OFFICE OF NAVAL RESEARCH

GRANT : N00014-89-J-3062

R&T Code 3132084

Technical Report No. 46

Purification of C_{70} Using Charcoal as a Stationary Phase in a Flash Chromatography Column

by

W. A. Scrivens, A. M. Cassell, K. E. Kinsey and J. M. Tour

Accepted for Publication in

Fullerenes, Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, Kadish, K. M.; Ruoff, R. S., Eds., Symposium Volume 94-24, Electrochemical Society: Pennington, NJ, **1994**, p 166.

Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

June 7, 1995

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	6-7-95	Technical Report

4. TITLE AND SUBTITLE
Purification of C_{70} Using Charcoal as a Stationary Phase in a Flash Chromatography Column

5. FUNDING NUMBERS
G- N00014-89-J3062
R&T 3132084
K. Wynne

6. AUTHOR(S)
W. A. Scrivens, A. M. Cassell, K. E. Kinsey and J. M. Tour

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Department of the Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
46

11. SUPPLEMENTARY NOTES
Fullerenes, Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, Kadish, K. M.; Ruoff, R. S., Eds., Symposium Volume 94-24, Electrochemical Society: Pennington, NJ, 1994, p 166.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Detailed procedures for obtaining multigram quantities of C_{60} and C_{70} are outlined. The procedure involves the use of a flash chromatography column packed with charcoal and silica gel and an eluant of toluene/1,2-dichlorobenzene.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

Purification of C_{70} Using Charcoal as a Stationary Phase in a Flash Chromatography Column

*Walter A. Scrivens, Alan M. Cassell, Kenneth E. Kinsey, and James M. Tour**
Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina 29208

Described is a method for the purification of C_{60} and C_{70} using a flash chromatography column that contains charcoal as the stationary phase. A number of functionalized aromatic solvents are studied and their efficacy for extraction, NMR spectral acquisition, and chromatographic purification of fullerenes is discussed. Ortho-dichlorobenzene was chosen as the best solvent for these applications and examples of its use in the extraction of higher fullerenes (>C_{84}) and in the rapid acquisition of ^{13}C NMR spectra are given. Finally, single column purification of both C_{60} and C_{70} is discussed. Starting with a typical arc-derived mixture of soluble fullerenes, 5.97 g of C_{60} at >99.9% purity and 1.58 g of C_{70} at >97% purity were produced in a single column pass.

A limitation to fullerene research is the difficulty in producing gram quantities of C_{60} and C_{70} free of the higher molecular weight fullerenes. We describe here a simple and low cost method that uses common laboratory glassware and reagents for the purification of even gram quantities of C_{60} and C_{70} using activated charcoal as a stationary phase in a flash chromatography column.

SOLUBILITY STUDIES

A severe difficulty in working with fullerenes is that they are sparingly soluble in most common solvents, typically on the order of a few mgs mL^{-1} (1). Solvents in which fullerenes are more soluble could be extremely useful for developing new inexpensive purification methods for fullerenes (2), the extracting of higher fullerenes, and facilitating ^{13}C NMR acquisition of the fullerenes and their derivatives. A number of groups have used carbon disulfide as an NMR solvent to get higher concentrations of fullerenes into solution (3-5). High-boiling aromatic solvents such as 1,2,4-trichlorobenzene, quinoline, and 1,2,3,5-tetramethylbenzene have been used in extracting fullerenes from soot in order to give higher yields or to better extract the higher molecular weight fullerenes (3,6,7). With the exception of benzene, toluene, and carbon disulfide, all of the solvents reported are poorly solublizing (<1 mg mL^{-1}). Since benzene and toluene, both aromatic compounds, were among the best solvents reported, a number of common and not-so-common aromatic liquids were investigated to facilitate the dissolution and NMR acquisition of fullerenes.

Solubility data was obtained gravimetrically as follows. Approximately 5 mL of the appropriate solvent was added to an excess of C_{60} such that undissolved C_{60} always remained. The mixture was sonicated in a room temperature water bath for 30 min. The mixture was centrifuged for about 5 min and the solution at 24.5-25.5°C was then passed through a 0.45 μm HPLC syringe filter. Three 1.0 mL samples of this solution were removed and placed into pre-weighed vials. The vials were then placed into a heated oil bath (typically 100°C but 150°C oil bath was used for some of the higher boiling solvents) and solvent was gently removed via a stream of N_2. The vials were then cleaned of the

exterior oil and weighed. The average of the three weights was recorded and a summary is presented in **Table # 1**.

Table # 1.

Room Temperature Solubility of C_{60} in Various Solvents.[a]

SOLVENT	SOLUBILITY (mg mL^{-1})[b]	SOLUTION COLOR
benzene	1.5	magenta
toluene	2.9	magenta
ethylbenzene	2.6	magenta
n-propylbenzene	1.5	magenta
iso-propylbenzene	1.2	pink
n-butylbenzene	1.9	magenta
sec-butylbenzene	1.1	pink
tert-butylbenzene	0.9	pink
1,2-dimethylbenzene	8.7	magenta
1,3-dimethylbenzene	1.4	pink
1,4-dimethylbenzene,	5.9	magenta
1,2,3-trimethylbenzene	4.7	magenta
1,2,4-trimethylbenzene	17.9	magenta
1,3,5-trimethylbenzene	1.7	magenta[c]
1,2,3,4-tetramethylbenzene	5.8	magenta/brown
1,2,3,5-tetramethylbenzene	20.8	brown/yellow
fluorobenzene	1.2	pink
chlorobenzene	5.7	magenta
bromobenzene	2.8	magenta
iodobenzene	2.1	magenta
1,2-dichlorobenzene	24.6[d]	dark purple
1,2-dibromobenzene	13.8	magenta
1,3-dichlorobenzene	2.4	magenta
1,3-dibromobenzene	13.8	magenta
1,2,4-trichlorobenzene	10.4	magenta[e]
1-methylnaphthalene	33.2	brown/green
1-bromo-2-methylnaphthalene	34.8	brown
quinoline	7.2	brown
pyridine	0.3	pink[f]
thiophene	0.4	pink

