.043	0.028

$\alpha = (T_{RC70} - T_{R0})/(T_{RC60} - T_{R0})$.
T_{R0} = Retention time at void volume.
$k' = (T_R - T_{R0}) / T_{R0}$.
$R = (T_{RC70} - T_{RC60}) \times 2.35 / (W(50)_{C70} - W(50)_{C60})/2$.
W(50) = Peak width at half height.
Columns : Envirosep 300 x 7.8 mm, 40 °C.
Eluent : 2.0 mL/min of 100% methylene chloride.

Effect of Column Dimension

Separation of C_{60} and C_{70} on seven Envirosep-ABC columns containing 10 μm O.D. PSDVB bead and different column dimensions and packing pore sizes were studied. These columns were:
300 x 7.8 mm, 50 Å ; 300 x 7.8 mm, 100 Å ;
300 x 7.8 mm, 500 Å ; 300 x 15.0 mm, 50 Å ;
300 x 22.5 mm, 50 Å ; 300 x 22.5 mm, 100 Å ;
300 x 22.5 mm, 500 Å.

Table 2 shows the results obtained with the seven columns. All columns show some degree of separation. The large difference in capacity factor observed with these two types of columns is in direct proportion to the surface area (i.e. thickness and pore size) of the PSDVB layer. Resolution is higher for the 100 Å column packing for both column sizes, and increases with increasing column size. As expected, selectivity and capacity factor decrease with increasing pore size, and are unaffected by column size.

Effect of Sample Size, Sample Solvent, and Mobile Phase on Separation of C_{60} and C_{70}

The low solubility of C_{60} and C_{70} in organic solvents limits chromatographic effectiveness and preparative

TABLE 2. Effect of Column Size and Pore Size of PSDVB Gel Packing on Separation of C_{60} and C_{70} Fullerenes.

Column	R	α	k' C_{60}	k' C_{70}
Envirosep-ABC				
300 x 7.8 mm				
50 Å	1.84	1.34	3.58	4.79
100 Å	2.19	1.29	2.80	3.61
500 Å	2.04	1.25	2.41	3.01
300 x 15.0 mm				
50 Å	1.88	1.34	3.64	4.85
300 x 22.5 mm				
100 Å	2.59	1.29	2.84	3.67
500 Å	2.27	1.25	2.37	2.97

Eluent Flow Rate : Methylene Chloride at 5 mL/min.
Column Temperature : Ambient.

throughput. The solubility of C_{60} in benzene at room temperature is about 5.0 mg/mL, while its solubility in methylene chloride is an order of magnitude lower. Co-solubilities of a mixture of C_{60}/C_{70} (6/1 ratio) in binary mixture solvent systems of toluene and methylene chloride, as determined by HPLC, are shown in Figure 6.

Solubility decreases nearly linearly with increasing methylene chloride mixture composition. Parallel solubility profiles indicate that solubilities of C_{60} and C_{70} are similar. Maximum solubility of C_{60}+C_{70} in toluene is thus an order of magnitude higher than in methylene chloride, and chromatography of saturated solution samples of fullerenes in toluene with methylene chloride mobile phase may thus be severely limited by solubility. The fullerenes may precipitate on the stationary phase, and thereby introduce another rate limiting step, i.e. solubility, in addition to adsorption, which would tend to increase peak tailing and reduce chromatographic separation efficiency. Thus, in order to increase sample

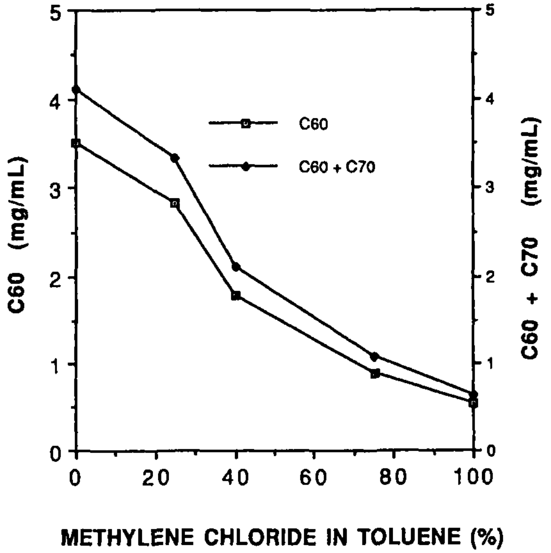

FIGURE 6. Co-solubility of a 7/1 Mixture of C_{60} and C_{70} in Toluene:Methylene Chloride Binary Mixtures.

capacity, it would be desirable to employ a mobile phase that has higher affinity for fullerenes than methylene chloride. Toluene and CS_2 appear to be good candidates for such a task. We first examine the effects of toluene on chromatographic separation.

