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FULLERENES AND GIANT FULLERENES: SYNTHESIS, SEPARATION, AND MASS SPECTROMETRIC CHARACTERIZATION

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Abstract—We report a detailed procedure for the production of fullerenes and giant fullerenes in very high yield. Our high yields are obtained by a combination of fine control of the arc gap distance, optimal convection in the apparatus, and careful Soxhlet extraction with selected solvents. Our extraction and mass spectrometry results confirm the existence of giant fullerenes with masses in excess of 3000 amu. We find that 94% of the soot can be extracted in N-methyl-2-pyrrolidinone, indicating that a large portion of the soot has a molecular fullerene-type structure. We also present a new one-step method for the rapid separation of pure C_{60} directly from raw soot. An overview of recent results in the area of synthesis and purification of fullerenes and giant fullerenes is also presented.

Key Words—Fullerene synthesis, mass spectrometry, soot, fullerene separation.

1. INTRODUCTION

In 1984, the group at Exxon reported the observation of only even-numbered carbon cluster ions in the range C_{40} to C_{200} generated by laser ablation of graphite[1]. In the next year, the collaborative group of Kroto, Curl, Smalley, and graduate students Heath and O'Brien, proposed the structure of the truncated icosahedron to explain the exceptional stability of a carbon molecular ion consisting of 60 carbon atoms in the mass spectrum of laser ablated graphite[2]. This molecule was given the name buckminsterfullerene. Five years passed before this material was isolated in macroscopic quantities. In early 1990, Krätschmer *et al.* reported evidence for the presence of C_{60} in a sample of carbon dust prepared from vaporized graphite[3] and were able to isolate macroscopic quantities of C_{60} and C_{70}[4]. Reports of the synthesis of gram quantities of C_{60} and C_{70}[5–15] have generated a huge amount of interest in this new class of closed-caged carbon molecules. This paper discusses our recent results on improvements in the synthesis, separation, and characterization of fullerenes and presents an overview of the work of other groups in this area.

The methods used to synthesize fullerenes are of five types: evaporation of high purity carbon by using resistive heating[5,6,10]; use of an AC or DC arc discharge source[7–9,11–15]; flame production of soot from carefully controlled combustion of benzene [16]; laser ablation of a rotating carbon disc in a furnace under flowing argon[8]; and most recently, a high frequency inductive heating method[17]. These methods produce carbon "soot" from which the fullerenes are extracted by use of appropriate solvents. Table 1 summarizes some of the experimental conditions reported in the literature for the synthesis of fullerene-containing soot by the arc discharge and resistive heating methods. The arc discharge process appears to be more efficient than the resistive heating method[7,18] since the power is dissipated in the arc rather than in heating the entire electrode[7]. Pang *et al.*[13] reported the synthesis of fullerenes from coke rods prepared from demineralized coal, and they note that DC power rather than AC power improves the percentage yield of soot for both graphite rods and rods prepared from coal. Shinohara *et al.*[15] also report that DC current is more efficient than AC current, but others report no difference in yield[19]. Koch *et al.*[12] found that lower currents gave better yields than very high AC currents. An examination of some of the conditions used for the arc synthesis (shown in Table 1) indicates that toluene- or benzene-soluble yields of about ten percent can typically be obtained for a wide range of experimental conditions. Our group uses a plasma-arc DC discharge that gives benzene soluble yields of 14% when extracted by reflux and the yield increases to 26% when Soxhlet extraction is used. This difference indicates that reflux extraction methods may be limited by solubility rather than the fullerene content of the soot. Pradeep and Rao[20] have reported a generator that produces,

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Table 1. Summary of some fullerene synthesis methods. Yields are based on total soluble material extracted per weight of soot used except where indicated. The column labeled "Soluble yield" reports yields for which it is unclear from the reference if AC or DC current was used in the synthesis. Extraction is in benzene unless otherwise noted. Gravity feed is a special case of the contact arc method

Soluble Yield %	DC Yield %	AC Yield %	Current (A)	Voltage (V)	He Pressure (Torr)	Contact Method	Extraction Method	Ref.
	8(3†)	8 (3†)	100	50	37–75	resistive	Soxhlet	[5],[19]†
14	?	?	140–180	?	225	resistive	boiling toluene	[6]
	—	10 ± 2	100–200	10–20	100	contact arc	Soxhlet	[7]
	—	10–15	150	27	100	contact arc	?	[8]
25–40	?	?	40–60	?	200	gravity	boiling toluene	[9]
5–10	?	?	?	?	100–200	resistive	?	[10]
	—	10	200	20	150	contact arc	?	[11]
	—	7.7	55	?	100	gravity	?	[12]
	—	3	130	?	100	gravity	?	[12]
	16.2	9.3	105–110	24	250	contact arc	Soxhlet	[13]
	26	—	70	20	200	plasma arc	Soxhlet	[14]
	12		200–250	?	20	contact arc	reflux	[15]
8–12	—	—	—	-	110	high freq.	toluene	[17]

†3% is the yield of pure C_{60}; 8% is the yield of extractable material.

under certain operating conditions, pure C_{60} as measured by NMR and mass spectrometric methods. The purity is unlikely to be better than 98% since they report a red toluene soluble extract rather than the magenta color of toluene solutions of pure C_{60}[5]. A small amount of contamination of C_{60} with C_{70} leads to the red color due to the strong absorption of C_{70} in the blue region where C_{60} is transparent[6].

Separation and purification of the fullerenes is typically performed by first extracting the soot with benzene or toluene. This extract is stripped of most of the solvent in a rotary evaporator and the concentrated solution is then placed at the top of a neutral alumina column and eluted with hexane[5,6] or hexane/toluene mixtures[21] to obtain fractions containing pure C_{60} and pure C_{70}. The separation is difficult because of the low solubility of C_{60} and C_{70} in most organic solvents[6] and to the minor solubility differences among the fullerenes. Hawkins *et al.*[22] found good separation on a Pirkle column but poor separation by flash chromatography on silica gel and HPLC on silica gel. Cox *et al.*[23] report good separation by normal phase HPLC with dinitroanilinopropyl silica using a gradient from *n*-hexane to 50% methylene chloride. Vassallo *et al.*[24] have reported an improved separation of C_{60} and C_{70} by liquid chromatography using a graphite column that allows larger amounts to be purified (tens of milligrams). Repeated chromatography of the benzene soluble portion on neutral alumina has afforded the separation of the higher fullerenes C_{76}, C_{84}, C_{90}, C_{94}, and $C_{70}O$[25] and Kikuchi and co-workers[26] have recently reported the separation of milligram quantities of these species and C_{96} with high efficiency using preparative HPLC with CS_2 as eluent. Recently, Meier and Selegue have reported[27] an efficient preparative separation of C_{60} and C_{70} using gel permeation chromatography (GPC) with toluene as the mobile phase. We have recently developed a one-step method for the extraction and purification of pure C_{60}[28] that is much faster and uses much less solvent than previously reported methods. This will be presented in further detail below.

Much of the characterization of fullerenes has relied on mass spectrometric analysis of the various extracts. For example, the first direct mass spectroscopic evidence for the presence of C_{60} in carbon soot was reported by Krätschmer *et al.*[4]. Meijer and Bethune[29] also reported direct evidence for the presence of C_{60} in an experiment that used laser desorption of the material followed by postionization of the desorbed neutral species. An isotope-scrambling experiment showed that the fullernes were not formed in the analysis step but were formed in the original deposition process. Taylor *et al.*[5] used fast atom bombardment (FAB) mass spectrometry to further characterize the soot and extracts. Aije *et al.* have compared the fragmentation resulting from electron impact mass spectrometry with FAB and laser desorption mass spectrometry[6]. There are many other reports of the use of mass spectrometry in the characterization of fullerenes, and the reader is referred to excellent reviews for further details[30,31]. We also rely extensively on mass spectrometry to characterize the fullerenes[32] and details of our mass spectrometers are presented below.

There have been a number of recent reports on the "giant" fullerenes (i.e., fullerene molecules whose mass exceeds 1000 amu)[14,15,33–37]. There has been some controversey over the existence of these large carbon clusters in soot produced by the arc synthesis method. For instance, large carbon clusters including C_{60} and C_{70} and larger species have been produced and detected mass spectrometrically by the laser ablation of a number of carbonaceous species such as graphite[2], polyimide[38], ethylene-tetrafluoroethylene copolymer[39], and diamondlike carbon films[39], and coal[40]. In view of these results, it has been suggested that the giant fullerenes are produced in the laser desorption step of the analysis and not in the laboratory-produced soot. Hertel and coworkers have shown that at increasing laser fluences for the desorption step, fragmentation, and aggregation to form larger carbon clusters can occur[41]. They also suggest that laser desorption mass spectrometry alone is not sufficient evidence to prove the existence of the giant fullerenes in arc produced carbon soot[41]. In contrast to this, we will present evidence from recent work in our laboratory that confirms the existence of giant fullerenes in arc-produced soot.

