Fast One-Step Separation and Purification of Buckminsterfullerene, C_{60}, from Carbon Soot[†]

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We have found a convenient method to obtain pure C_{60} in a single step from fullerene-containing soot produced in a carbon-arc soot generator. Since the discovery in 1985 of the stable carbon cluster consisting of sixty atoms,[1] there have been several reports of the preparation of macroscopic quantities of C_{60} and C_{70}.[2-8] The fullerenes are commonly prepared by decomposition of graphite in an electric arc by resistive heating. Typically, the soot resulting from the decomposition is extracted with benzene or toluene, with subsequent separation of C_{60} and C_{70} by column chromatography.[3,6,7] Although excellent separation is achieved with hexane on neutral alumina,[3] it is tedious and time-consuming. Due to the low solubility of C_{60} in hexane, several liters of eluant are required. We sought a simple one-step method that combined extraction and chromatography in a single apparatus to isolate pure C_{60} *directly* from the raw soot. We report our results that provide yields of 4-6% in only a few hours with a minimum amount of solvent.

Our previous work on fullerene synthesis and extraction[8] showed that higher yields were obtained by using Soxhlet instead of reflux, presumably because the soot is continually washed with fresh hot solvent in the former method. About 18% of the soot was extracted into hexane and this extract contained primarily C_{60} and C_{70}.[8] Following our success with hexane Soxhlet extraction of the soot, we sought to combine the efficiency of Soxhlet extraction with the selectivity of the chromatographic method to provide a one-step method for C_{60} purification. The idea was to use the solvent recycling mechanism of a Soxhlet extraction apparatus adapted for a chromatographic column. Fortunately, such a device is commercially available and is known as a Kauffman chromatographic column which is ideally suited to the purification of poorly soluble compounds.[9] After the initial success with a commercial column, we fabricated a larger scale Kauffman apparatus.

In a typical experiment, aluminum oxide was loaded in the inner column of the apparatus, and a small amount of raw soot was added on top of the alumina. The alumina was held in place by a porosity B frit at the bottom of the inner column. To prevent the soot from "flying" due to air currents and static charge, we added additional alumina on top of the soot. The inner column was then placed within the outer column and tightly attached with a nylon bushing and CAPFE O-ring. The column was fitted with a condenser and was placed above a preweighed flask containing hexane. Once reflux begins, the solvent vapors from the boiling flask rise through the space between the inner and outer columns and continue through the holes near the top of the inner column into the condenser. The condensate then falls onto the raw soot, extracts the fullerenes, and passes through the alumina column. The violet C_{60} band is readily separated from the band containing C_{70}. Hexane and the purified C_{60} flows into the boiling flask, and hexane is again vaporized while the purified C_{60} remains in the flask. Yields of 4-6% were obtained by this procedure.

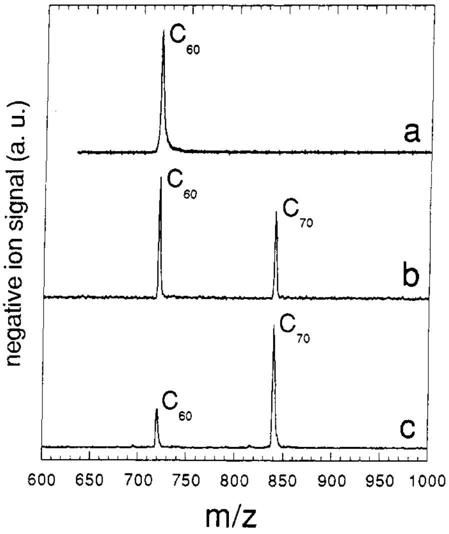

Figure 1. Time-of-flight mass spectrum of the fullerene solutions obtained after Kauffman column chromatography. Panel a shows that pure C_{60} is obtained in the first fraction eluted from the column (5 h). Successive fractions shown in panels b (20 h) and c (additional 20 h after fraction b was removed) show the increasing enrichment of C_{70} in the solution.

The product was analyzed by laser desorption time-of-flight mass spectrometry.[8,10] Panel a of Figure 1 shows that the violet solution contains only C_{60}. No other species were detected at a signal-to-noise ratio of 100:1. Continuing the run for longer times results in a solution highly enriched in C_{70} as shown in panels b and c of Figure 1. Pure C_{70} was not obtained directly from the raw soot since C_{60} is continually extracted from the soot and contaminates the C_{70} band as it moves down the column.

In summary, we have obtained pure C_{60} in a one-step procedure from raw soot with yields of 4-6%. The method provides continuous solvent feed so that the process does not have to be monitored constantly. Much less solvent is needed compared to the previous method. Additionally, the new method requires one-tenth the time required in earlier methods involving sequential Soxhlet extraction,

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chromatographic separation, and rotary evaporation. Furthermore, we believe the new method to be relatively inexpensive. More work is being carried out to optimize the yield of C_{60} and perhaps to obtain pure C_{70} and the higher fullerenes by use of different solvents.

Experimental Section

The soot was prepared from graphite rods (United Graphite Products Co., Inc., Bay City, MI) as reported previously.[8] *n*-Hexane (American Burdick & Jackson) was supplied by American Scientific Products. Aluminum oxide (activated neutral; 150 mesh, 58 A) was supplied by Aldrich Chemical Co. The Kauffman chromatographic column was obtained from Ace Glass.