Effect of Mobile Phase and Sample Size on Semi-Preparative Separation of C_{60} and C_{70}

Based on the previous results, the 300 x 22.5 mm column packed with 100 Å, 10 μm particles was selected for the semi-preparative separation of C_{60} and C_{70}. The effects of sample size, sample solvent (100% toluene vs 50% toluene/CH_2Cl_2, v/v), and mobile phase (toluene to methylene chloride ratio) on chromatographic separation are given in Table 3. Chromatographic resolution is seen

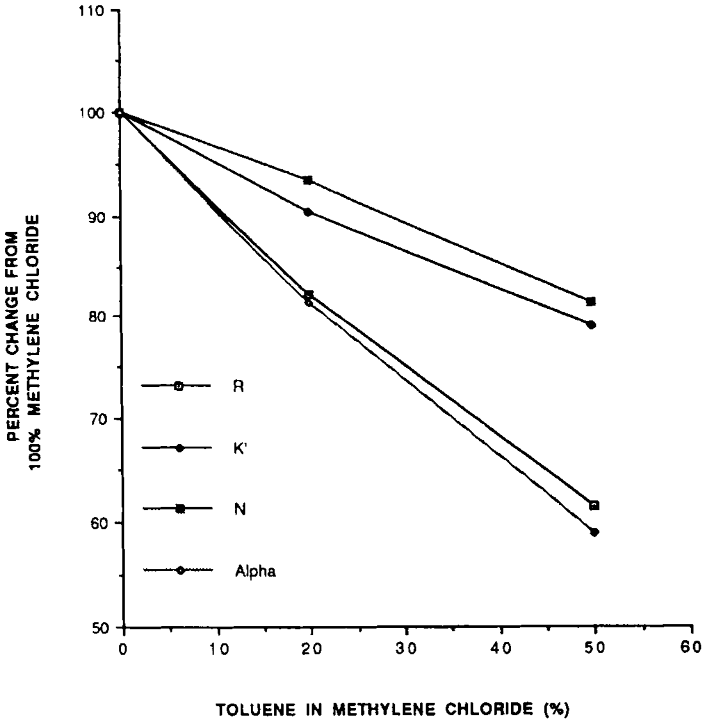

FIGURE.7. Influence of Toluene:Methylene Chloride Ratio on Chromatographic Separation of C_{60} and C_{70}.

to decrease with increasing sample size and increasing ratio of toluene/methylene chloride in the sample solvent or in the mobile phase. Sample size has little effect on selectivity or capacity factor. Selectivity and capacity factor are negatively affected by increasing ratio of toluene/methylene chloride in the mobile phase.

Figure 7 illustrates these results. The decrease in retention time and separation efficiency of both fullerenes with increasing toluene concentration in the methylene chloride:toluene mobile phase is further evidence for the proposed π-π electron interaction separation mechanism.

TABLE 3. Effect of Sample Size, Sample Solvent, and Mobile Phase on Separation of C_{60} and C_{70} Fullerenes.

Sample Size (mL)	R	α	k' C_{60}	k' C_{70}	HEIGHT/AREA C_{60}	HEIGHT/AREA C_{70}
Elution Solvent: 20% Tol. in $MeCl_2$						
0.1	2.17	1.25	2.65	3.31	0.015	0.011
1.0	2.01	1.25	2.61	3.26	0.013	0.010
2.5	1.58	1.25	2.62	3.26	0.011	0.009
5.0	0.92	1.23	2.64	3.26	0.007	0.006
5.0*	1.58	1.25	2.67	3.32	0.011	0.009
Elution Solvent: 50% Tol. in $MeCl_2$						
1.0	1.59	1.20	2.35	2.83	0.014	0.011
5.0	0.86	1.19	2.39	2.84	0.008	0.008

Column : Envirosep-ABC, 300 x 22.5 mm, 10 μm, 100 Å.
Sample : Saturated fullerene mixture in toluene diluted 500 times with toluene. (*) : Saturated fullerene mixture in toluene diluted 500 times with 50% toluene in methylene chloride. Column at ambient temperature.