2. RESULTS

2.1 *Fullerene synthesis*

Figure 1 shows a scale diagram of the generator used to produce the fullerene containing soot. Since our initial report[14], we added cooling coils on the outside of the generator and a pressure relief valve for increased safety. The apparatus is housed in a modified 8-in. four-way Conflat cross and pumped by a mechanical pump to a base pressure of 10^{-2} Torr. The entire apparatus is positioned in a vented fume hood for safety. After pump-down, the chamber is isolated from the pump and then backfilled with high purity helium to a pressure of 200 Torr. The production of fullerenes is carried out within the water-cooled shield region shown on the right-hand side of Fig. 1. The water cooled shield is actually a Perkin-Elmer cryoshroud (designed for ultrahigh vacuum pumping) through which we flow cold water. This region is lined with stainless steel shims kept cool by contact with the water-cooled shield. At the end of a run, these shims can be easily removed and the soot scraped and collected using a paint brush. The large (½ in.) graphite rod ("Ultra Purity Spectroscopic Graphite Electrodes," United Carbon Products Company, Inc., Bay City, MI) is attached to a 2-in. linear feedthrough drive. A grounding strap is attached from the feedthrough shaft to the chamber to provide a low-resistance path for the high electrical current to flow to ground. This avoids high currents passing through the delicate bearings and bellows of the linear motion feedthrough. The smaller carbon rod (¼ in., National, "Special Spectroscopic Electrodes") is held in a stainless steel holder that can be fed into the chamber by means of an Ultra-Torr union. This allows almost the entire length (12 in.) of the rod to be "burned" without breaking vacuum. The holder is attached to the positive lead of the power supply. A ceramic-to-metal insulator electrically isolates the smaller carbon rod from the chamber. The negative lead of the power supply is attached to the grounded chamber. The power supply is a regulated 100 A, 50-V DC power supply.

Synthesis of the fullerenes is accomplished by first positioning the two carbon rods so that they are touching. The power supply is maintained at 25 V. Resistive heating occurs while the rods are touching and the rods are not consumed. The power supply draws full current (100 A) when the rods are touching. We quickly move the electrodes apart to ignite the arc, using the fine control provided by the linear motion feedthrough, until the plasma is burning

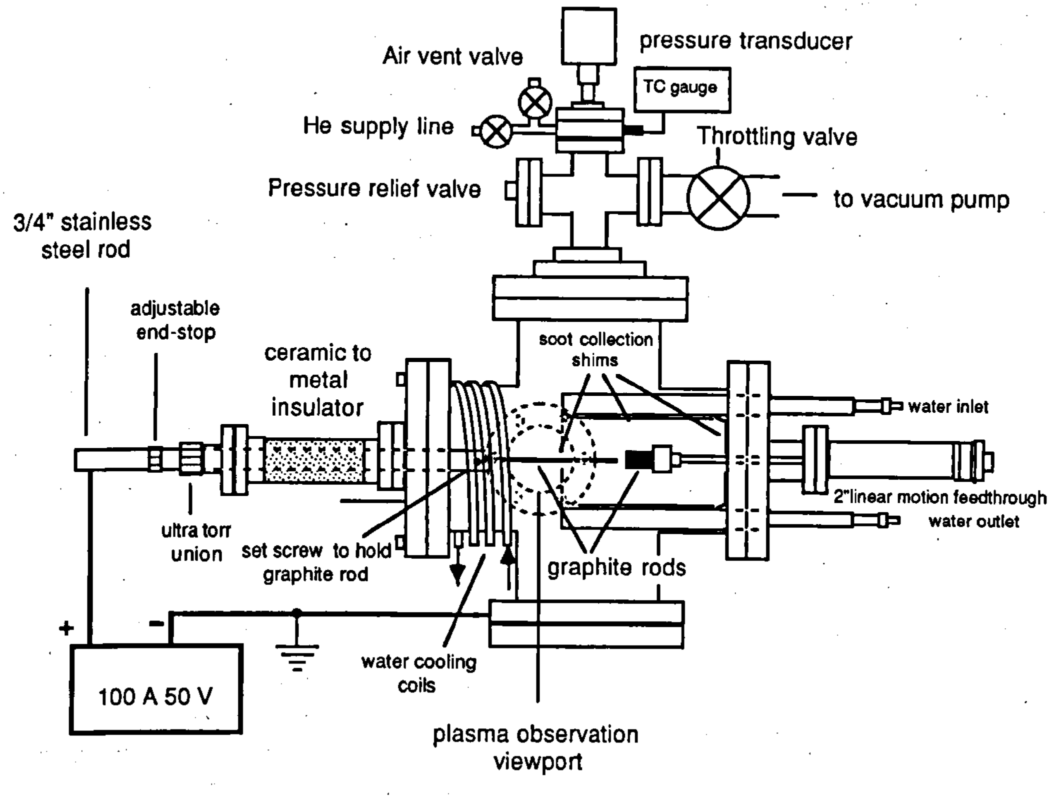


Fig. 1. Scale diagram of the apparatus used to produce fullerenes from graphite rod.

steadily. As the rod is consumed, we continually turn the linear motion feed while observing the plasma indirectly through a viewport. We adjust the gap between the electrodes to attain maximum brightness of the plasma. Under these conditions the plasma draws 60–80 A from the power supply. We do not observe the plasma directly under normal operating conditions. Instead, we observe the light emitted from the end of the collection region that is aligned directly in front of the viewport. On occasion, we have moved the electrode gap region in front of the viewport for observation (using welding goggles to observe the plasma). In this manner, we are able to determine that the gap between the rods is about 4 mm during operation. The typical power requirement under these conditions is 1–2 kW (25 V at 60–80 A). We consume the ¼ in. (positive) electrode at a rate of about 0.5 in. per minute and the larger (negative) electrode shows no detectable consumption. Occasionally, the smaller electrode is not consumed but instead transforms to look something like "popcorn." This popcorn, which is light grey in color, often breaks off and is collected with the soot, but is discarded before solvent extraction. We have not yet determined what causes the formation of this popcorn. At the end of a run, the apparatus is filled to atmospheric pressure with He. The chamber is then opened, the collection shims removed and the soot scraped from the shims and collected for further purification. Gloves and a face mask are worn during this step to avoid exposure to the very fine soot particles. With this method, tens of grams of soot per day can be produced. The addition of the cooling coils to the outside of the chamber (Fig. 1), allows the system to be operated continuously, without waiting for cooling between runs.

2.2 *Mass spectrometry*

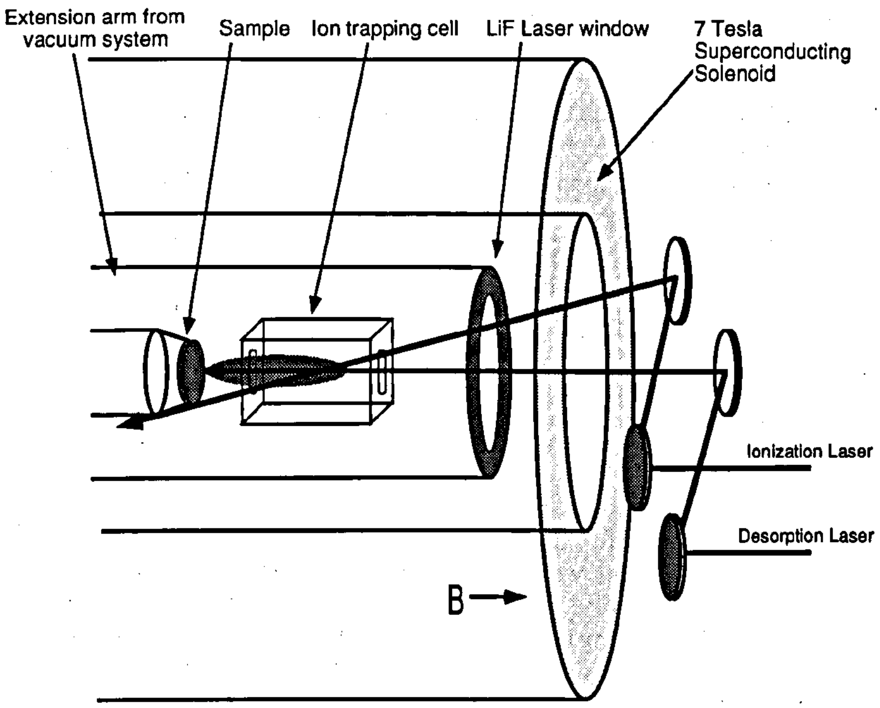
We use two different mass spectrometers to characterize the soot and extracts. Our laser desorption time-of-flight (TOF) mass spectrometer has been described in more detail in a previous publication[42]. Briefly, the TOF mass spectrometer consists of a sample plug, an ion optics stack for ion acceleration, deflection plates, a field free region, and a dual microchannel plate assembly for detection of ions. The experiment measures the mass spectrum of negative ions or positive ions emitted directly from the sample in the desorption process. The mass resolution (m/Δm) of the apparatus is usually 400 under these experimental conditions. The base pressure of the system is typically 2×10^{-9} Torr. Neutral and ionized fullerene clusters are desorbed from the stainless steel substrate by a XeCl excimer laser (308 nm) or by 532 nm (266 nm) light from the doubled (quadrupled) output of a Q-switched mode-locked Nd^{3+}:YAG laser. The fluence of the desorption laser is held constant at approximately 10–100 mJ/cm^2, which is just above the threshold for ion production. The laser desorption at these intensities produces a minimum of fragmentation of the desorbing fullerene molecules[43]. However, at slightly higher intensities, significant fragmentation occurs.