[a]See text for the method of solubility determination. [b]Solubility data is approximately ±0.5 mg mL^{-1}. [c]An olive-drab-colored precipitate formed. [d]A value of 33 mg mL^{-1} was reported in ref 1. [e]A purple-black colored iridescent precipitate formed. [f]Pyridine appeared to be reacting slowly with the C_{60} (8).

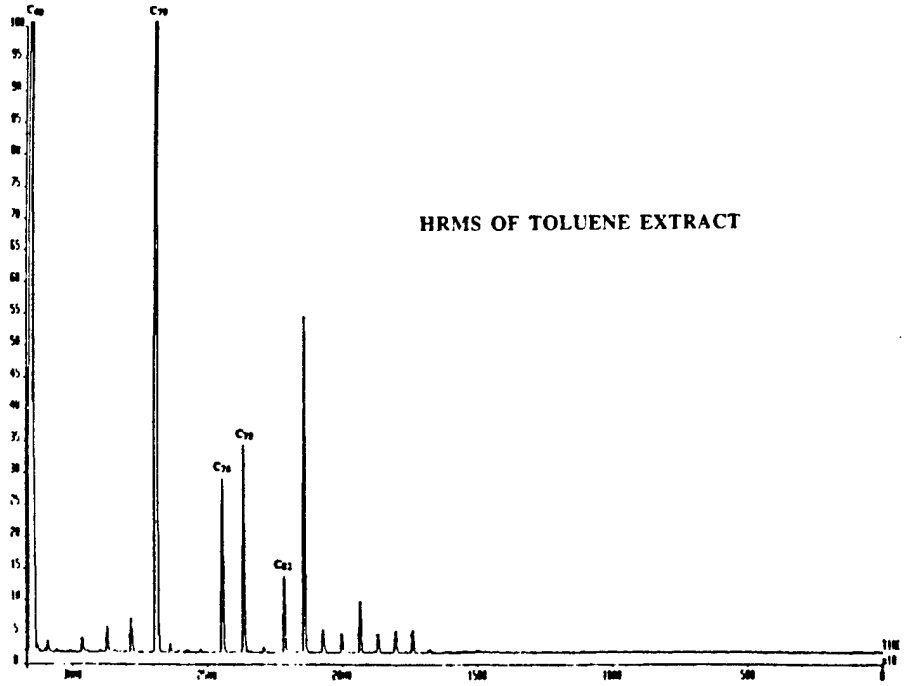
The results indicate that many substituted aromatic solvents were superior to benzene and toluene for the dissolution of C_{60}. Substituted naphthalenes and 1,2-dichlorobenzene are approximately 10 times better solvents than toluene.

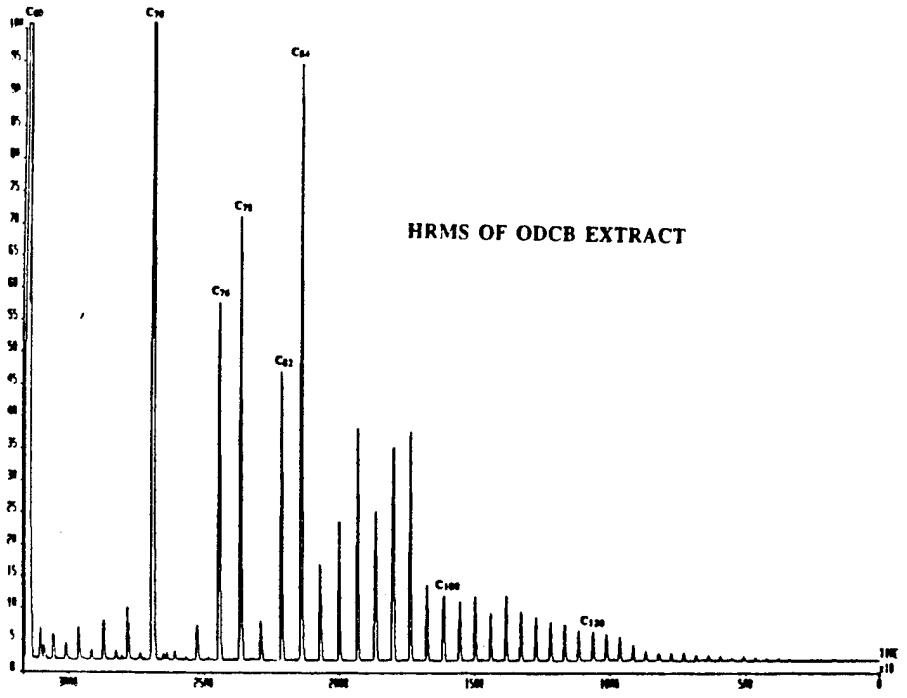
Initial evaluation of the solubility data showed no readily obvious relationship between the solubility of C_{60} in a particular solvent and properties of the solvent. Moreover, a number of the solutions showed a distinct green or brown color that was different from the commonly observed magenta/pink/purple-colored solutions. In the case of 1,3,5-trimethylbenzene and 1,2,4-trichlorobenzene, unusual precipitates formed during sonication of the C_{60} mixtures. Complexes of C_{60} and benzene have been reported by the very slow crystallization of C_{60} from benzene solutions (9), however, precipitate formation between C_{60} and 1,3,5-trimethylbenzene or 1,2,4-trichlorobenzene was so unusually rapid that it was concluded that unusual complexes/adducts had formed. At the end of this initial solubility study it was concluded that 1,2-dichlorobenzene would be a good solvent for use in a variety of areas in fullerene research because it is very solubilizing, readily avalable in high purity, and has a reasonably low boiling point.

