

ARTICLES

Fullerene Molecular Weight Distributions in Graphite Soot Extractions Measured by Laser Desorption Fourier Transform Mass Spectrometry

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Received: July 30, 1992; In Final Form: October 9, 1992

Fullerenes were extracted from graphite soot produced by the Huffman–Krätschmer process by using a number of solvents, including refluxing in xylenes, 1,3,5-trimethylbenzene, 1,2,4-trichlorobenzene, α,α,α -trichlorotoluene, and 1-methylnaphthalene, and by using high-pressure, high-temperature *o*-xylene and supercritical carbon tetrachloride. The extract was dried and analyzed using laser desorption/Fourier transform mass spectrometry in order to measure fullerene molecular weight distributions. Positive and negative ion mass spectra were taken of all samples in order to compare the types of spectra. It is expected from mechanistic considerations and from past results that negative ion spectra should be less sensitive to growth or fragmentation of the fullerenes. The determination of the most reliable fullerene distributions requires a comparison of both positive and negative ion mass spectra, however. The highest mass distribution, with fullerenes to 2500 amu, was found for 1-methylnaphthalene extract, although there was evidence for dimers, trimers, and tetramers of the solvent in the extract. High-pressure *o*-xylene yielded fullerene distributions to 2000 amu. It was found that, for some solvents, residual solvent or solvent polymerization affected the reliable measurement of fullerene distributions by laser desorption. Extraction with supercritical carbon tetrachloride degraded the fullerenes or the soot into perchlorinated aromatic molecules.

Introduction

Following the discovery of the process for making bulk quantities of buckminsterfullerene from soot prepared by graphite evaporation by Krätschmer, Huffman, and co-workers,¹ there has been an interest in obtaining higher molecular weight fullerenes as well as buckminsterfullerene from the soot. A number of studies have succeeded in extracting larger fullerenes from the soot using a variety of solvents and conditions.^{2–8} Fullerenes up to C₉₄² and C₉₆⁵ have been isolated by liquid chromatography and identified by laser desorption mass spectrometry. In other studies, higher mass fullerenes have been identified in the extracted material using static SIMS,⁴ fast atom bombardment (FAB),⁶ scanning tunneling microscopy (STM),⁷ or laser desorption mass spectrometry (LDMS), using a number of different laser wavelengths.^{3,4,7,8} The variety of extraction

methods and of detection techniques confirms that higher mass fullerenes are present in graphite soot and can be extracted.

A considerable amount of work has been done to determine the optimal methods for extracting fullerenes and for determining the molecular weight distributions.^{2–8} One method of characterizing the extraction is by measuring the total weight of extractable fullerenes for a given solvent.^{2–4,8} Smart and co-workers⁴ found that a maximum of 37 wt % of virgin soot could be extracted using 1,2,4-trichlorobenzene. They found a correlation between the boiling point of the solvent and extracted weight with refluxing. This result implied that the solvation of the giant fullerenes in the soot was a thermally activated process, although some solvents deviated from the general trend. Parker and co-workers have reported producing soot which is 44% extractable in successive extractions with benzene, pyridine, and 1,2,3,5-tetramethylbenzene³ and 94% extractable using *N*-methyl-2-pyrrolidinone (NMP) as solvents.⁸

Another method of characterizing the fullerene extract is by measuring the molecular weight distribution of the fullerenes.

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However, determining the fullerene distribution in the extract, especially by LDMS, can be complicated by several effects. Since LDMS is a commonly used method for analyzing extracted fullerenes, it is worth considering some of the complications in order to determine an optimal experimental approach.

It is well-known that laser ablation of some types of non-fullerene-containing materials can produce fullerenes in the positive ion mass spectra.⁹⁻¹⁴ This has been explained by gas-phase growth processes during the laser ablation in which the fullerenes form from reactive fragments in the ablation plasma.¹³⁻¹⁵ It is also possible that fullerenes can be fragmented during the desorption process. These processes could affect the fullerene distributions that are observed from LDMS of soot extract.

Negative ion LDMS mass spectra have been used in some studies to detect fullerenes.^{3,5,16} However, no detailed studies of comparisons of positive to negative ion LDMS fullerene spectra have been reported which would indicate which type of spectra are preferable for large fullerenes.