In a typical run, 110 g of neutral alumina was loaded in the inner column to which 0.356 g of soot was added. Extraction was begun with 135 mL of *n*-hexane in a previously weighed flask. The extraction was stopped after 6 h when the violet band was eluted from the column. The C_{70} and higher fullerenes remained on the column. The flask was removed, and solvent was stripped from the extract in a rotary evaporator. The flask was weighed, and from the difference, the amount of pure C_{60} obtained was 0.015 g for a yield of 4%. The large-scale apparatus gave similar results using 4.5 g of soot, 200 g of alumina, and 250 mL of hexane to obtain a yield of 0.268 g of pure C_{60} (6%) after 11 h of extraction.

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Registry No. C_{60}, 99685-96-8; C_{70}, 115383-22-7; C, 7440-44-0; aluminum oxide, 1344-28-1.

A Simple Soxhlet Chromatographic Method for the Isolation of Pure C_{60} and C_{70}

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Large isolable quantities of C_{60} and smaller amounts of C_{70} can be obtained by striking an arc between two graphite rods at 60–150 A in a He (100 Torr) atmosphere in a modified evaporator,[1] followed by extraction of the resulting soot with toluene. Purification of the toluene extract by column chromatography over neutral alumina (5% toluene in hexane as eluent)[2] affords pure C_{60} and C_{70} (contaminated with C_{60}). This chromatographic process is inexpedient because (a) it often requires constant attention and involvement of at least one person for a whole day, (b) it makes use of large amounts of solvents (for a 0.5-g amount of the mixture, for example, one may require as much as 12 L of hexane and 0.6 L of toluene), and (c) the C_{70} obtained this way is generally contaminated with C_{60} and higher fullerenes.

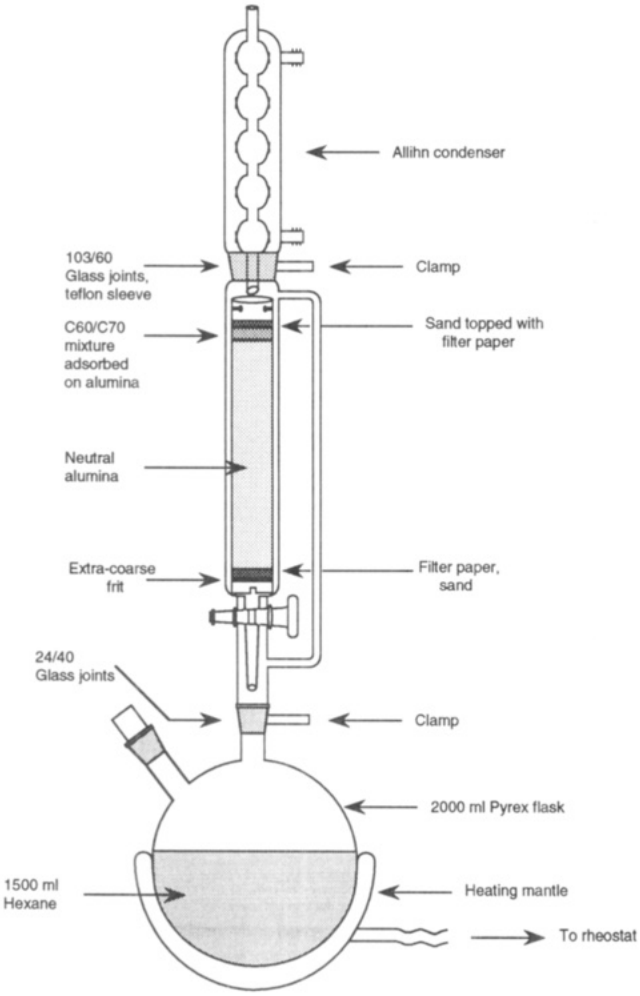

Figure 1. Schematic representation of the modified Soxhlet chromatography apparatus.

In this publication we describe a very simple process for the purification of C_{60} and C_{70} from the soot extracts; this procedure, combined with our fullerene benchtop reactor (FuBR),[3] allows easy preparation of gram quantities of pure C_{60} and tenth gram quantities of *pure* C_{70}. Our setup, once assembled and started, does not require constant monitoring and uses only about 1.5 L of pure hexane[4] per run.[5] The apparatus is shown schematically in Figure 1. In essence, the equipment is nothing but a regular alumina column with continuous solvent recycling using a modified Soxhlet extractor.[6] The glassware is very easily fabricated by simple glass-shop modifications (as per the specifications shown in Figure 2) of the following commercially

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[3] Koch, A. S.; Khemani, K. C.; Wudl, F. *J. Org. Chem.* **1991**, *56*, 4543. We noticed that the quality of the Corning 4-L kettle reactor varied unpredictably from batch to batch, in some cases resulting in unprovoked cracking of the vessel. We therefore suggest use of a stainless steel kettle reactor lined with a Pyrex sleeve. The Cu guide sleeve was replaced with a tantalum guide to prevent melting of the metal.

[4] The solvent used was actually "hexanes" (ACS reagent grade) from Fisher.

[5] If a clean, efficient rotary evaporator is used, then the solvent waste is essentially zero because the recovered solvent can be used for the next batch.

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