Not surprisingly, *o*-dichlorobenzene (ODCB) is a superb solvent for the Soxhlet extraction of higher fullerenes from carbon arc soot. Carbon arc-generated soot (7.74 g) was extracted with toluene via sonication for 1 h to yield 509 mg of extract. The soot was then further extracted with toluene using a Soxhlet extractor for 2 d to yield an additional 69 mg of extract. Further Soxhlet extraction of the soot with 1,2-dichlorobenzene afforded 95 mg of extract that is toluene insoluble and containes numerous higher fullerenes with up to C_{152} being clearly observed by mass spectrometry (**Figure #1**).

Figure #1

Comparison of Toluene and ODCB as Extraction Solvents for Fullerenes

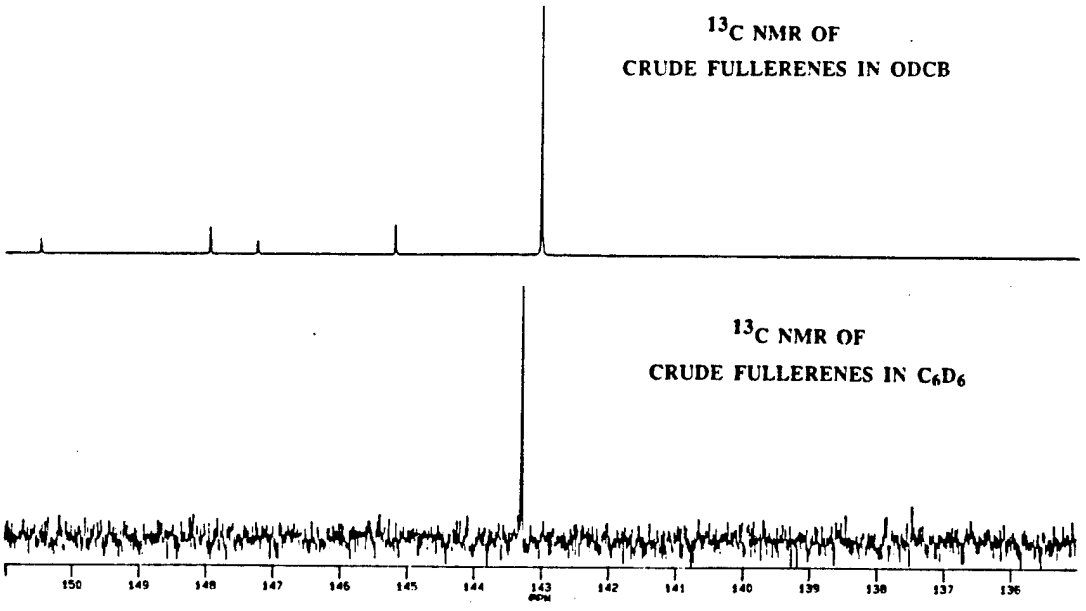




The efficacy of 1,2-dichlorobenzene (ODCB) as a ^{13}C NMR solvent was then explored. Our ^{13}C NMR parameters were optimized by maximizing the signal to noise ratio on a sample of pure C_{60} in C_6D_6 by varying the pulse width (**Figure #2**).

Figure #2

Comparison of ODCB and Benzene as ^{13}C NMR Solvents for Fullerenes



The optimal parameters (125 MHz) determined were: (a) pulse width = 2.0 μs, (b) pulse width for 90° tip ($\pi/2$) = 6.1 ms, (c) acquisition time = 1.704 s, and (d) delay = 0.005 s. A C_{60}/C_{70} mixture in ODCB(with 5% (v/v) C_6D_6 added for the internal deuterium lock signal) was compared with the spectra obtained in C_6D_6 as the only solvent

All of the NMR samples were saturated with the fullerene mixture. The 1,2-dichlorobenzene peaks appear at δ 132.68, 130.60, 127.86 ppm. Note that the C_{70} peak at δ 132.7 ppm (not shown in the spectra but commonly observed at d 130.9 ppm in C_6D_6) is coincident in chemical shift with one of the three 1,2-dichlorobenzene peaks. Dramatic increases were noted in the signal to noise ratio for the spectra obtained in 1,2-dichlorobenzene as compared with C_6D_6 alone. For the ^{13}C NMR of pure C_{60} saturated 1,2-dichlorobenzene (plus 5% C_6D_6) and C_6D_6 only, the signal to noise ratios after 28 min of scanning were 470:1, and 13:1, respectively. In the C_6D_6 spectra, the C_{70} peaks can not even be resolved in the 28 min time period used for the analysis. Therefore, ODCB may prove to be particularly effective for obtaining the ^{13}C NMR spectra of the higher fullerenes which are generally less soluble than C_{60} and have less intense ^{13}C signals due to the range of magnetically dissimilar carbons.