The laser desorption Fourier transform mass spectrometer (FTMS) consists of a three-region vacuum chamber with each region separated by gate valves and differential pumping apertures. The first region is a turbo-pumped rapid sample transfer region. The second region is also turbo-pumped and contains an argon ion sputter gun and gas dosing capabilities. The third region contains the optical path for an FTIR spectrometer, additional gas dosing capability, a resistive heater for vapor deposition of fullerenes, and an extension arm containing the analyzer cell for FTMS. In this region, a typical base pressure of 1×10^{-10} Torr is achieved by a cryopump. The entire apparatus is on a cart that can be moved to place the analyzer cell in the bore of a 7-T superconducting magnet. The sample is transferred between the various regions of the apparatus by a 1.5-in. polished transfer rod, and the sample can be resistively heated and cooled with liquid nitrogen. The FTMS experiments are performed with an Ionspec Omega data acquisition system. RF chirp excitation is used to accelerate the ions into cyclotron orbits inside the cell. Figure 2 shows a schematic of the FTMS cell and laser ports.

2.3 *Extraction of the fullerenes*

In the early stages of this work, we first determined that the fullerene synthesis was successful by stirring a portion of the soot in warm benzene for one hour. Filtration of this mixture yields a dark red solution indicating the presence of C_{60} and C_{70} and small amounts of higher fullerenes. We analyzed this solution by two procedures. First, a small amount of solution was evaporated onto a stainless steel sample holder and laser desorption TOF mass spectrometric measurements were performed on the residue. The TOF mass spectrum of this sample[14] showed primarily C_{60} and C_{70} with small amounts of C_{78} and C_{84}. Extractions were also performed with toluene and carbon tetrachloride, which gave nearly identical results. In the second procedure, we evaporated the fullerenes obtained from the same solution onto the Pd substrate using the fullerene doser in the FTMS apparatus. FTMS is more sensitive at higher molecular weights than our TOF spectrometer due to the velocity dependent detection sensitivity of the microchannel plates in the TOF detector. Figure 3 shows the FTMS spectrum indicating that small amounts of the higher fullerenes are indeed present in the benzene extract. A spectrum acquired with ejection of the ions below mass 850 is shown in the expanded portion of the spectrum. Ion ejection is accomplished with selective rf chirp excitation and does not alter the intensity of the remaining ions in the analyzer cell. This spectrum clearly shows that fullerenes up to cluster size C_{266} can be identified in the benzene extract prepared from soot formed in our fullerene generator.

We have compared the efficiency of Soxhlet extraction with the reflux technique using benzene as



Laser Desorption Fourier Transform Mass Spectrometer

Fig. 2. Schematic diagram of the FTMS apparatus showing the position of the analyzer cell and laser entrance port. The ionization laser was not used in these experiments.

the extraction solvent. Both extractions were carried out for 24 h yielding strongly colored red solutions. Small amounts of the extract were saved for later analysis by mass spectrometry. The remainder of the sample was stripped of solvent in a rotary evaporator and then dried under high vacuum over a 105°C oil bath to determine the yield relative to the initial amount of soot used in the extraction. The insoluble material in the thimble was also dried over a hot oil bath under high vaccuum. In all of our extractions, we obtained a mass balance to within ~2% by measuring the weight loss of the soot compared to the weight of the dry extract. We found that the Soxhlet extraction worked much better than simple reflux, giving a 26% yield of soluble material. By contrast, the reflux extract gave a 14% yield of soluble material. Since Soxhlet extraction resulted in yields almost twice as high as with reflux, all subsequent extractions were performed by the Soxhlet method. From Table 2, it is seen that after four hours of extraction, not all

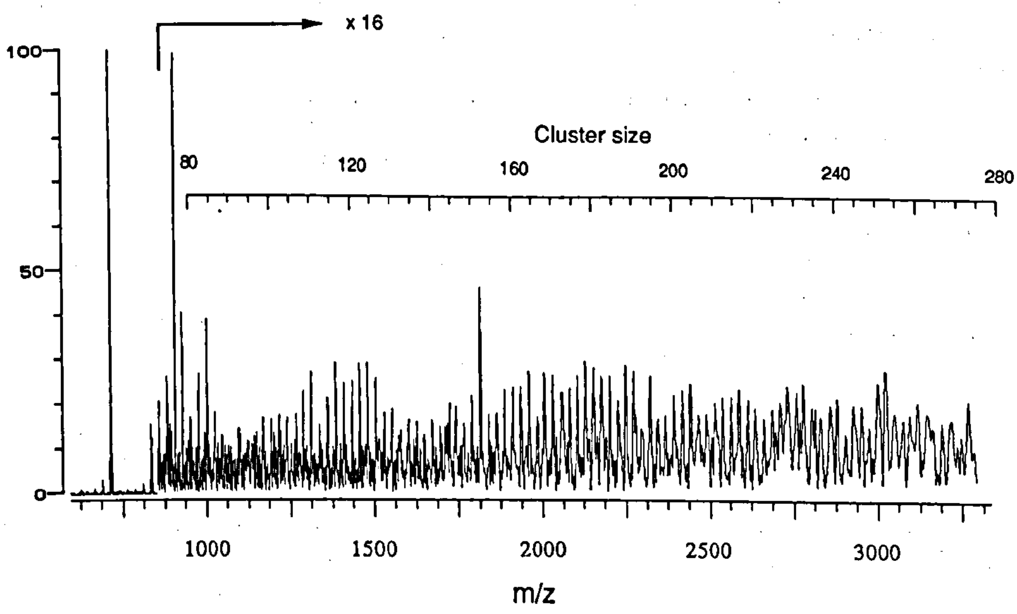


Fig. 3. Fourier transform mass spectrum of fullerenes extracted by washing in benzene, showing C_{60} and C_{70}. The inset, shown at a scale factor of 16×, depicts a spectrum acquired by ejecting ions with m/z less than 850, showing that fullerenes up to cluster size C_{266} are produced in our apparatus.

Table 2. Experimental results for Soxhlet extraction of soot with *n*-hexane and benzene

Extraction Solvent	Yields	He Pressure (Torr)	batch†/sample number‡	Extraction Time
n-hexane	18%	200	batch #1 sample b	4 h
n-hexane	§18.6%	200	batch #6 sample b	4 h
n-hexane	21%	200	batch #1 sample a	24 h
n-hexane	20%	200	batch #6 sample a	24 h
benzene	24%	200	batch #1	24 h
benzene	27%	200	batch #2 sample a	24 h
benzene	26%	200	batch #2 sample b	24 h

†Batch numbers refer to different sample of soot produced either by different experimenters or on different days or both.

‡Sample numbers refer to different samples of the same batch of soot.

§"Blind" analysis performed by an independent laboratory.

of the fullerenes are extracted compared to the 24-h extraction. Consequently, all extractions were performed for 24 hours unless noted otherwise with cycling times of 25 min per cycle. The cycling time and total time are important parameters to consider when comparing results between laboratories since these two parameters determine the total volume of solvent washed through the soot. A run carried out at a slower

At first, we were surprised by these high yields since they are considerably higher than yields previously reported (Table 1) with the exception of the work by Diederich *et al.*, which also reports yields in this range[25]. We spend considerable time verifying these results and a summary of several of our experimental runs using *n*-hexane and benzene extraction solvents is shown in Table 2. This table shows that the results are quite reproducible and we consistently obtain these high yields, unlike the work reported in Refs. [6,9, and 25] which gives a wide range of yields (25–35%). Our yields have been repeated by several operators and with several different Soxhlet extraction apparatus.

We were concerned that some of the yield could be attributed to insoluble micron-sized particles escaping through the cellulose Soxhlet thimble without actually becoming dissolved. If this occurred, a good mass balance would still be obtained but the yield would be artificially high. To ensure that this was not contributing to our high yields, we filtered some of the solutions through a 0.8-μm Nucleopore polycarbonate membrane filter or a 0.45-μm millipore filter. No particulates were trapped by the filter indicating that the extract is a true solution and does not contain insoluble particulates. Because benzene is a carcinogen, we now use toluene or *n*-hexane for routine extractions. The fullerenes are less soluble in toluene than benzene. Only 17% soluble material is extracted in toluene compared to 26% for benzene. Figure 4A gives the TOF mass spectrum of the material isolated from the benzene Soxhlet extractions showing that the benzene solvent dissolves primarily C_{60} and C_{70} in a ratio of approximately 3:1 with very small amounts of higher fullerenes up to mass 1200. The mass spectrum of the sample prepared by reflux was identical. However, the mass spectrum of a toluene extract is similar to the mass spectrum obtained for benzene extraction, indicating that the solubility differences are largely independent of mass. We also found that if the extraction is performed under a nitrogen atmosphere, the yields are slightly higher (3–4%) than when extracted under ambient conditions. Also, it is important to cover the Soxhlet apparatus with foil during the extraction to keep light from the solution that will degrade the fullerenes. We refluxed a solution of pure C_{60} in toluene exposed to room light

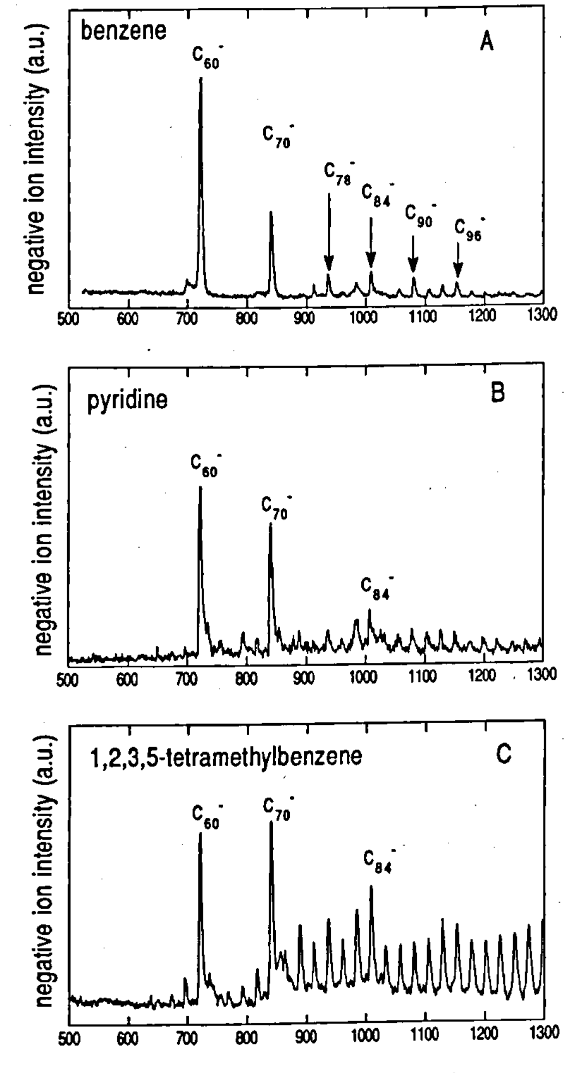


Fig. 4. Laser desorption TOF mass spectra of soot extracts resulting from sequential extractions with (A) benzene, (B) pyridine, and (C) 1,2,3,5-tetramethylbenzene. The spectra are plotted on the same mass scale for comparison.