Separation efficiency, i.e. highest yield of purified C_{60} and C_{70} per unit time and cost, is the deciding factor in determining optimum conditions for preparative chromatography. Toluene was therefore selected as sample solvent and a 50/50, v/v, mixture of toluene and methylene chloride was selected as mobile phase, as this mixture provides lower retention times.

Semi-preparative isolation runs of C_{60} and C_{70} were made using the chromatography conditions shown in Table 4. Data were obtained on sample size effects on the purity and recovery of C_{60} and C_{70}. Equivalent fractions from the multiple runs were pooled and the purity and amount of fullerenes in these fractions were analyzed. Figure 8 shows the collection windows.

Table 5 shows that recovery of C_{60} decreases slightly with increasing sample size. Pooled fraction 1 contains a small amount of C_{60} (ca. 5%) and several unresolved unknown peaks that eluted before the C_{60} peak. These

TABLE 4. HPLC Conditions for Semi-Preparative Isolation of C_{60} and C_{70}

Column:	Envirosep, 300 x 22.5 mm,10 µm, 100Å.
Flow-rate:	5.0 mL/min.
Elution Solvent:	50% methylene chloride in toluene, v/v, at ambient T.
Inject. Volume:	4.5 mL.
Detector:	330 nm, +/- 40 nm
Sample Solution:	2.43 mg of (C_{60} + C_{70})/mL of toluene (MER sample).
Collection Times:	(See Figure 7)
Fraction 1:	14.0-21.0 min. Toluene and unknown peaks.
Fraction 2:	21.0-23.8 min. C_{60}.
Fraction 3:	23.8-25.0 min. C_{60} and C_{70}.
Fraction 4:	25.0-26.8 min. Mainly C_{70}.
Fraction 5:	26.8-34.0 min. Mainly C_{74-84} and higher MW fullerenes.

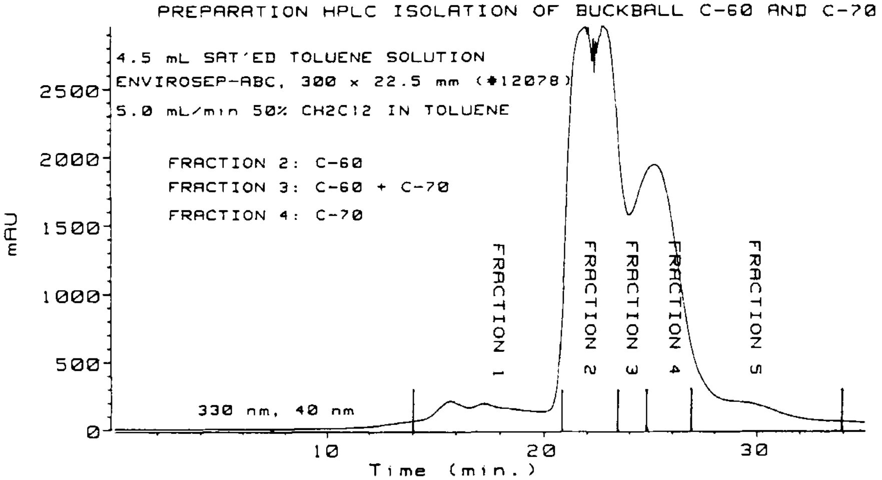

FIGURE 8. Semi-Preparative Separation of Fullerenes on a 22.5 mm I.D., 300 mm Long Envirosep-ABC Column.

