282 *J. Org. Chem.* **1993**, *58*, 282–283

[2-(1-Pyrenyl)ethyl]silyl Silica Packing Material for Liquid Chromatographic Separation of Fullerenes[1]

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As the interest in the fullerenes increases, better purification methods are being sought for C_{60}, C_{70}, and related compounds existing in crude soot. Two major problems encountered in the preparative separation of carbon clusters by HPLC,[2,3] poor peak shape and limited loading capacity, are due to the facts that the fullerenes show limited solubilities in the solvents employed and that the retention provided by the stationary phases was also limited. The silica gel bonded with nitro aromatic groups possessing π-acidity showed the improved separation and the greater loading capacity than alkyl-bonded silica stationary phases,[2] especially at high temperatures.[2c] Stationary phases containing phenyl and naphthyl groups also showed increased retention.[2d,3] The amount of fullerenes that can be separated under these conditions, however, was still much smaller than that of ordinary substances.[2c] Here we report that the PYE silica,[4] having π-basic character, can provide much greater loading capacity and higher efficiency in an aromatic solvent such as benzene or toluene, permitting much easier preparative separations of carbon clusters than the reported methods.

Although most fullerene separations have been carried out by employing a poor solvent as a mobile-phase component to effect the separation, the use of a more retentive stationary phase with better solvents is desirable for preparative purposes. Aromatic solvents generally showed better solubilities for fullerenes than polar solvents and alkanes usually employed for chromatographic separations. The solubilities of C_{60} and C_{70} in toluene were found to be 3.2 and 5.2 mg/mL, respectively, while that of C_{60} in hexane is less than 50 μg/mL.[5] We have chosen toluene as a mobile phase in this study for the reason of safety and convenience, although 1,2,4-trichlorobenzene and carbon disulfide showed higher solubilities than toluene.

Table I. Retention of C_{60} and the Separation Factor between C_{60} and C_{70} on Various Silica-Based Stationary Phases

stationary phase (R)[a]	k' (C_{60})	α $k'(C_{70})/k'(C_{60})$	k' (coronene)
silica	0.40	1.26	1.27
octyl (C_8)	0.10	1.30	0.09
dodecyl (C_{12})	0.27	1.40	0.24
octadecyl (C_{18})	0.70	1.77	0.48
triacontyl (C_{30})	2.03	1.72	0.82
NPE	2.60	2.04	3.22
phenyl	0.62	1.41	0.40
2-(2-naphthyl)ethyl	3.77	2.27	0.84
PYE[b]	13.7	3.14	1.77
PYE[c]	4.24	2.42	0.84

[a] Mobile phase: hexane, 30 °C. All the stationary phases were prepared from silica particles (Cosmosil; particle diameter, 5 μm; pore size, 11 nm; surface area, 330 m^2/g) by the reaction with alkyldimethylchlorosilane, $RSi(CH_3)_2Cl$.[6] [b] Mobile phase: hexane/toluene = 80/20 (v/v). [c] Mobile phase: hexane/toluene = 50/50 (v/v).

In order to find a better stationary phase than the reported ones, the retention of C_{60} was compared with various stationary phases in hexane. With the increase in size of the bonded alkyl groups, a greater increase in retention was observed for C_{60} than for coronene, a planar aromatic compound, as shown in Table I. The effect of the size of the bonded moiety was more pronounced with the aromatic stationary phases, which showed greater retention than alkyl-bonded silicas. [2-(1-Pyrenyl)ethyl]silyl (PYE) silica, resulting in prolonged retention in hexane, seems to be best suited for the preparative separation of fullerenes among these stationary phases. The results can be explained in terms of the charge-transfer interaction between electron-donating pyrene moieties and the electronegative fullerenes, whereas the interaction between [2-(nitrophenyl)ethyl]silyl (NPE) silica,[4b] an electron acceptor, and the fullerenes was not so effective as with a planar aromatic compound, e.g. coronene. C_{60} undergoes increased interaction with aromatic compounds with sterically matched structures.[3,7] The strong influence of molecular size and shape of bonded moieties as well as solvents[8] also suggests the importance of structural matching and dispersion forces in the chromatographic process.[9]

Figure 1 shows the effect of toluene content of the mobile phase on the retention of C_{60}. Although the NPE phase showed longer retention than C_{18}, the stationary phase cannot be used in toluene for the separation of fullerenes. PYE phase showed adequate retention ($k' = 0.91$) for C_{60} in toluene for the first time[10] with the separation factor of 1.80 between C_{60} and C_{70}, which compares favorably with the results on the other stationary phases in much weaker solvents. A slight decrease in retention was observed at higher temperatures.

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[5] C_{60} was dissolved to saturation in these solvents at refluxing temperatures. After cooling to 25 °C, the solution was filtered and analyzed by HPLC. The solubility in toluene was also examined gravimetrically by evaporating the solvent to dryness.

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[10] Benzene was employed as a mobile phase for the separation of fullerenes using a recycle system with polymer gel columns which showed very small retention. See: Kikuchi, K.; Nakahara, N.; Honda, M.; Suzuki, S.; Saito, K.; Shiromaru, H.; Yamauchi, K.; Ikemoto, I.; Kuramochi, T.; Hino, S.; Achiba, Y. *Chem. Lett.* **1991**, 1607–1610. Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Suzuki, S.; Shiromaru, H.; Miyake, Y.; Saito, K.; Ikemoto, I.; Kainosho, M.; Achiba, Y. *Nature* **1992**, *357*, 142–145.