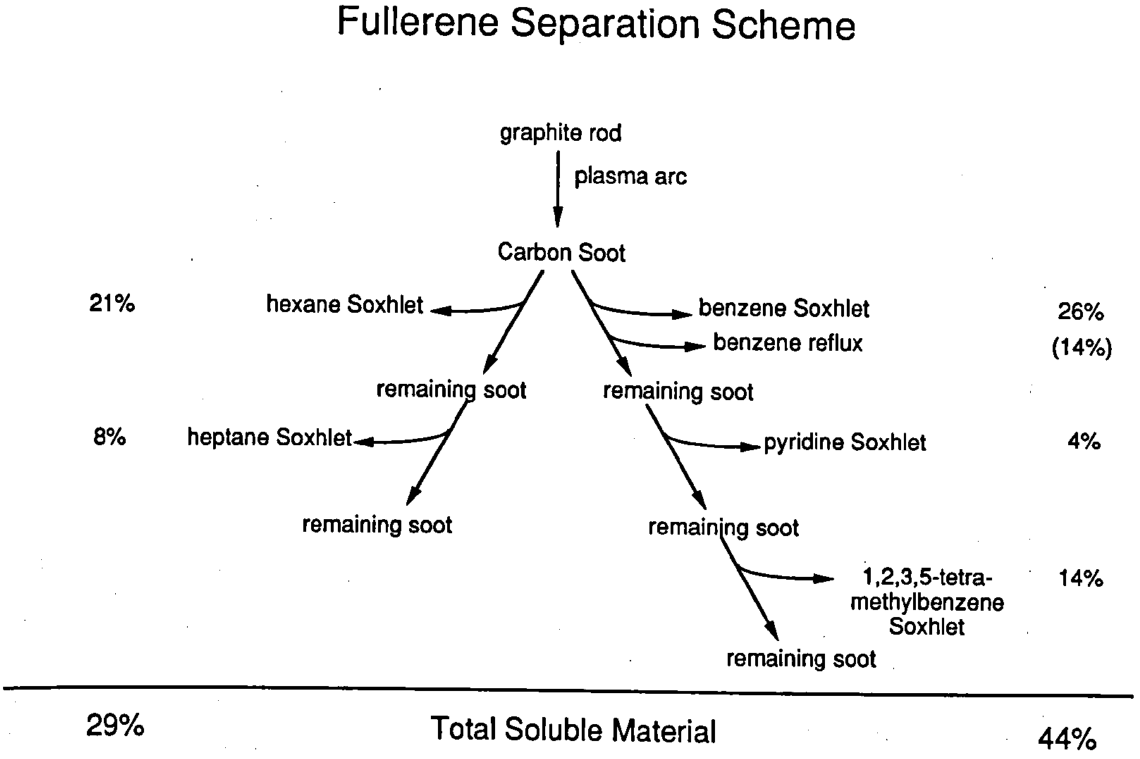


Fig. 5. Diagram of the sequential fullerene extraction scheme. The TOF mass spectra corresponding to the right-hand branch are shown in Figs. 4 and 6. The TOF mass spectra corresponding to the left-hand branch are shown in Fig. 11.

under ambient conditions. After 24 h of reflux, the solution had changed from the beautiful magenta color of pure C_{60} to an orange color, indicating decomposition of the C_{60}.

2.4 *Selective molecular weight extraction by varying the extraction solvent*

Following the observation of the small amounts of fullerenes up to mass 1200 in Fig. 4A, we thought that we could increase the solubility of these larger species by using higher boiling solvents. We performed the successive extraction scheme shown in the right-hand side of Fig. 5. We first attempted to isolate higher molecular weight fullerenes by extraction with a more polar solvent. The material remaining in the Soxhlet thimble was Soxhlet extracted with pyridine yielding an additional 4% yield of soluble material. The TOF mass spectrum of this material, depicted in Fig. 4B, shows C_{60} and C_{70} in a ratio of 2:1 with small amounts of the higher fullerenes. This extraction gives results very similar to the benzene extraction, and there appears to be no advantage to using pyridine over benzene. The material remaining in the thimble was then extracted with 1,2,3,5-tetramethylbenzene (TMB). This extraction yielded a dark greenish-brown solution with an additional 14% soluble material. TOF mass spectrometry (Fig. 6) shows that this solution contains significant concentrations of fullerenes up to mass 2400 (C_{200}). This TOF spectrum is also shown in Fig. 4C, where it is plotted on the same scale as the benzene and pyridine extracts for comparison. The spectrum (Fig. 6) shows only successive even-numbered peaks suggesting the presence of hollow fullerene cage molecules [44]. From peak areas and abundance considerations, it appears that C_{60} and C_{70} are present in concentrations of less than 1%. Because of the decreasing channel plate detection sensitivity for higher mass species in the TOF apparatus, we suspected that there may be even larger fullerene species present in the TMB extract. Using FTMS, and carefully optimizing the excitation conditions, using low desorption laser power to avoid fragmentation, and ejecting masses below 850 from the cell, the spectrum shown in Fig. 7 was obtained. Based on the yields from the successive extractions of the soot with benzene, pyridine, and 1,2,3,5-tetramethylbenzene, the total yield of soluble material consisting of fullerenes C_{60} to C_{466} is 44($\pm$2)% for this series of extractions.

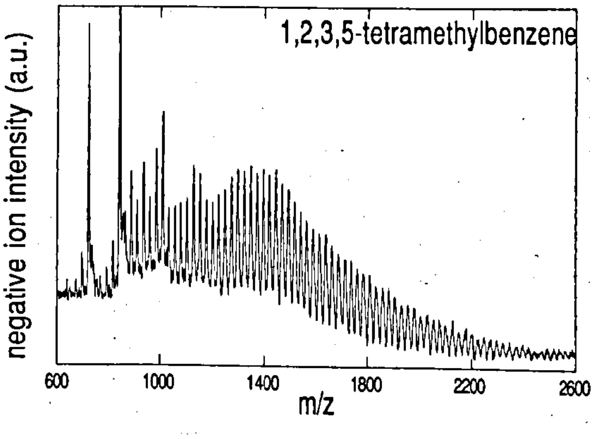


Fig. 6. Laser Desorption TOF mass spectrum of TMB extract prepared from soot previously extracted with benzene and pyridine according to the diagram shown in Fig. 5. A portion of this spectrum is also shown in Fig. 4(C).

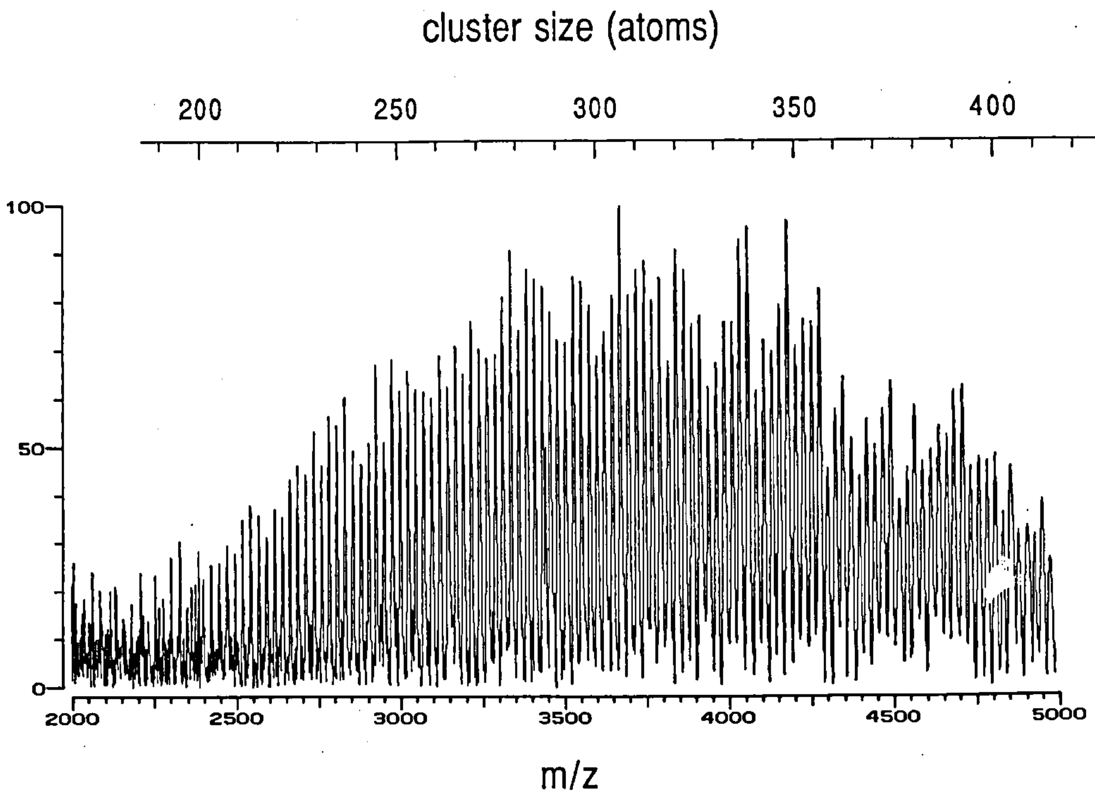


Fig. 7. Laser Desorption FTMS spectrum of the 1,2,3,5-tetramethylbenzene extract. The spectrum was acquired using low laser fluence, and ejecting masses below m/z = 850.