CHARCOAL COLUMN CHROMATOGRAPHY

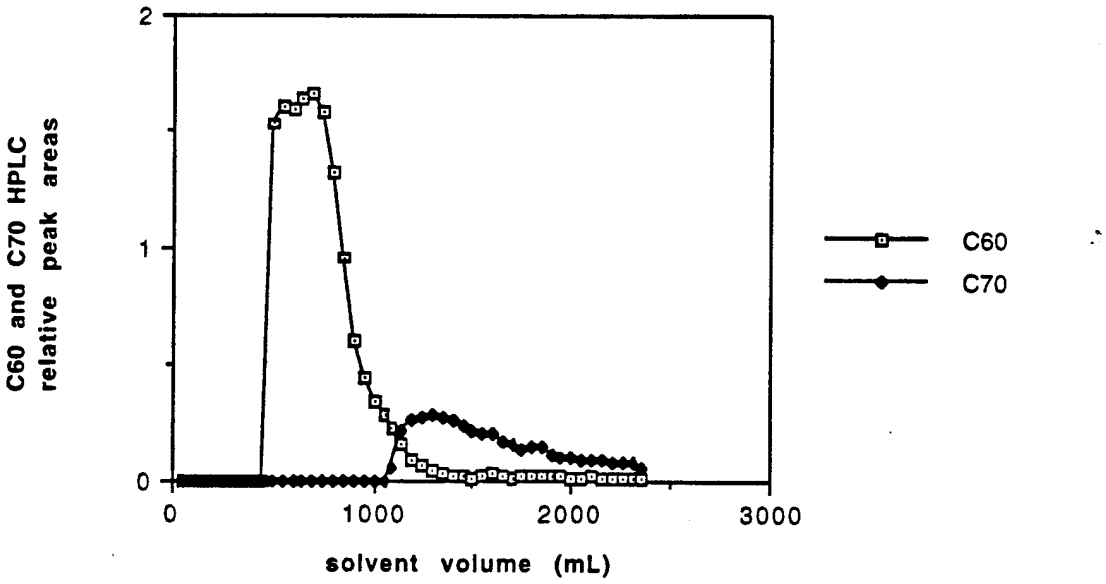
ODCB and toluene were then evaluated as eluents for the chromatographic purification of fullerenes. Crude fullerene extracts from carbon arc soot contain 65-85% C_{60} and 10-30% C_{70} with the remainder being higher fullerenes (10). The most common method for purifying fullerenes is by column chromatography on activity grade I neutral alumina (11). Our experience with this method has shown that to obtain 1 g of pure C_{60} takes 16-20 h and uses 10 kg of alumina and 50 L of solvent. About 50% of C_{60} of a possible 75% C_{60} present in the crude can be recovered since activity grade I alumina irreversibly adsorbs some of the C_{60} (11). Alumina columns within modified Soxhlet extractors can be used to significantly simplify this method but recovery yields are generally in the range of 33% to 43% out of a possible 75% of C_{60} present (12). Powdered graphite has been used as the stationary phase for chromatographic purification of C_{60} but the recovery of C_{60} is only 32% of a possible 75% (13). HPLC has been used for C_{60} purification but it is primarily useful only for small scale separations (14,15). Obtaining gram quantities of C_{70} by these methods is exceedingly difficult.

Activated carbon has been used extensively as a stationary phase for molecular size selection-based chromatography and it was this feature that promoted our initial investigation (16). It has also been used as a co-stationary phase with silica gel for the separation of PCBs (17); silica gel alone is not sufficient for the separation of large amounts of fullerenes (18). On the basis of on this information methods were developed for the purification of C_{60}. A typical gram-quantity C_{60} purification procedure using this method is as follows. A slurry of alkaline decolorizing carbon Norit®-A (36 g, Fisher Scientific Company) and silica gel (72 g, Silica Gel 60, EM Scientific) in toluene (200 mL) was poured into a typical glass flash chromatography column (38 mm diameter column, 45 cm long) that had a cotton plug at the bottom of the column. This is a typical flash chromatography set-up (19). The size of the column was chosen so that the length of the stationary phase in the column was at least 10 times longer than the diameter in order to help prevent cracking. The slurry was allowed to settle as the solvent *above* the stationary phase was allowed to drain under a 7.5 psi N_2 head pressure applied at the top of the column. Although there were no ruptures of the standard glass columns under 15 psi pressures, utilization of this procedure behind a protective transparent shield is recomended

to prevent injury if a rupture should occur. Additionally, tape-wrapped columns would provide added protection. The stationary phase must not be allowed to become solvent free or else cracking of the stationary phase can occur. A homogeneous saturated toluene (400 mL) solution of 1.85 g of crude fullerenes (sonication of the mixture was used to facilitate the dissolution process) extracted from carbon arc soot was slowly poured onto the top of the Norit®-A/silica gel stationary phase. A 7.5 psi N_2 head pressure was applied thus providing a ~16 mL/min elution rate. The deep purple-colored solution containing C_{60} started to elute from the column after 37 min. After 36 min more, the eluant was nearly colorless and collection of a second faction was then begun. The total volume of toluene needed for obtaining the C_{60} fraction (first fraction) was ~600 mL. After 3 min more, a red-brown band characteristic of C_{70} started to elute. Removal of the solvent from the purple fraction afforded 1.16 g of C_{60} (63% of a possible 75% of C_{60} in extractable fullerenes). Fractions were collected and analyzed by HPLC (**Figure #3**)