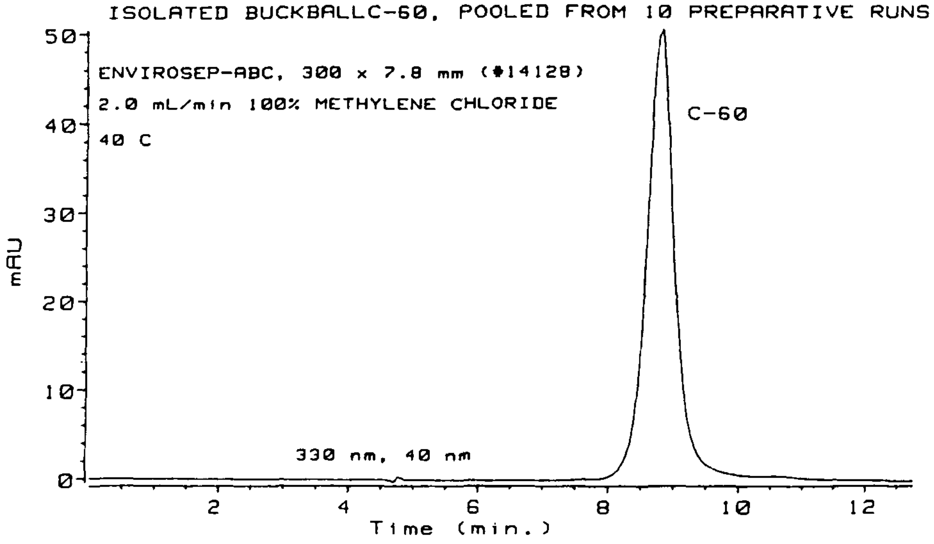

FIGURE 9. Isolation of C_{60} Fullerene from a Preparative Run (Fraction 2, Figure 8).

TABLE 5 : Effect of Sample Size on Semi-Preparative Separation of Fullerenes C_{60} and C_{70}

Vol. inj. (mL)	Mass Inj. (mg) C_{60} C_{70}	Amount (mg) and % Purity in Fraction						Total		C_{60} %Rec
		2 C_{60} C_{70}		3 C_{60} C_{70}		4 C_{60} C_{70}		mg C_{60} C_{70}	%Rec.	
2.5	4.65	3.62	96.3	0.156	26.2	0.251	25.1	4.03	86.7	90.0
	1.41	0.14	3.70	0.439	73.7	0.747	74.9	1.33	84.3	
3.5	6.58	4.95	95.9	0.172	26.5	0.348	22.3	5.47	83.1	90.5
	1.98	0.21	4.10	0.468	72.2	1.210	77.7	1.89	95.4	
3.5	6.58	4.70	96.5	0.247	33.2	0.354	22.9	5.30	80.6	88.7
	1.98	0.17	3.50	0.498	66.8	1.190	77.1	1.85	93.4	
4.0	7.44	5.87	96.8	0.314	39.4	0.554	27.5	6.74	90.6	87.1
	2.26	0.20	3.20	0.480	60.5	1.460	72.5	2.15	95.1	
4.5	8.37	No fractions collected						7.00	83.6	
	2.54							2.40	94.4	

MER Sample Composition : C_{60} : 1.860 mg/mL of toluene
C_{70} : 0.565 mg/mL of toluene

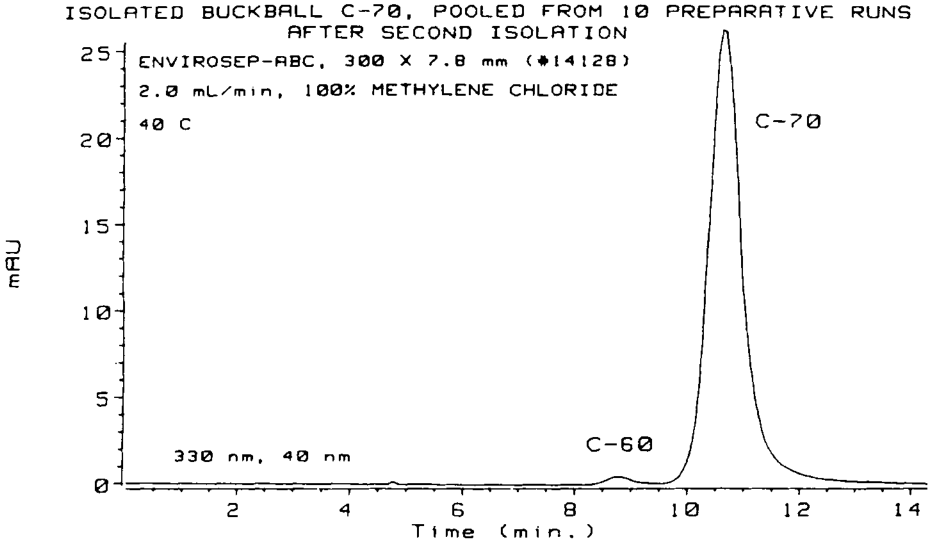

FIGURE 10. Isolation of C_{70} Fullerene from Two Consecutive Preparative Runs (Fraction 4, Figure 8).