We were concerned that perhaps C_{60} and C_{70} were reacting with the solvent to form a polymeric species that, upon laser desorption, readily recombined to give the higher fullerenes, much as reported by Brenna and Creasy for the laser ablation of other polymers[39]. To test this, we refluxed pure C_{60} with TMB for 20 h under nitrogen to determine if polymerization was taking place. The TOF mass spectrum (Fig. 8A) of this reaction mixture shows that the solvent has added to the fullerene cage, but we see no evidence of polymerization of the solvent or fragmentation and reaggregation to form giant fullerenes. Figure 8B shows a high resolution FTMS spectrum plotted for the region around the first adduct peak (centered at m/z 854). These experiments, comparing the TMB soot extract and the TMB C_{60} reaction product, were performed under similar conditions of laser fluence. This is very good evidence that the giant fullerenes are actually present in the extract solution and are not formed by a matrix effect during the desorption step due to polymerization by the solvent. It is possible, however, that the larger fullerenes are also reacting with the solvent thus contributing to the measured yield, and we do see a small amount of the C_{60}-TMB adduct in the mass spectrum of Fig. 4C at m/z = 854. However, in our high mass resolution FTMS spectrum of the TMB extract, we do not see any evidence for the adduct reaction products of the giant fullerenes. This reaction of C_{60} with TMB is very similar to the reactions reported by Hoke *et al.*[45] in which C_{60} was shown to add five to six molecules of toluene by refluxing this solution in the presence of $FeCl_3$. It is important to note that, in our work and in that of Hoke *et al.*, these species are not formed in the mass spectrometer. A solution of pure C_{60} in TMB (without refluxing) evaporated onto a sample holder shows only C_{60} in the mass spectrum. Interestingly, we do not require the presence of the Lewis acid $FeCl_3$ to catalyze the solvent addition to C_{60}. The reaction likely proceeds by a free radical addition mechanism. We have performed a 20-h reflux of pure C_{60} with 1,2-dimethylbenzene and 1,3,5-trimethyl benzene and we see no evidence of reaction.

We thought that it might be possible to obtain pure C_{60}, or at least greatly enriched C_{60}, by extracting the soot directly with alkanes. Two different types of experiments were performed: extraction of raw soot with different alkane solvents and successive extractions of soot residue with a series of different alkane solvents. We extracted the *raw* soot with *n*-pentane, *n*-hexane, and *n*-heptane and find that 14(±2)%, 18(±2)%, and 23(±2)% soluble material is extracted, respectively. The mass spectra of the *n*-pentane, *n*-hexane, and *n*-heptane extracts are shown in Fig. 9, panels A–C. The mass spectra of the extracts with saturated hydrocarbons are very similar but show larger amounts of higher fullerenes for the heptane extract. The total extracted amount from raw soot increases with increasing boiling point of the solvent for *n*-pentane, *n*-hexane, and *n*-heptane (boiling points are 36°C, 69°C, and 98°C, respectively). We can show this general trend in a plot of the amount extracted versus boiling point of solvent for all of the solvents we have used to extract raw soot (Fig. 10). We cannot make a

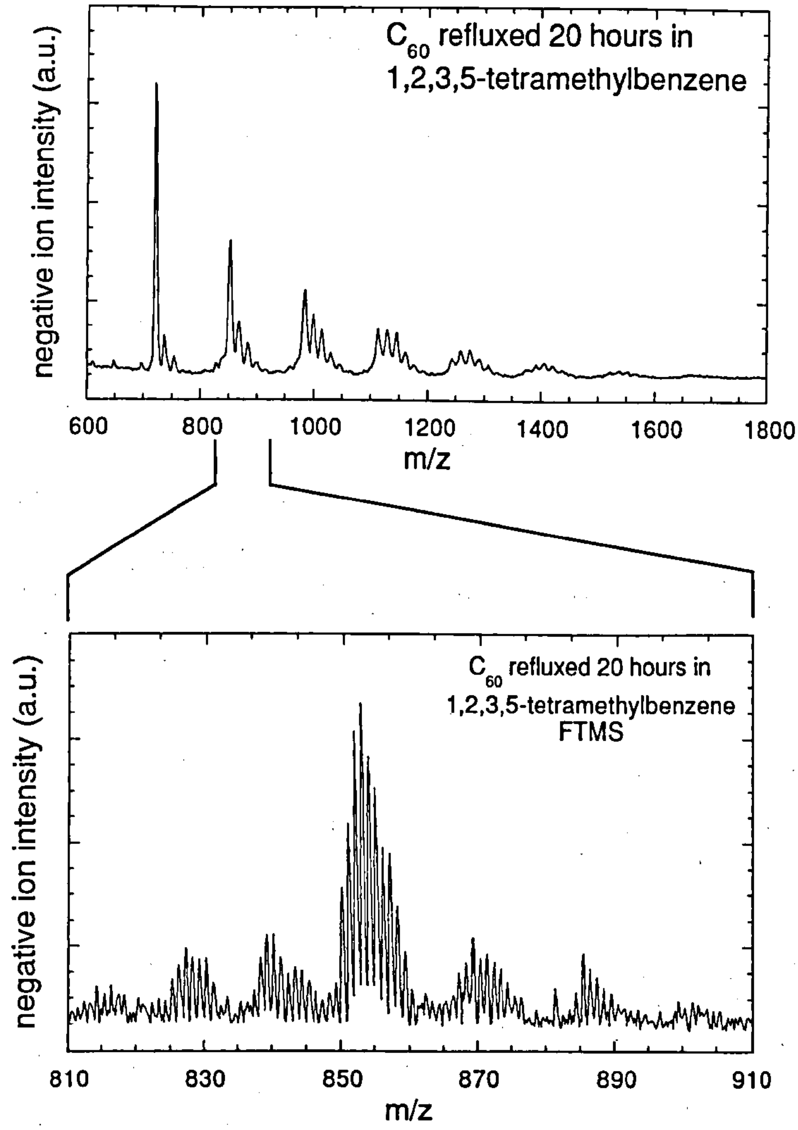


Fig. 8. The top panel shows the laser desorption TOF mass spectrum of C_{60} refluxed for 20 h in 1,2,3,5-tetramethylbenzene. The bottom panel shows a high resolution FTMS mass spectrum of the same sample, expanded about the region 810 to 910 mass units. The spectrum shows the adduct of one solvent molecule with C_{60} at mass 853. Methyl addition and methyl loss are evident in the multiplets on either side of the central peaks. Isotope peaks of carbon appear to be convoluted with hydrogen addition and loss in each of the multiplets.

van't Hoff plot as in Ref.[37] because we have used a nonequilibrium Soxhlet extraction method instead of equilibrium reflux. The van't Hoff analysis only works for processes at equilibrium.

For the successive extractions, a fresh portion of the soot was Soxhlet extracted with *n*-hexane for 24 h giving a pink solution. This extraction yielded 18(± 2)% soluble material. The mass spectrum shown in Fig. 11A indicates that *n*-hexane extracts C_{60} and C_{70} with only trace amounts of C_{76}, C_{78}, and C_{84} (<1%). The soot remaining in the Soxhlet thimble was then extracted with *n*-heptane, giving an orange-colored solution. This extraction yielded an additional 8% soluble material, bringing the total yield to 29(±2)% by weight. The TOF mass spectrum of this extraction is shown in Fig. 11B. The *n*-heptane extract is enriched in C_{84} compared to other extracts and contains C_{60}, C_{70}, C_{76}, C_{78} and C_{84}. The ratio of fullerenes in this extract is 2.0:1.4:0.5:1.0 for C_{60}, C_{70}, C_{78}, and C_{84}, respectively. The insoluble residue from the *n*-heptane extraction was then extracted with decane yielding a clear, light-yellow solution. This solution did not show any fullerenes in the TOF spectrum and may only contain trace hydrocarbons. The total yield for the hexane/heptane branch amounts of 29 ± 2%. This is lower yield than the benzene branch of the extraction, but the hexane/heptane branch does not extract fullerenes above C_{84}, whereas the TMB extracts fullerenes out to mass C_{466} and thus, the yield is expected to be lower for the hexane/heptane branch.