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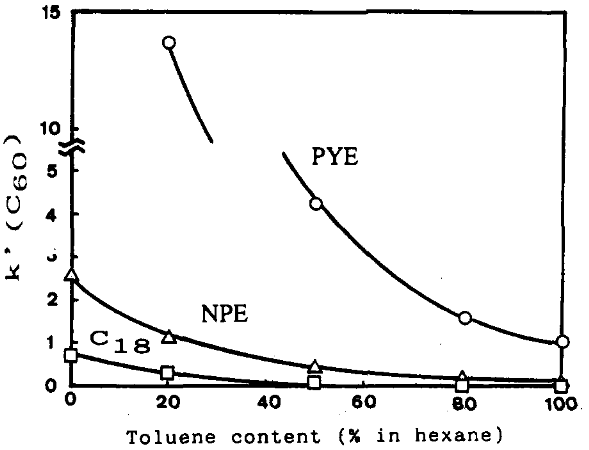

Figure 1. Effect of toluene content of the mobile phase on the retention of C_{60} on the column of C_{18}, NPE, and PYE, 30 °C.

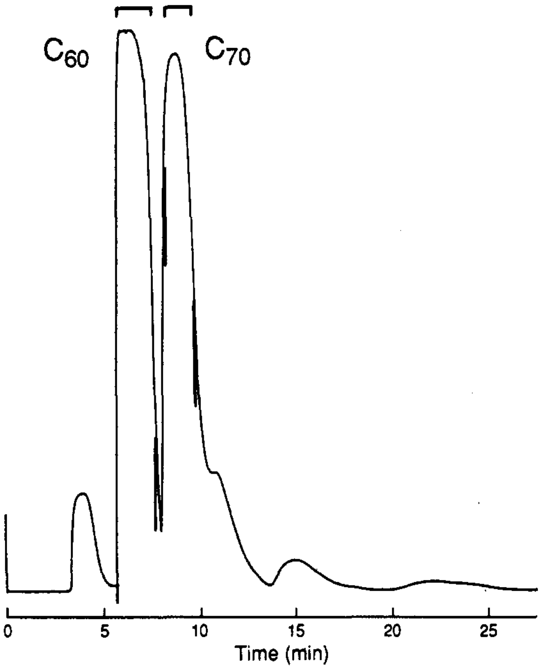

Figure 2. Preparative separation of crude carbon clusters on PYE silica in toluene. Sample: 20 mL of toluene extract of carbon soot. Column: PYE, 20-mm i.d., 25-cm length. Mobile phase: toluene. Flow rate: 18 mL/min. Temperature: 30 °C.

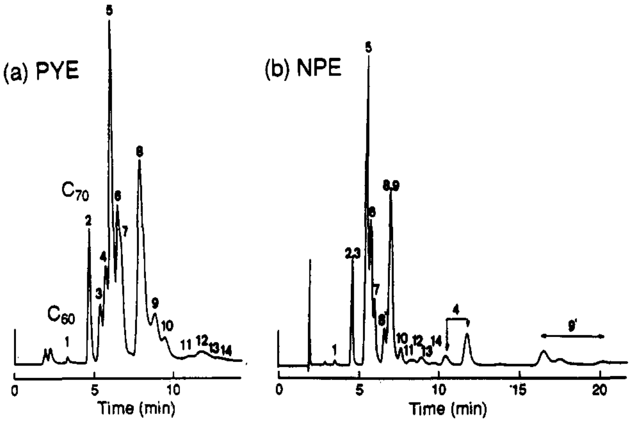

Figure 3. Separation of late-eluting products in carbon soot. Sample: Injection of 3 μL of combined fractions (ca. 4 mg) in toluene (10 mL) after removing C_{60} (peak 1) and C_{70} (peak 2) from carbon soot. (a) Column: PYE, 4.6-mm i.d., 15 cm. Mobile phase: toluene. Flow rate: 1 mL/min. (b) Column: NPE, 4.6-mm i.d., 15 cm. Mobile phase: toluene/hexane = 25/75 (v/v). Flow rate: 1 mL/min, 30 °C.

Figure 2 shows the separation of soot extract[11] in 20 mL of toluene with PYE silica packed in a semipreparative-scale column (20-mm i.d., 25-cm length) to produce 49.2 mg of C_{60} and 10.6 mg of C_{70} of higher than 99% purity along with 3.9 mg of late-eluting substances. Thus the PYE silica can separate more than 10 times as much fullerenes as the examples reported.[2,12]

Recently the separation and characterization of higher fullerenes as well as the oxygen-containing species in the late eluting peaks have been reported.[10,13] The PYE phase also allowed the improved separation of the late-eluting substances as shown in Figure 3a, where the combined fractions after removing most of the C_{60} (peak 1) and C_{70} (peak 2) from the crude soot extract were injected. Some of the peaks (4, 8, and 9 in Figure 3a), however, produced more than one peak on NPE, as shown in Figure 3b. Although the peaks have not been characterized yet, the present results strongly suggest the necessity of the careful examination of peak homogeneity in the isolation and characterization of late-eluting substances. The combination of the two aromatic stationary phases, π-basic PYE and π-acidic NPE, showing the opposite retention characteristics for aromatic molecules[4b] will be very useful for these purposes. Further studies are in progress for the characterization of the late-eluting species and the development of stationary phases for the improved separation of fullerenes and their derivatives.

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