An examination of the fullerene ion distributions from laser ablation of non-fullerene-containing materials can show the characteristics of the fullerene formation from the ablation process itself. From studies of ablation of graphite, polymers, and other materials, it has been found that positive ion fullerene distributions are observed much more often than the corresponding negative ion fullerene distributions.^{9,10,14,17-20} This is also the case for ²⁵²Cf plasma desorption mass spectrometry.²¹ Only a few exceptions have been observed of negative fullerene distributions from LDMS of non-fullerene materials. One example was reported by Brown and co-workers.¹¹ The distributions are observed from ablation of aromatic polymers with a pulsed CO₂ laser (10.6- μ m wavelength). The aromatic polymers that were studied were reaction products, and the exact components were not well characterized. Another case, reported by Lineman and co-workers,¹² showed a negative fullerene distribution from ablation of some polycyclic aromatic hydrocarbons with a 266-nm laser. In both cases, the spectra had poor signal-to-noise ratios. The positive and negative fullerene distributions were distinctly different from each other in their molecular weight distributions.

Other recent studies have also indicated that growth reactions occur for positively charged fullerenes but not for negative fullerenes. Yeretzyan and co-workers²² have shown that coalescence reactions can occur between laser-desorbed, positively charged fullerenes, but they are not observed for negatively charged fullerenes. Bunshah and co-workers²³ have produced fullerenes using electron beam evaporation of graphite. By using electrostatic deflection of the fullerenes which are produced, they collected positively charged products and neutral products but not negatively charged fullerenes. Thus, in this system, the fullerenes can grow as positive ions or neutrals but not as negative ions. They suggest that cationic intermediates may be important in fullerene growth reactions.²³

From mechanistic considerations, it is expected that negative ion mass spectra of fullerenes should be more immune from both fragmentation and growth processes than positive ion mass spectra. This is due to the competition between fragmentation and electron detachment which occurs for energetic negative ions. The extra electron on the negative fullerenes is easily detached by the excess energy that is required for fragmentation. The electron affinity (2.6-2.8 eV for C₆₀, but increasing for larger fullerenes²⁴) is less than the energy threshold for fragmentation (4.5 eV for C₆₀, although considerably more internal energy is required for fragmentation on microsecond time scales due to kinetic considerations²⁵). Thus, any negative cluster which is hot enough to fragment is also capable of losing the extra electron. Similar considerations affect the growth process, which is effectively the reverse reaction to fragmentation. The addition of small carbon

units (condensation) is a heating process which adds energy to the cluster,¹⁵ also tending to detach an electron.

Therefore, most of the hot negative ions, if they are formed, will detach the electron and neutralize, so they will not be observed in the negative ion spectrum. The remaining negative ions, which are observed, are the least energetic ions. The energetic positive ions are not neutralized by a corresponding process, and the ions will still be observed after fragmentation or growth processes have occurred. As a result of these processes, the negative ions which are observed in the mass spectrum should be more representative of the species which are desorbed intact and with little internal energy from the surface and which are subject to fewer gas-phase interactions. These ions should be closely related to the species which are present in the extract. The observed positive ions may or may not be directly related to surface species.

The formation of negative ions must still involve the attachment of an electron, unless anions are present on the surface. The electron attachment may involve collisional cooling, implying some gas-phase interactions take place. However, it has been observed that thermal electrons can attach to fullerenes even in low-pressure environments without collisional cooling.²⁶ The abundances of the fullerene anions relative to each other may be affected by electron capture cross sections, however, which would skew the observed distribution.²⁶ The process of electron attachment could also be affected by the presence of other species with high electron affinities in the laser ablation plasma. For example, large concentrations of chlorine or cyanide in the ablation plasma could scavenge the electrons, decreasing the probability for formation of fullerene negative ions. In this case, fullerenes would be desorbed but not observed as negative ions. Therefore, the observed distribution in the LDMS spectra could be affected by interfering impurities such as the presence of residual or polymerized solvent in the extract or by the laser desorption conditions, sample thickness, and substrate material.

Due to these considerations, it seems that the observation of both positive and negative ion fullerene distributions which are similar provides reasonable criteria for concluding that fullerenes are present in the extract and that the distribution is not affected by the laser conditions. The mechanisms for forming positive and negative ions should be sufficiently different that the same interferences will not affect both types of spectra. On the other hand, differences between the positive and negative spectra suggest that other processes could be occurring. The absence of a negative ion distribution could mean that positive ions are formed by growth processes from non-fullerene samples or that the negative fullerene ions are not formed due to competing effects.