Figure #3

HPLC Analysis of Fullerene Fractions from a Charcaol Column



The HPLC analysis shows that there is nearly baseline separation of C_{60} and C_{70}. Unfortunately the C_{70} and C_{60} tail and this tailing prevents the collection of pure C_{70} fractions. HPLC was done using an Alltech Econosphere silica gel column (250 mm x 4.6 mm I.D.) with 2% toluene in hexane at 1 mL/min. UV detection was used at 356.6 nm. At this wavelength, C_{60} and C_{70} have nearly equivalent molar absorptions (20). The retention times for C_{60} and C_{70} were 4.40 and 4.84 min. respectively. Higher fullerenes had retention times >5.00 min. The crude material showed a mixture of C_{60}, C_{70}, and other higher fullerenes. HPLC on silica gel showed only C_{60} in the first fraction; no other fullerenes were detected. While the second band eluted from the column was red-brown, it did contain some C_{60}. One more smaller chromatographic run on the initial red-brown portion afforded 74 mg more of C_{60} and 120 mg of a sample that was 1 : 5 in C_{60} : C_{70} as

judged by peak height comparison of the MS signals and 1 : 10 in C_{60} : C_{70} as judged by HPLC analysis. Thus the combined yield of purified C_{60} after two columns was 67%.

^{13}C NMR (125 MHz, C_6D_6) analysis of the C_{60} showed only one peak at δ 143.29 ppm with no other peaks in the spectrum while the signal to noise ratio was 68 : 1. Likewise, mass spectrometric (MS) analysis showed a peak at 720 amu with no detectable peaks for higher molecular weight fullerenes.

Although this procedure was done with 1.85 g of extractable fullerenes, it works equally well on a smaller scale using the proportionately smaller stationary phases and solvent volumes. Norit®-A alone as the stationary phase without silica gel as a co-phase worked excellently for C_{60} separations on smaller scales (i.e., 100 mg of crude fullerenes with 2.0 g of Norit®-A); however, the silica gel prevents cracking of the stationary phase in the larger columns and allows for higher flow rates. The reproducibility of the C_{60} separations were verified by using Norit®-A from a different distributor (Matheson Coleman & Bell) and the results were nearly identical. Norit®-A/Celite®-521 as a stationary phase is inferior to the Norit®-A/silica gel because with the former, packing is more difficult and cracking of the stationary phase occurs easily. Molecular sieves (13X pellets ground to a fine powder and packet in a column), and carbon soot were used as stationary phases and proved to be inadequate for C_{60} purifications. SEM analysis showed no obvious topological features for why activated charcoal works so well and molecular sieves and soot do not work.

The purification procedure as described above works well for the purification of C_{60}, but from the standpoint of C_{70} recovery, modifications had to be made. 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 the column. On the basis of on our percentage recovery values for these charcoal columns, it was thought that most of the C_{60} had come off the column but that a large amount of C_{70} still remained tightly adsorbed to the charcoal. It was assumed that if one could flush off the rest of the C_{70} from the column, one could substantially increase recovery and purity.

On the basis of on our solubility studies, it was concluded that ODCB was a good potential mobile phase for the purification of C_{70} for a number of reasons. 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 band width. 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 be impractical to use. 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 re-chromatographing or multiple benzene crystallizations to obtain <100 mg quantities of purified C_{70} (21).

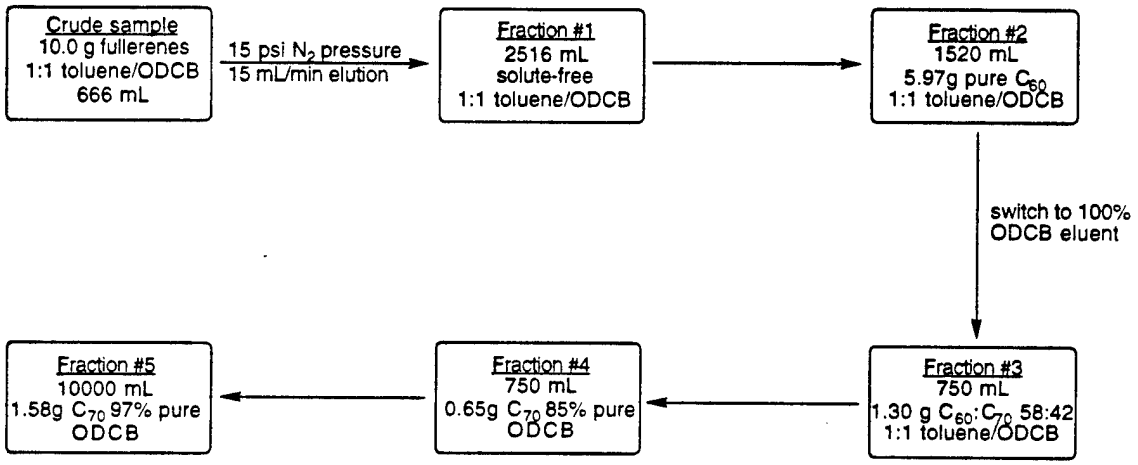
Small test columns on 100 mg samples of crude fullerenes were run using different ratios of activated charcoals/silica gel/crude fullerenes/toluene and ODCB. The silica gel is necessary to prevent cracking of the stationary phase. Fractions were collected and analyzed by HPLC to determine the optimum conditions for C_{70} purification. When ODCB was used as the only mobile phase, separation of C_{60} from C_{70} was poor; C_{60}

nearly co-eluted with C_{70}. However, it was pleasing to find that the recovery of fullerenes from the column was >95%. In fact, a golden yellow fraction enriched in higher fullerenes (fullerenes >C_{70}) was collected after prolonged elution of the column. It was eventually found that the optimum conditions for the recovery of purified C_{70} are to initially run the column with a 1:1 mixture of ODCB/toluene in order to remove most of the C_{60} then to elute with pure ODCB to remove the purified C_{70} fraction. Also, it was found that Norit A, a relatively inactive form of activated charcoal, is superior to more active forms including Darco G60 (Fluka), which has been shown to work well for obtaining C_{60} (22).