The solvent N-methyl-2-pyrrolidinone (NMP, bp = 202°C) was used as this is an excellent solvent for dissolving carbonaceous materials such as coal[46]. This polar aprotic solvent penetrates deep into the coal structure and swells the coal. It is also commonly used in the separation of olefins and aromatics and

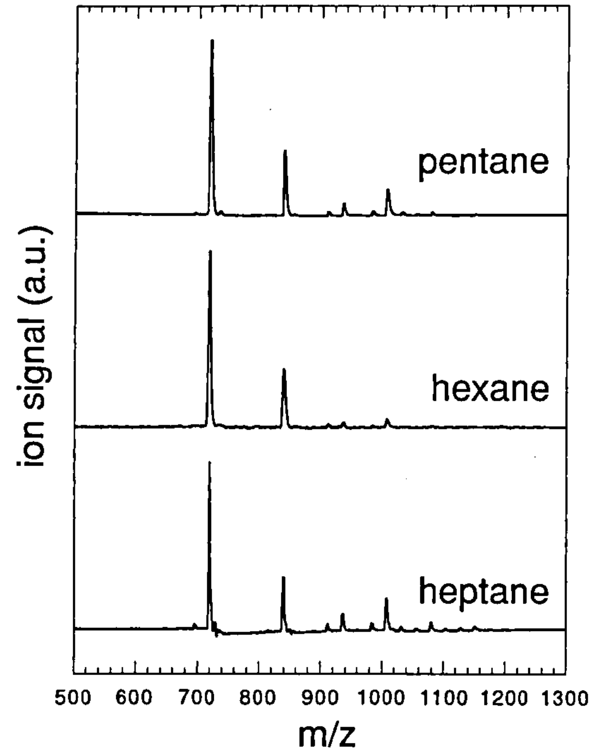


Fig. 9. Laser desorption TOF mass spectrum of pentane, hexane and heptane extracts of raw soot.

for refining oil[46]. We found that 94% of the raw soot could be desolved in this material resulting in a black solution. NMP gives high solubilities probably because of increased solvent penetration into the soot matrix, interrupting the polarization forces that hold the extractable fullerenes within the soot. The solution was evaporated onto a plug and examined by TOF MS. The result is shown in Fig. 12. Along with C_{60} and C_{70}, and giant fullerenes a significant number of smaller carbon clusters (m/z <300) were also observed in the mass spectrum.

Additionally, we have extracted giant fullerenes with 1,2,4-trichlorobenzene (TCB). We performed this extraction on soot previously extracted with toluene to deplete the soot of C_{60} and C_{70}. Figure 13 shows two LD FTMS spectra taken at different laser fluences (532-nm direct positive ion desorption). At low laser fluences, the mass distribution peaks at m/z = 2300 with fullerenes present up to m/z = 3500 and, importantly, *no* C_{60} *is observed.* C_{60} and C_{70} are observed for higher laser fluences along with the fragment clusters C_{68}, C_{66}, C_{58}, and C_{56} (panel B). At high laser fluence, the mass distribution peaks at a lower mass of 1500 and the high mass tail has moved down to 3000 mass units. This indicates that substantial fragmentation occurs at higher laser fluences to produce lower molecular weight fullerenes in the desorption step. At low laser fluences no C_{60} and only a trace of C_{70} is observed indicating that very little fragmentation is occurring. Thus, the spectrum in panel A likely represents the nascent distribution of giant fullerenes extracted with TCB. At worst, this spectrum is a lower limit for the mass distribution in the extract.

We have also repeated the experiment first reported by the group at Arizona[36] where toluene in a bomb reactor at high temperature and pressure was used to extract soot that had been previously extracted with toluene to deplete the soot of C_{60} and C_{70}. This result is shown in Fig. 14. We only extract about 3% of the soot in this manner. We indeed observe

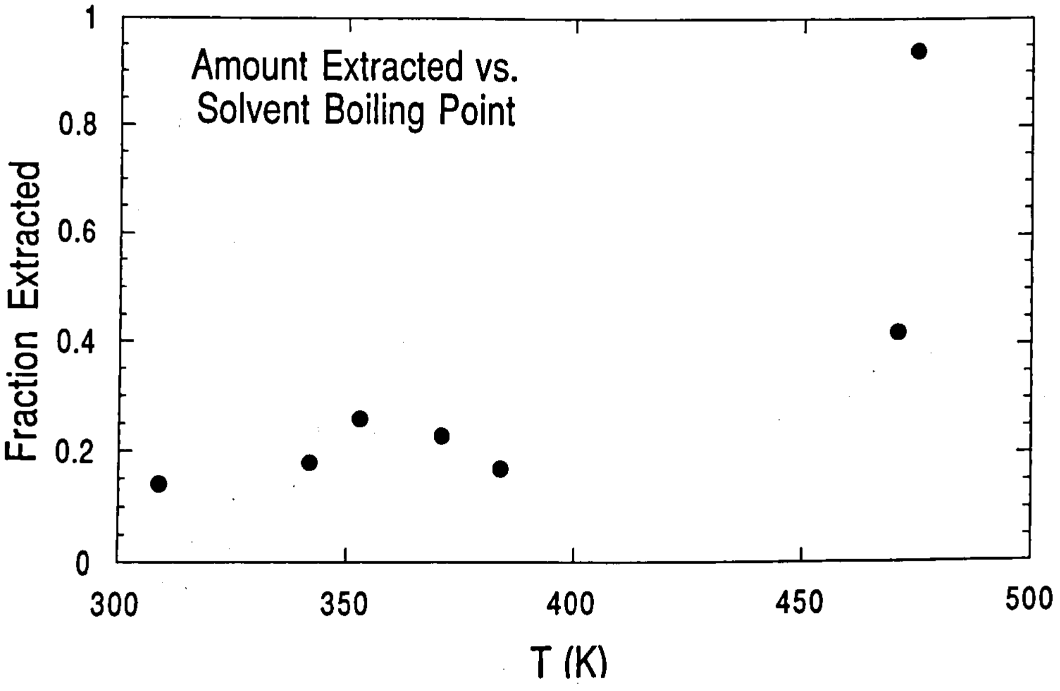


Fig. 10. Plot of fraction extracted versus solvent boiling point. The boiling points for the solvents are listed in Table 3.

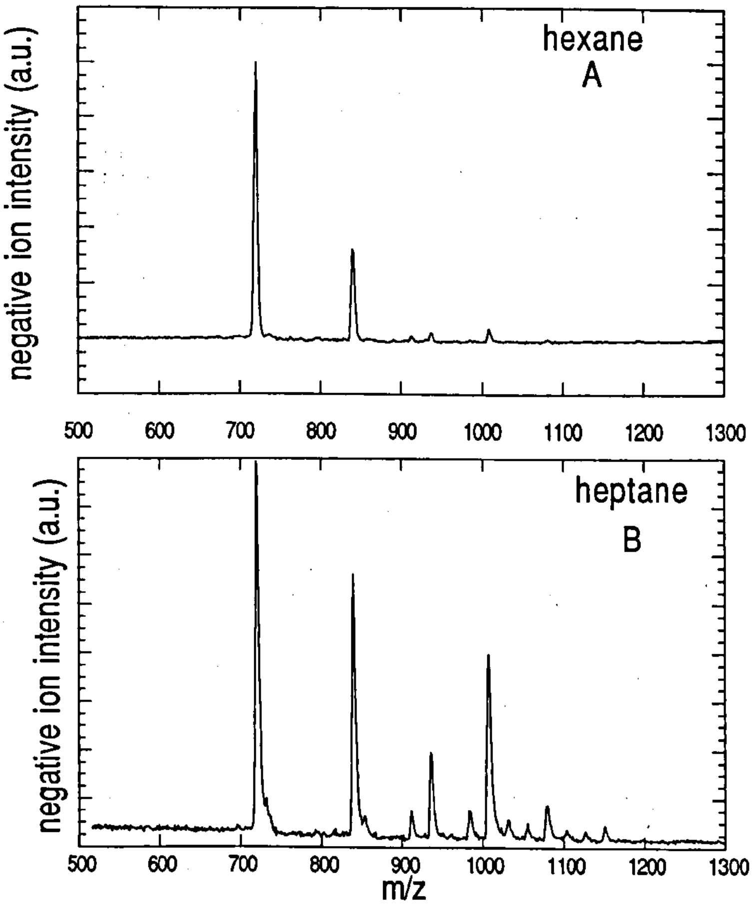


Fig. 11. Laser TOF mass spectra of extract prepared by sequential solvent extraction with (A) hexane, and (B) heptane.

higher fullerenes in this extract, but we do not observe masses as high as reported previously, probably due to difference in experimental conditions of temperature and pressure. Also, we find that once extracted from the soot, the fullerenes can be redissolved in lower boiling solvents such as hexane and methylene chloride. Further incidental evidence for the different molecular weight ranges extracted in different solvents is in the color of the solutions. These are summarized in Table 3.