peaks could be low MW polynuclear aromatic hydrocarbons (having lower π-electron density), or partially formed fullerenes. The fraction was rechromatographed on a 500 Å column and no change in separation was noted. Pooled fraction 2 contains mainly C_{60} (> 95%) for all sample sizes. Purity of this fraction is thus unaffected by sample size. Pure C_{60} was obtained by slightly narrowing the window of collection.

Figure 9 shows the HPLC of isolated C_{60} from the pooled fraction 2. Pooled fraction 3 includes 22-27% C_{60}. Pooled fraction 4 contains slightly more C_{70} than fraction 3, but still contains some C_{60}.
Thus, for semi-preparative samples, C_{60} elution tails into the next peaks and contaminates the C_{70} fraction. A second isolation run was performed on this fraction and the C_{60} content was reduced to 3% (Figure 10). Pooled

fraction 5 Contains a minor peak. Its UV spectrum and elution position indicate that it is either C_{74}, C_{76}, C_{82} or possibly C_{84}. C_{84} is reported to be the most significant fraction in fullerene soots besides C_{60} and C_{70} (19). Small quantities of C_{60} and C_{70} were still present in this fraction. About 2 mg of this substance were obtained, and were used to generate the chromatogram in Figure 1.

An Optimized Semi-Preparative Column Set

In separation of large amounts of low solubility substances such as fullerenes, the use of a guard column in series with a more costly full-size column is recommended to avoid possible damage to this latter. The limitations in sample capacity and resolution of the 300x22.5 mm column led to the development of an optimized set of semi-preparative columns consisting of a guard column and a modified semi-preparative column with improved flow design and separation efficiency. Figure 11 shows the effect of sample size on chromatographic separation of C_{60} and C_{70} with an Envirosep-ABC guard (60x21.2 mm) column in series with a full size column (350x21.2 mm), using a 50% toluene/methylene chloride mobile phase. Sample weight does not appear to affect separation efficiency of the fullerenes, and loading capacity is now limited primarily by the low solubility of the fullerenes in the sample solvent (toluene). This column set is thus capable of processing at least 14.5 mg of fullerenes C_{60} and C_{70}, and obtain 85% of the C_{60} in pure form.

Separation of C_{60} and C_{70} Using CS_2/Methylene Chloride Mobile Phase

Preliminary results on the effects of CS_2 in the mobile phase are now reported. The high solubility of fullerenes in CS_2 appears to result from the interaction

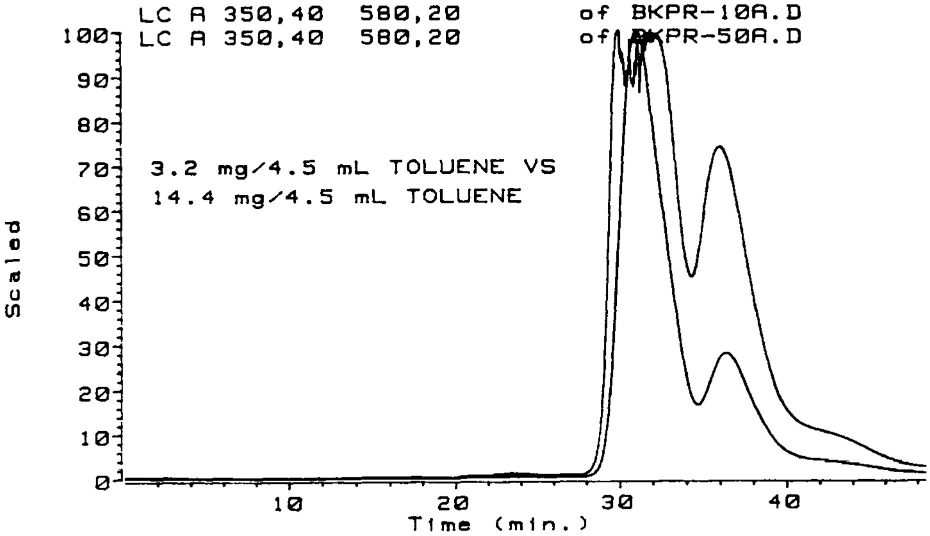

FIGURE 11. Effect of Sample Size on Preparative Separation of Fullerenes on a 21.2 mm I.D., 350 mm long Envirosep-ABC Column.