A typical gram-quantity C_{70} purification procedure is outlined in **Figure #4.**

Figure #4

Improved Methodology for the Purification of C_{60} and C_{70}



A slurry of alkaline decolorizing carbon Norit-A (400 g, Aldrich) and silica gel (800 g, Silica Gel 60, EM Science) in 1:1 toluene/ODCB 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. 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. 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 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. As more solvent was needed, the stopcock at the bottom of the column was closed, the pressure released, and more solvent was added. After 2516 mL (fraction 1) of solute-free mobile phase had eluted from the column, elution of a purple C_{60} band occurrs, 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 brought with it most of the C70, and fraction 4 was begun. Fraction 4, an enriched C_{70} fraction was collected and monitored by

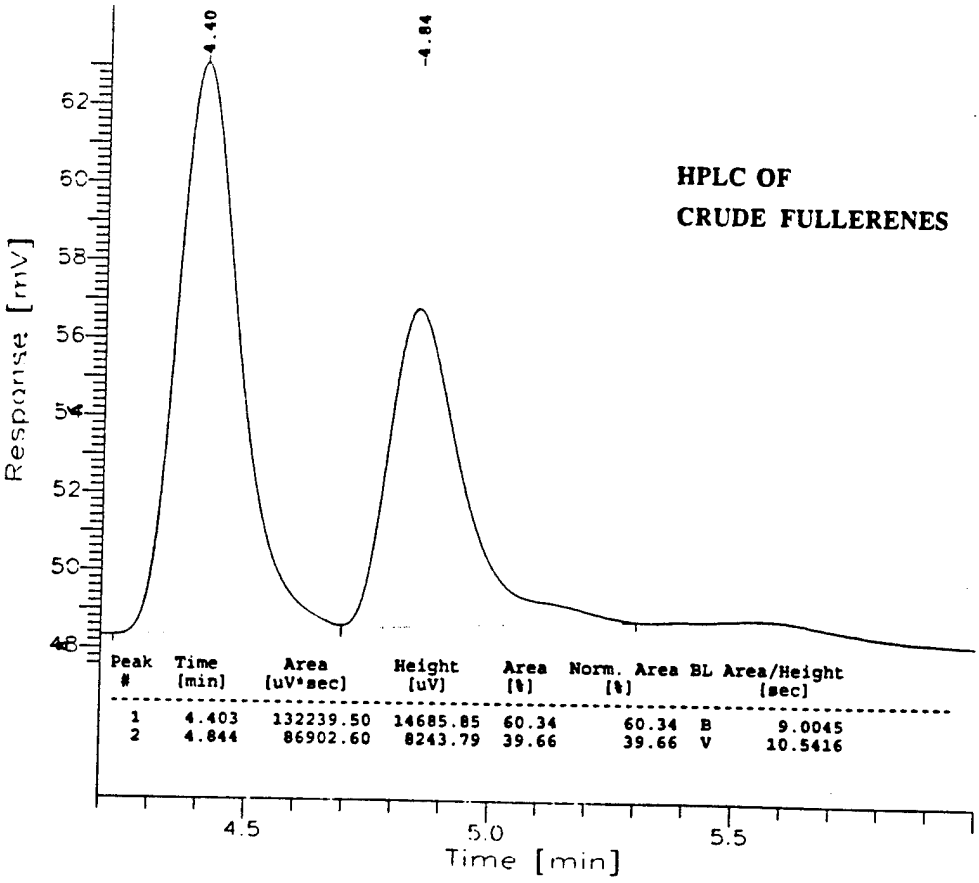
HPLC until the purity of the C_{70} in the eluant had reached 90%. Fraction 4 was 750 mL and contained 0.65 g of C_{70} at 85% purity. Collection of fraction 5, the final C_{70} fraction, was begun. Fraction 5 was 10 L and contained 1.58 g of C_{70} at >97% purity

