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Single Column Purification of Gram Quantities of C_{70}

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Until recently the lack of gram quantities of pure fullerenes has somewhat limited the development of the fullerene field. Alumina columns have been used for fullerene separation, but the cost of the alumina is quite high.[1] With the use of inexpensive activated charcoal columns for obtaining gram quantities of >99.9% pure C_{60}, this cost limitation has been lifted for the most abundant of the fullerene allotropes.[2] Unfortunately, C_{70}, present in 10–35% of the crude fullerenes produced by the carbon arc method,[3] is still difficult to obtain in large amounts, and a gram quantity recovery has never been described. Outlined here is a method for the purification of gram quantities of C_{70} from a crude fullerene mixture using activated charcoal (Norit A) and silica gel as a stationary phase in a flash chromatography column, after a single column pass, with toluene and *o*-dichlorobenzene (ODCB) as the mobile phases.

We developed a Norit A/silica gel-based method for the purification of gram quantities of C_{60}.[2] From the standpoint of C_{70} recovery, however, the major disadvantage of activated charcoal columns is that they are too active. The C_{70} is retained so well that severe band broadening and tailing occurs, resulting in poor recoveries and purities of the C_{70} while using the normal toluene eluant. Similarly, the higher fullerenes never come off of the column. Based on our % recovery values for these charcoal columns, we knew that most of the C_{60} had come off of the column but that a large amount of C_{70} still remained tightly adsorbed to the charcoal. We assumed that if we could flush off the rest of the C_{70} from the column, we could substantially increase recovery and purity.

A number of studies have been done on the solubility of C_{60} in different solvents.[4] Based on these studies, we concluded that ODCB was a good potential mobile phase for the purification of C_{70} for a number of reasons.[5] C_{60} is about 8 times more soluble in ODCB than in toluene (the mobile phase typically used in charcoal columns). The resulting decrease in solution volume introduced onto the top of the column could significantly enhance separation by decreasing the bandwidth. While there are other compounds, like 1-chloronaphthalene, that are better solvents for C_{60}, it was felt that these significantly more expensive and higher boiling solvents would have been impractical to use.

In our studies, small test columns on 100 mg samples of crude fullerenes were run using different ratios of activated charcoals/silica gel/crude fullerenes/toluene and ODCB. The silica gel aids in preventing cracking of the stationary phase. Fractions were collected and analyzed by HPLC to determine the optimum conditions for C_{70} purification.[6] When ODCB was used as the only mobile phase, separation of C_{60} from C_{70} was poor; C_{60} nearly coeluted with C_{70}. However, we were pleased to find that the recovery of fullerenes from the column was >95%. In fact, we were also able to collect a golden yellow fraction enriched in higher fullerenes after prolonged elution of the column. By HPLC, 49% (three peaks at 5.1, 5.4, and 5.6 min) of the golden yellow fraction consisted of fullerenes > C_{70}.[6] No attempt was made to further purify this fraction. We eventually found that the optimum conditions for the recovery of purified C_{70} was to initially run the column with a 1:1 mixture of ODCB/toluene in order to remove most of the C_{60}, followed by elution with pure ODCB to remove the purified C_{70} fraction. Also, we found that Norit A, a relatively inactive form of activated charcoal, was superior to more active forms including Darco G60 (Fluka), which has been shown to work very well for obtaining C_{60}.[7]

A typical gram-quantity C_{70} purification procedure is as follows. A slurry of alkaline decolorizing carbon Norit A[8] (400 g) and silica gel[9] (800 g) in 1:1 toluene[10] /ODCB[11] was poured into a typical glass flash chromatography column (7 cm diameter column, 120 cm long) that had a cotton plug at the bottom of the column.[12] The slurry was allowed to settle as the solvent above the stationary phase was allowed to drain under a 15 psi N_2 head pressure applied at the top of the column.[13] The stationary phase must not be allowed to become solvent free or else cracking of the stationary phase can occur. The settled stationary phase was 75 cm long. A solution of carbon arc soot-extracted[14] crude fullerenes (10.00 g, 36% C_{70} by HPLC analysis) in 1:1 ODCB/toluene (666 mL) was slowly introduced to the top of the column, and a N_2 head pressure of 15 psi was applied, providing a 15 mL/min elution rate.[13] As more solvent was needed, the stopcock at the bottom of the column was closed, the pressure released, and more solvent added. After 2516 mL (fraction 1) of solute-free mobile phase had eluted from the column, elution of a purple C_{60} band occurred, and collection of fraction 2 was started. Fraction 2 totaled 1520 mL and contained 5.97 g of C_{60} that was >99.9% pure by HPLC analysis. After fraction 2 had become almost colorless, the red/brown color of C_{70} was first noticed. At the first indication of the C_{70}, fraction 3 was collected, and the mobile phase was changed to pure ODCB. Fraction 3 was 750 mL and contained 1.30 g of a mixture of C_{60} and C_{70} in a 58:42 ratio. At the end of fraction 3, the color of the eluant darkened from a light red/brown to a nearly black, indicating that the pure ODCB had reached the bottom of the column. The ODCB

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(1) (a) Koch, A. S.; Khemani, K. C.; Wudl, F. *J. Org. Chem.* **1991**, *56*, 4543. (b) Bhyrappa, P.; Penicaud, A.; Kawamoto, M.; Reed, C. A. *J. Chem. Soc.. Chem. Commun.* **1992**, 936. (c) Chatterjee, K.; Parker, D. H.; Wurz, P.; Lykke, K. R.; Gruen, D. M.; Stock, L. M. *J. Org. Chem.* **1992**, *57*, 3253. (d) Khemani, K. C.; Prato, M.; Wudl, F. *J. Org. Chem.* **1992**, *57*, 3254.