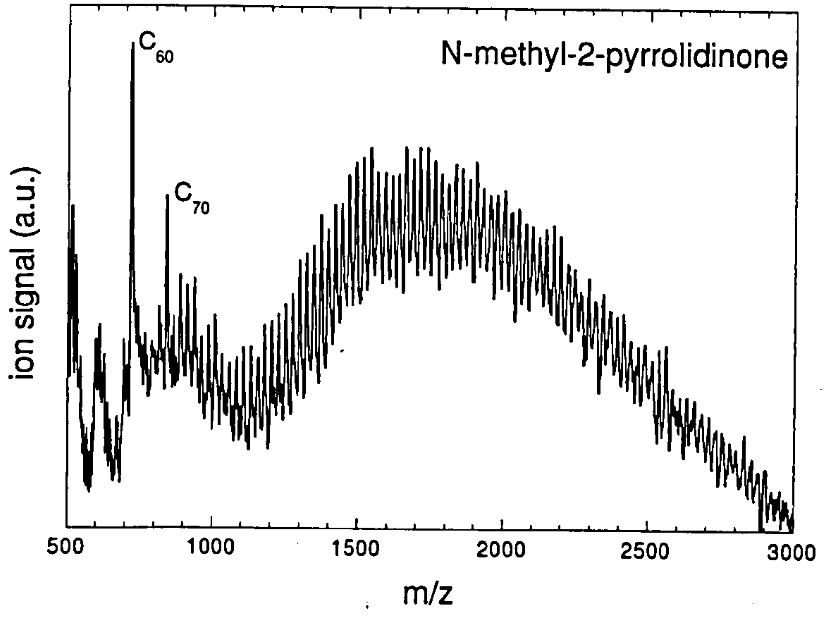


Fig. 12. Laser desorption TOF mass spectrum of raw soot extract prepared by Soxhlet extraction with N-methyl-2-pyrrolidinone.

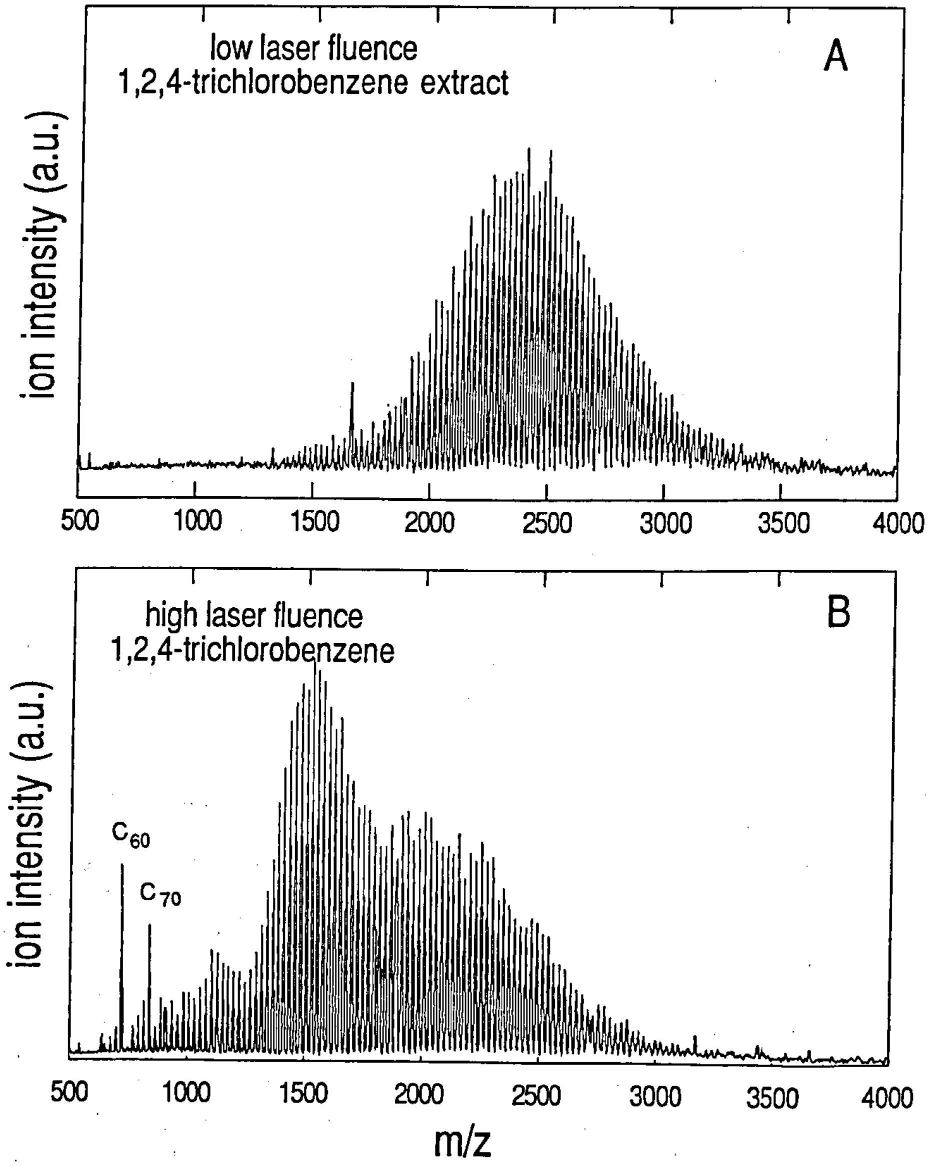


Fig. 13. Laser desorption FTMS spectra of 1,2,4-trichlorobenzene extract prepared by Soxhlet extraction of soot previously extracted in toluene to deplete the soot of C_{60} and C_{70}. Panel A depicts data collected with low laser fluence showing no C_{60} peak. Panel B shows data collected with high laser fluence, resulting in considerable fragmentation. Noise spikes have been removed from the spectrum.

2.5 *Separation of pure C_{60}*

The previously reported methods of purification of C_{60} suffer from a number of drawbacks. The liquid chromatography method on neutral alumina requires large amounts of solvent and a great deal of patience but affords excellent separation. The HPLC method is limited by the amount of material that can be injected on the column. The GPC method requires less solvent since toluene is the mobile phase, but the amount of material injected is still a limitation. Also, the HPLC and GPC methods require a considerable investment in equipment. The one-step method that we demonstrate uses only a minimum amount of solvent and runs continuously so that it does not have to be monitored constantly.

Table 3. Raw soot extract color in various solvents

Solvent	Boiling Point (K)	Color
pentane	309	pink
hexane	342	pink
heptane	371	orange
toluene	384	red
benzene	353	red
TMB	471	green-brown
NMP	475	black

Our simple one-step method involves the combination of extraction and chromatography in a single apparatus. As discussed above, higher yields were obtained by using Soxhlet extraction instead of reflux, presumably because the soot is continually washed with hot pure solvent in the former method. We also found that 18% of the raw soot was extracted into *n*-hexane and this extract contains primarily C_{60} and C_{70}[14]. We sought to combine the efficiency of Soxhlet extraction with the selectivity of the chromatographic method to provide a one-step method

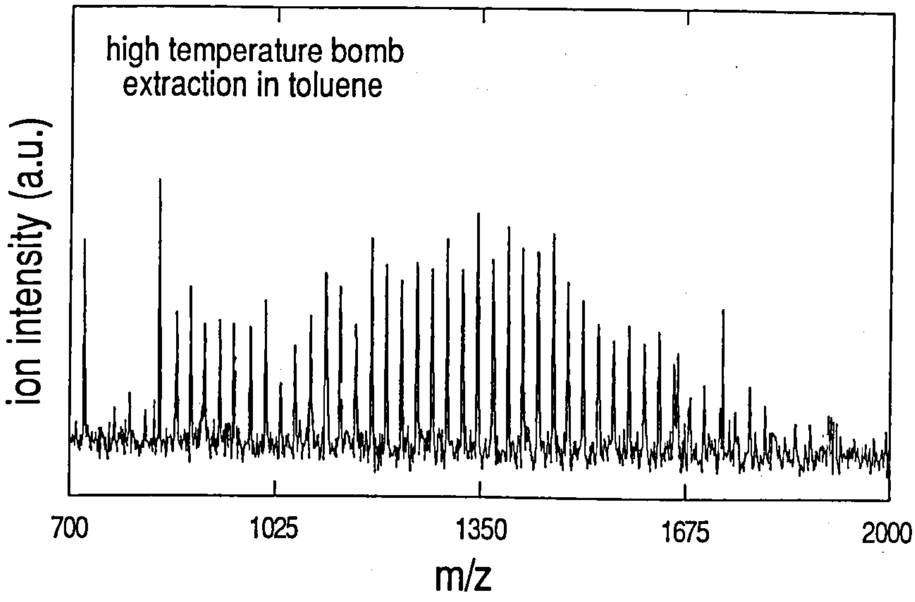


Fig. 14. Laser desorption FTMS spectra of high pressure/high temperature toluene extract prepared with soot previously extracted in toluene to deplete the soot of C_{60} and C_{70}. Noise spikes have been removed from the spectrum.

for C_{60} purification. A device to carry this out is commercially available and is known as a Kauffman chromatographic column (Ace Glass Co.). The Kauffman column is ideally suited to the purification of poorly soluble compounds[47]. In a typical experiment, aluminum oxide (200 g) was loaded in the inner column of the apparatus and raw soot (4.5 g) was added on top of the alumina. The alumina is held in place by a frit at the bottom of the inner column. Additional alumina was placed on top of the soot to immobilize it. 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 *n*-hexane (250 mL). 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 magenta C_{60} band is readily separated from the band containing C_{70}. Hexane and the purified C_{60} flow into the boiling flask and *n*-hexane is again vaporized while the purified C_{60} remains in the flask. A yield of 0.27 g (6%) of pure C_{60} was obtained by this procedure after 11 h of extraction.