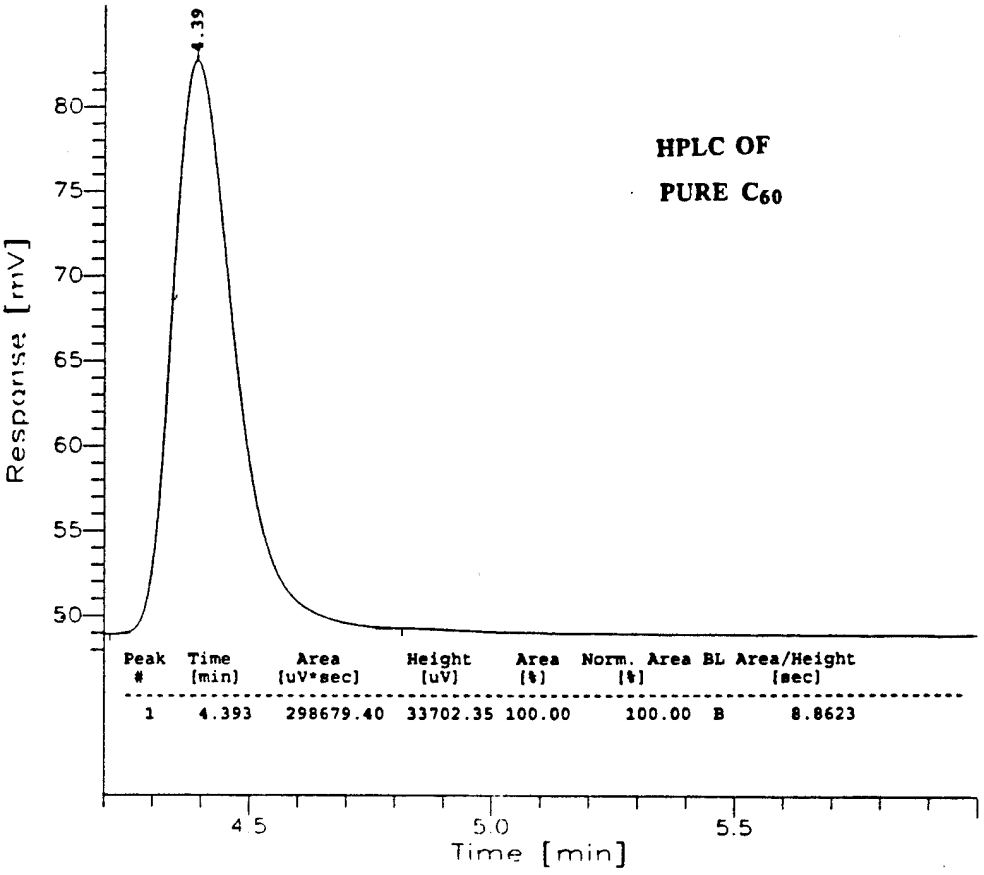
The combined fractions weighed 9.50 g giving 95% mass recovery from the column. If one assumes that the remaining mass is due to higher fullerenes, one can conclude that this purification method is nearly quantitative. Additional column work on the impure fractions could yield ~3 g of >97% pure C_{70} 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. Over the course of this purification, 13 L of ODCB were used, and 12.4 L were recovered giving a 95% recovery of ODCB (**Figure #5**).

Figure #5

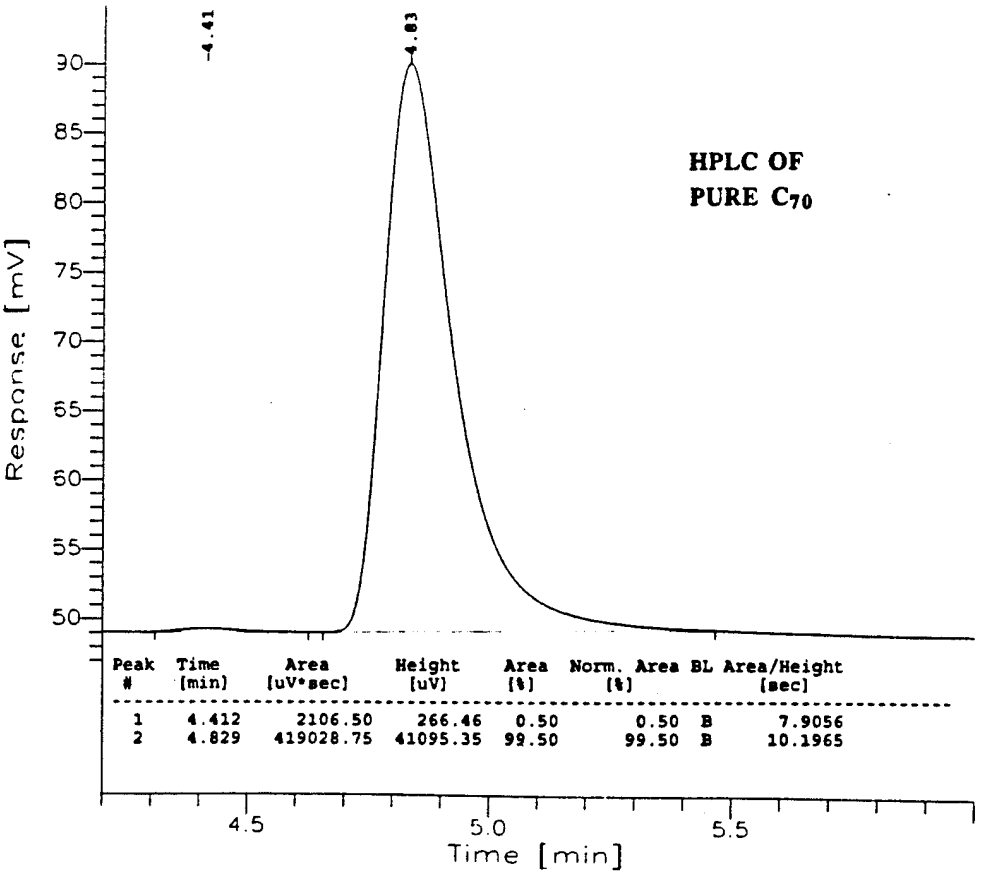
HPLC Plots of Crude Fullerenes, Pure C_{60} and C_{70}





HPLC OF
PURE C_{60}

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	4.393	298679.40	33702.35	100.00	100.00	B	8.8623



HPLC OF
PURE C_{70}

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	4.412	2106.50	266.46	0.50	0.50	B	7.9056
2	4.829	419028.75	41095.35	99.50	99.50	B	10.1965

During the solvent removal from the test column studies, several noteworthy observations were made. Initially, the recovery of ODCB through fractional distillation at atmospheric pressure was attempted. During the distillation of ODCB from the C_{70} fractions, it was noticed that the distillate was slightly brown in color. It was 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, it was concluded that the fullerenes were co-distilling with the ODCB. It should be noted that no co-distillation occurred when ODCB was removed via rotary evaporation. This co-distillation 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 compared to the crude. Also 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. 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 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.