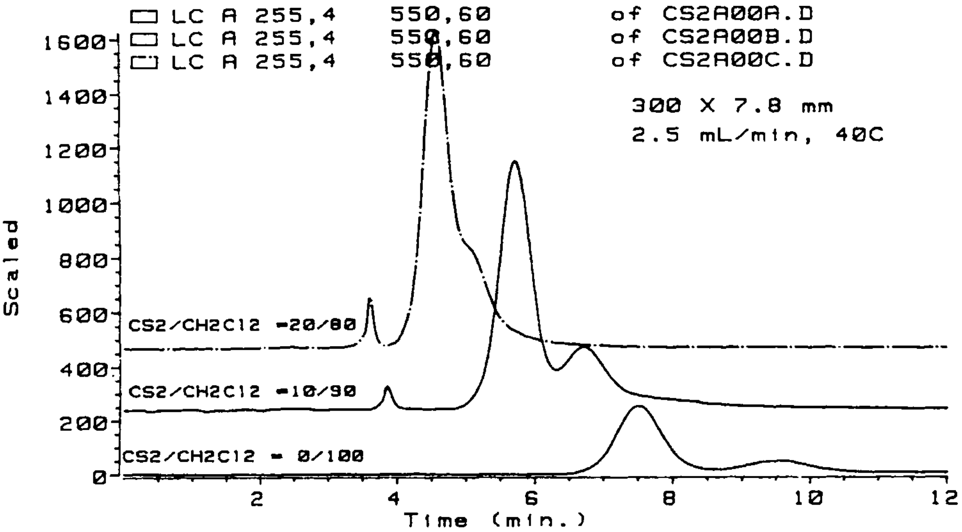

FIGURE 12. Effect of CS_2 in Methylene Chloride Mobile Phase on Retention and Chromatographic Separation of C_{60} and C_{70} Fullerenes.

between the high electronic density d-orbitals of sulfur with the π-electrons of the fullerenes. Figure 12 shows the change in chromatographic separation of fullerenes C_{60} and C_{70} with increasing CS_2 content in methylene chloride mobile phase. A sample of 0.2 μl of a 10 μg (C_{60}+C_{70})/μl of CS_2 solution was injected in each run. The smaller peak eluting prior to C_{60} and C_{70} was not identified. The reduction in elution time and the rapprochement of both fullerene peaks with increasing CS_2 content in the mobile phase is an indication of attenuation of fullerene adsorption on the stationary phase, and of conversion of the separation mechanism from adsorption chromatography to size exclusion chromatography. Separation obtained with 20% CS_2 mobile phase is similar to that obtained with 100% toluene mobile phase. Because of the small difference between the molecular sizes of both fullerenes, further increase in CS_2 content of the mobile phase to 60% causes the fullerenes to co-elute. For CS_2 concentrations greater than 80%, k' for both C_{60} and C_{70} are low, and C_{60} elutes after C_{70}, indicating that size exclusion dominates the separation mechanism.

In order to take advantage of the high solubility of fullerenes in CS_2, we have developed a new stationary phase that is a least five order of magnitude more interactive with the fullerenes than PSDVB. Investigation of the optimum conditions of stationary phase pore size and mobile phase CS_2 content on chromatographic separation and capacity in underway. We will report applications using this new column in a separate paper.

CONCLUSIONS

Fullerenes C_{60} and C_{70} are well separated with the Envirosep-ABC columns. Analytical columns provide high resolution separation between C_{60}, C_{70} and C_{74+} in less than

15 minutes. Sample capacities greater than 14.5 mg of fullerenes are obtained using a 60x21.2 mm guard column in series with a 350x21.2 mm full size column. The presence of either toluene or CS_2 in the mobile phase attenuates π-electron interactions. The separation mechanism becomes predominantly size exclusion chromatography for CS_2 concentration in the mobile phase $\geq$ 80%.

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