The product was analyzed by laser desorption TOF mass spectrometry which showed only C_{60} with no other species detected at a signal-to-noise ratio of 100:1 (Fig. 15, panel a). Pure C_{70} cannot be obtained by this method since C_{60} is continually extracted from the soot and contaminates the C_{70} band as it moves down the column (Fig. 15, panels b and c). This one-step method for the purification of C_{60} provides several advantages. The refluxing solvent provides continuous solvent feed so that the process does not have to be monitored constantly. Much less solvent is needed compared to the previous methods: 300 mL compared to 2–3 L for C_{60}. The new method requires one-tenth the time required in earlier methods involving sequential Soxhlet extraction, chromatographic separation, and rotary evaporation. However, not all of the C_{60} is eluted from the column. Some C_{60} continues to elute with C_{70}, contaminating the C_{70} band, and at present, the C_{70} has not been isolated in pure form with this technique. Even so, we obtain yields of 6% pure C_{60}. Pure C_{70} can be obtained by extracting the alumina with toluene to recover the remaining C_{60} and C_{70}, and using the ordinary neutral alumina liquid chromatography method on the C_{70}-enriched fraction.

3. DISCUSSION

3.1 *Fullerene synthesis*

The use of fine control over the gap distance is a logical development in the synthesis of fullerene soot since virtually no carbon vaporizes when the electrodes touch[18] and yields are generally lower when there is little control over the gap distance, such as under gravity-feed conditions or spring-held positions. Combining the improved yield that results from fine control over the arc gap in the generation process with efficient Soxhlet extraction generates higher yields of soluble fullerenes than are generally reported. In contradistinction to our results, Smalley's group finds that the yield does not depend on the gap spacing[8]. Another important design feature is the convection rate that determines the rate of annealing (cooling) of the carbon once it leaves the plasma. This factor is known to be important for fullerene formation from results of the laser ablation jet expansion experiments of Smalley's group that show

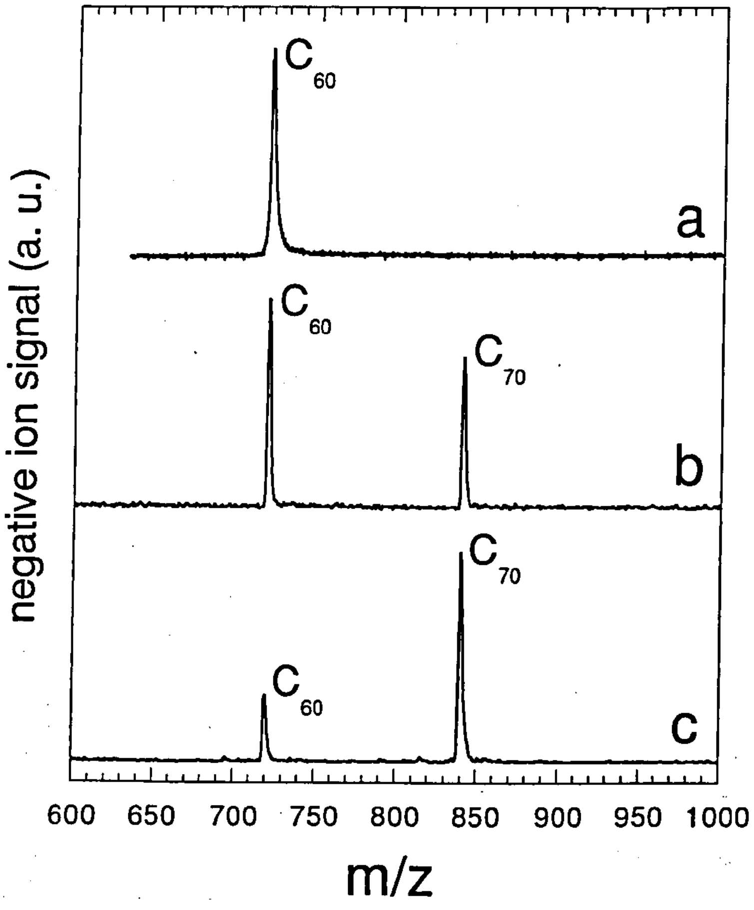


Fig. 15. Time-of-flight mass spectrum of the fullerene solutions obtained after Kauffman column chromatography. Panel a shows that pure C_{60} is obtained in the first fraction eluted from the column (5 h). Successive fractions shown in panels b (20 h) and c (additional 20 h after fraction b was removed) show the increasing enrichment of C_{70} in the solution.

dramatic differences in the carbon cluster formation depending on the nozzle conditions[2,44]. We find that, when the end shims are removed, the observed convection pattern in the chamber is markedly different and the yields of soluble materials are lower *by over a factor of two:* 8% Soxhlet extracted in toluene compared to 17% extracted in toluene with the shims in place. It is likely that careful design of a plasma arc apparatus that combines effective convection conditions with continuous graphite feed could result in a fullerene generator with even higher yields, and it may be possible to "tune" the conditions to produce fullerenes of a desired molecular weight. Even so, as the data in Table 1 indicate, fullerene generation in significant quantity can easily be performed in a wide variety of experimental setups, enabling any ordinary chemical laboratory to produce fullerenes.

3.2 *Giant fullerene extraction*

Our experiments[14] were the first to report the mass spectra showing the dissolution of giant fullerenes in high boiling point solvents, although Diederich and co-workers mentioned a similar experiment in trichlorobenzene in a note added in proof in their *Science* paper[25]. Since that time, other reports of similar results have appeared in the literature. Smart and co-workers report solvation of giant fullerenes in xylenes, 1,3,5-trimethylbenzene, 1,2,4-trichlorobenzene, and 1-methylnapthalene. They raise the question, "How much of the soot is fullerenes?" From our data using TMB, it appears that nearly half of the soot consists of fullerenes. Even more of the soot may have a molecular fullerene-type structure given the tremendous amount of soot—94%—that is soluble in NMP. The helium pycnometry experiments of Ruoff *et al.*[35] support this idea. The pycnometry experiment determines an upper bound to the density of the soot that is much lower than the density of graphite. This suggests the presence of large amounts of carbon cage molecules and very little graphite. Our NMP solvation experiment suggests this as well since graphite does not dissolve in NMP. We are presently working on experiments to determine the structure and identity of the NMP soluble portion. Shinohara *et al.* have also been successful in extracting very large fullerenes from arc-produced soot using quinoline (bp 238°C). They report that fullerenes up to C_{300} are extracted with quinoline from the benzene insoluble soot. Even though they employ the highest boiling liquid used so far for the extraction of fullerenes, they do not detect fullerenes higher than 3600 mass units in their fast atom bombardment mass spectrometer, nor do they report the sharply peaked mass distributions reported by us, Lamb *et al.*[36], and Smart *et al.*[37]. In these latter three studies, the mass distributions peak about 1600—2500 mass units and taper off at about 3500 mass units.

As mentioned in the Introduction, there has been some controversy over the existence of the giant fullerenes. For example, Hertel's group states, "We are able to show that the samples prepared by Krätschmer and collaborators contain almost pure C_{60} and C_{70} molecules and that higher laser fluences can easily lead to substantial fragmentation and reaggregation forming rather large carbon clusters." Part of this statement is certainly true: Higher laser fluences can cause fragmentation and reaggregation to form large carbon clusters. This is well known from the laser ablation experiments of Smalley and collaborators[2], and from the polymer ablation experiments of Creasy and Brenna[39] and other experiments in Hertel's group[41]. However, because they see no fullerenes higher than C_{84} at lower laser powers does not mean that they are not present. It could well be that it is a detection sensitivity problem.

Let us examine the evidence for the giant fullerenes in more detail. As laser power is increased, the fragmentation of C_{60} occurs by loss of C_2 units to form C_{58} and smaller fullerenes. Fragmentation of larger fullerenes will of necessity generate C_{60} since this is an extremely stable fragmentation product. Previous experiments from our research group on pure C_{70} have shown that increasing the intensity of the positionization laser results in the creation of fragment clusters[48]. These previous experiments showed that at the highest laser fluence, the C_{60} ion signal resulting from the fragmentation of C_{70} becomes larger than the C_{70} ion signal. In our experiment with the TCB extract, we depleted the sample of C_{60} and C_{70} by Soxhlet extraction in benzene. At low laser power, we see no C_{60} and only a trace of C_{70}. As the laser power is increased, the C_{60} peak appears, as well as the C_{58} fragmentation peak, indicating that significant fragmentation is occurring. If we were using high enough laser intensity to cause the formation of significant amounts of giant fullerenes, then we should also see significant amounts of the fragmentation products C_{60} and C_{58}. Since we do not see C_{60} in our TCB extract at lower laser fluences, this is very good evidence that the giant fullerenes are indeed produced in arc-generated soot and not in the analysis step. Additional evidence fo the existence of giant fullerenes comes from the recent work of Lamb *et al.*[36] in which giant fullerenes are extracted in a bomb at high temperature and pressure. The species extracted in this manner were imaged with STM, showing spherical fullerenes containing up to 330 carbon atoms. Taken together, the results of our work, the He pycnometry experiments, and the STM images provide convincing evidence for the existence of giant fullerenes.

4. CONCLUSIONS

We have reported a detailed procedure for the production of fullerenes and giant fullerenes in very high yield. Our experiments indicate the fine control of the arc gap combined with proper convection in the apparatus and careful Soxhlet extraction all contribute to our high yields of fullerenes. We report several different kinds of mass spectrometric evidence for the presence of giant fullerenes extracted in high boiling solvents. Our results also indicate that the majority of the soot has a molecular fullerene-type structure and dissolves in organic solvents. We have also developed a quick one-step method for the isolation of pure C_{60} that is a factor of ten faster and uses a factor of ten less solvent than previous methods.

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