(2) Scrivens, W. A.; Bedworth, P. V.; Tour, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 7917.

(3) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(4) (a) Sivaraman, N.; Dhamodaran, R.; Kaliappan, I.; Srinivasan, T. G.; Rao, P. R. V.; Mathews, C. K. *J. Org. Chem.* **1992**, *57*, 6077. (b) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379. (c) Scrivens, W. A.; Tour, J. M. *J. Chem. Soc.. Chem. Commun.* **1993**, *15*, 1207.

(5) During the course of our investigations, Walton et al. carefully described the use of Elorit carbon/toluene columns, followed by multiple ODCB Soxhlet extractions and then rechromatographing or multiple benzene crystallizations to obtain <100 mg quantities of purified C_{70}. See: Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc.. Chem. Commun.* **1994**, 15.

(6) HPLC was carried out on an Alltech Econosphere silica gel column (250 mm × 4.6 mm i.d.) with hexane at 1 mL/min using UV detection at 356.6 nm. At this wavelength, C_{60} and C_{70} have nearly equivalent molar absorptions (Lamb, L. D., University of Arizona, personal communication). The retention times for C_{60} and C_{70} were 4.4 and 4.8 min, respectively. Higher fullerenes had retention times > 5.0 min.

(7) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231.

(8) Alkaline decolorizing carbon Norit A was purchased from Aldrich Chemical Company.

(9) (a) Flash chromatography grade Silica Gel 60 (230–400 mesh ASTM, 0.040–0.063 particle size) was purchased from EM Science. (b) Silica gel alone is not sufficient for the separation of fullerenes, see: Heath, J. R.; Hawkins, J. M.; Alivasatos, P. A.; Sakally, R. J.; Lewis, T. A.; Loren, S. D.; Meyer, A.; Shibato, Y.; Tolbert, S.; Shang, J. *Mater. Res. Soc. Proc.* **1991**, *206*, 667.

(10) ACS grade purchased from EM Science and used without purification.

(11) Purchased from Aldrich Chemical Co. and used without purification.

(12) The design of a typical flash chromatography column can be found in the following: Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(13) ***CAUTION***: Though we experienced no rupture of the standard glass columns under 15 psi pressures, we recommend utilization of this procedure behind a protective transparent shield to prevent injury if a rupture should occur. Additionally, tape-wrapped columns would provide added protection. In smaller columns, adequate flow rates can be maintained with pressures of 7–10 psi.

(14) Scrivens, W. A.; Tour, J. M. *J. Org. Chem.* **1992**, *57*, 6932.

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brought with it most of the C_{70}, and fraction 4 was begun. Fraction 4, an enriched C_{70} fraction, was collected and monitored by HPLC until the purity of the C_{70} in the eluant had reached 90%. Fraction 4 was 750 mL and contained 0.65 g of C_{70} at 85% purity. We then began collection of fraction 5, the final C_{70} fraction. Fraction 5 was 10 L and contained 1.58 g of C_{70} at >97% purity. The combined fractions weighed 9.50 g, giving 95% mass recovery from the column. If one assumes that the remaining mass is due to higher fullerenes, one can conclude that this purification method is nearly quantitative. Additional column work on the impure fractions could yield ~3 g of >97% pure C_{70} from a 10 g batch of crude.

Solvent was removed from the different fractions via rotary evaporation with aspirator pressure and an ice-cooled condenser. In fractions containing mixed solvents, the toluene was first removed at 40 °C, and the ODCB was then recovered at 85 °C. This proved to be a fast and efficient method of solvent recovery.[15] Over the course of this purification, 13 L of ODCB was used, and 12.4 L was recovered giving a 95% recovery of ODCB.

During the solvent removal from the test column studies, we made several noteworthy observations. Initially, we tried to recover the ODCB through fractional distillation at atmospheric pressure. During the distillation of ODCB from the C_{70} fractions, it was noticed that the distillate was slightly brown in color. We assumed that bumping had occurred, so the distillation was repeated more carefully through a 20-cm Vigreux column. The distillate was initially clear, but as the solution of C_{70} became saturated, the refluxing solvent began to turn brown. Eventually, a light brown liquid began to distill, and since no observable bumping or spattering had occurred, we concluded that the fullerenes were codistilling with the ODCB. It should be noted that no codistillation occurred when ODCB was removed via rotary evaporation. This codistillation process was repeated several times with crude fullerenes. Again, colored material was distilled. When crude fullerenes were subjected to the same conditions, the ratio of C_{60}:C_{70} was monitored, and no change was detected in the distillate when it was compared to the crude. Further investigations of this potentially useful process for removing lower fullerenes from extracts are currently in progress.

During the solvent removal of the C_{70} enriched fractions, it was noticed that, if one carefully removes most of the ODCB via rotary evaporation at 85 °C, saturated solutions of C_{70} are made. These saturated solutions indicate a much higher solubility of C_{70} in hot ODCB than the known value of 24 mg/mL for C_{60} at room temperature.[4c] Initial observations indicate that solubilities of >50 mg/mL may be obtained using hot ODCB. These solutions, if allowed to sit overnight, produce an abundance of long C_{70} crystals with 99.5% purity by HPLC analysis.

Finally, since higher fullerenes did come off of a charcoal test column, and since the solubility of C_{70} seems to be very temperature dependent, the potential for the purification of higher fullerenes on shorter, heated charcoal columns using ODCB as eluant seems to exist.

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[15] A standard laboratory rotary evaporator (Büchi RE111) was used, and ODCB was removed at a rate of approximately 3–4 L/h.