ACKNOWLEDGMENTS

We are grateful for support from the Office of Naval Research, the National Science Foundation, and generous industrial contributors to the NSF Presidential Young Investigator Award Program: Molecular Design Ltd., Hercules, IBM, Ethyl, Shell, Eli Lilly, Farchan, Polaroid, and Exxon Corporations. We would also like to thank NASA and the American Vacuum Society for scholarships.

REFERENCES

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

(2) (a) W. A. Scrivens and J. M. Tour, J. Org. Chem., **57**, 6932 (1992). (b) W. A. Scrivens, P. V. Bedworth and J. M. Tour , J. Am. Chem. Soc., **114**, 7917 (1992).

(3) F. Diederich, R. Ettl, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K. C. Khemani and A. Koch, Science, **252**, 548 (1991).

(4) F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, I. Chao and M. M. Alvarez, Science, **254**, 1768 (1991).

(5) R. Taylor, G. J. Langley, T. J. S. Dennis, H. W. Kroto and D. R. M.Walton, J. Chem. Soc., Chem. Comm., 1043 (1992).

(6) D. H. Parker, P. Wurz, K. Chatterjee, K. R. Lykke, J. E. Hunt, M. J. Pellin, J. C. Hemminger, D. M. Gruen and L. M. Stock, J. Am. Chem. Soc., **113**, 7499 (1991).

(7) H. Shinohara, H. Sato, Y. Saito, M. Takayama, A. Izuoka and T. Sugawara, J. Phys. Chem., **95**, 8449 (1991).

(8) A. Hirsch, Q. Li and F. Wudl, Angew. Chem. Int. Ed. Engl., **30**, 1309 (1991).

(9) (a) U. Geiser, S. K. Kumar, B. M. Savall, S. S. Harried, K. D. Carlson, P. R. Mobley, H. H. Wang, J. M. Williams, R. E. Botto, W. Liang and M. H. Whangbo, Chem. Mater., **4**, 1077 (1992). (b) M. F. Meidine, P. B. Hitchcock, H. W. Kroto, R. Taylor, D. R. M. Walton, J. Chem. Soc., Chem. Comm., 1534 (1992).

(10) (a) H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature* , **318**, 162 (1985). (b) W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature* , **347**, 354 (1990). (c) R. Taylor, J. P. Hare, A. K. Abdul-Sada and H. W. Kroto,*J.* Chem. Soc., Chem. Comm., **20**, 1423 (1990). (d) H. Ajie, M. Alvarez, S. J. Anz, R. D. Beck, F. Diederich, K. Fostiropoulos, D. R. Huffman, W. Krätschmer, Y. Rubin, K. E. Schriver, D. Sensharma and R. L. Whetten, J. Phys. Chem., **94**, 8630 (1990). (e) F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, I. Chao and M. M. Alvarez, Science, **254**, 1768 (1991). (f) R. L. Whetten, M. M. Alvarez, S. J. Ans, K. E. Schriver, R. D. Beck, F. N. Diederich, Y. Rubin, R. Ettl, C. S. Foote, A. P. Darmanyan and J. W. Arbogast, Mat. Res. Soc. Symp. Proc., **206**, 639 (1991). (f) For a recent review on fullerenes, see: F. W. McLafferty, (Ed) Acc. Chem. Res., **25**, 97 (1992).

(11) (a) A. S. Koch, K. C. Khemani and F. Wudl, J. Org. Chem., **56**, 4543 (1991). (b) P. Bhyrappa, A. Penicaud, M. Kawamoto And C. A. Reed, J. Chem. Soc. Chem. Comm., 936 (1992).

(12) (a) K. Chatterjee, D. H. Parker, P. Wurz, K. R. Lykke, D. M. Gruen and L. M. Stock, *J.* Org. Chem., **57**, 3253 (1992). (b) K. C. Khemani, M. Prato and F. Wudl, J. Org. Chem., **57**, 3254 (1992).

(13) A. M. Vassallo, A. J. Palmisano, L. S. K. Pang and M. A. Wilson, J. Chem. Soc., Chem. Comm., 60 (1992).

(14) M. S. Meier and J. P. Selegue, *J.* Org. Chem., **57**, 1924 (1992).

(15) (a) K. Jinno, K. Yamamoto, T. Ueda, H. Nagashima and K. Itoh, J. Chromatogr., **594**, 105 (1992). (b) A. Gügel, M. Becker, D. Hammel, L. Mindach, J. Rader, T. Simon, M. Wagner and K. Müllen, Angew. Chem. Int. Ed. Engl., **31**, 644 (1992).

(16) A. J. Gordon and R. A. Ford, The Chemist's Companion. A Handbook of Practical Data, Techniques, and References, p. 373, Wiley, New York (1972).

(17) J. L. Sericano, A. M. El-Husseini, T. L. Wade, Chemosphere, **23**, 915 (1991).

(18) J. R. Heath, J. M. Hawkins, P. A. Alivasatos, R. J. Sakally, T. Lewis, S. D. Loren, A. Meyer, Y. Shibato, S. Tolbert and J. Shang, Mat. Res. Soc. Proc., **206**, 667 (1991).

(19) W. C. Still, M. Kahn and A. Mitra, J. Org. Chem., **43**, 2923 (1978).

(20) L. D. Lamb, Univ. of Arizona, personal communication.

(21) A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, J. Chem. Soc., Chem. Commun., 15 (1994).

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