In this study, several extracts, which were made by extracting the same batch of soot with different solvents, are compared using LDMS. Laser desorption/Fourier transform mass spectrometry, with both positive and negative ion spectra, is used to measure the fullerene distributions. Results for positive ion spectra of some of the extracts were presented previously,⁴ but comparisons to the negative ion spectra will be given. The positive and negative spectra will be compared to determine whether they can be used to assess a reliable fullerene distribution.

Experimental Section

Mass spectrometry was done using the Laser Microprobe Fourier transform mass spectrometer (FTMS) which has been described previously.²⁷ In brief, a 266-nm laser pulse (fourth harmonic from a Nd:YAG laser) is focused on a sample. Ions produced by the laser pulse are trapped and detected in the cell of an Extrel FTMS-2000 Fourier transform mass spectrometer²⁸ with a 4.8-cm cubic cell and a 3-T superconducting solenoid magnet. Positive or negative ion spectra were taken using a +2 or -2 V trapping potential on the cell plates, respectively. Typical detection conditions consisted of a bandwidth of 333 kHz and 16K data points for fullerenes, which generally gave the highest

resolution with good signal levels and without mass discrimination. Higher bandwidth and more data points were used for lower mass ions.

Laser power was adjusted to be the lowest level at which ion signal was observed, by adjusting a variable attenuator. Increasing the laser power by small amounts was not observed to make a significant difference in the fullerene distributions. Due to the complexity of the optical path, it has not been possible to accurately measure the laser power and focal spot size on the sample, which are necessary to measure the power density in the ablation.

We consider the optimal laser wavelength for fullerene analysis to be the 266-nm output of the Nd:YAG (or another ultraviolet wavelength). Due to the strong optical absorption of fullerenes in the ultraviolet, the 266-nm wavelength allows desorption and ionization with the lowest laser power, which should minimize fragmentation due to multiphoton absorption. The wavelength is also preferable since the laser radiation penetrates as little as possible into the sample. This tends to maximize the desorption from the surface of the sample and cause less thermal degradation to the sample. For longer laser wavelengths, more power is necessary to desorb and ionize material, which consequently leads to greater heating of the substrate prior to desorption. Thermal desorption has a similar problem, since the sample may thermally degrade before desorption occurs. Less penetration and lower power also minimize the amount of ablated material. With less ablated material, there is less likelihood for gas-phase growth of the fullerenes due to the lower density in the ablation plasma. For example, for ablation of graphite, fullerenes can form using 532- or 1064-nm radiation but have not been observed for 266-nm ablation.⁹ However, these qualitative arguments are based on general experience with laser desorption rather than detailed modeling of the process, which is very complex.

For all extractions, samples of the same lot of soot were used. The soot was obtained from Research Materials, Inc., who had previously extracted the soot with toluene to remove the readily soluble C₆₀ and C₇₀, which was about 10 wt %. (No details of this first extraction are available.) The techniques used for most of the solvent extractions have been reported previously.⁴ To summarize, extractions using mixed xylenes, 1,3,5-trimethylbenzene, 1,2,4-trichlorobenzene, α,α,α -trichlorotoluene, and 1-methylnaphthalene were done by refluxing the solvent and the soot for 24 h under dry nitrogen. The solution was then filtered twice with filter paper to remove insoluble material. Samples for LDMS analysis were made by drying extracted solutions on glass slides at ambient temperatures or by gently heating to <100 °C to remove the solvent.

An extraction was also done using high-temperature, high-pressure *o*-xylene, which was similar to one reported previously by Lamb and co-workers.⁷ Samples of 0.1 g of soot were placed in glass vials with 10 mL of reagent grade *o*-xylene and placed in a stainless steel chamber. The chamber was purged with nitrogen gas and sealed with OFHC copper gaskets. The chamber was placed in an oven at 300 °C, giving a calculated pressure of about 30 atm. After 24 h, the chamber was removed and cooled, and the solutions were filtered. About half of the solvent remained in the glass vials, since some of it recondensed on the bottom of the chamber. The solvent in the bottom of the chamber had a yellowish color, possibly from polymerization, and was discarded. Due to the small sample size, the percentage yield by weight was not determined.

Other extractions with high-temperature, high-pressure toluene, xylene, and carbon tetrachloride were done in an autoclave.²⁹ Only mass spectra from extractions using supercritical carbon tetrachloride will be presented here.

Results

First, LDMS mass spectra were taken of mixed C₆₀ and C₇₀ from a toluene extraction. Figure 1 shows both the positive and

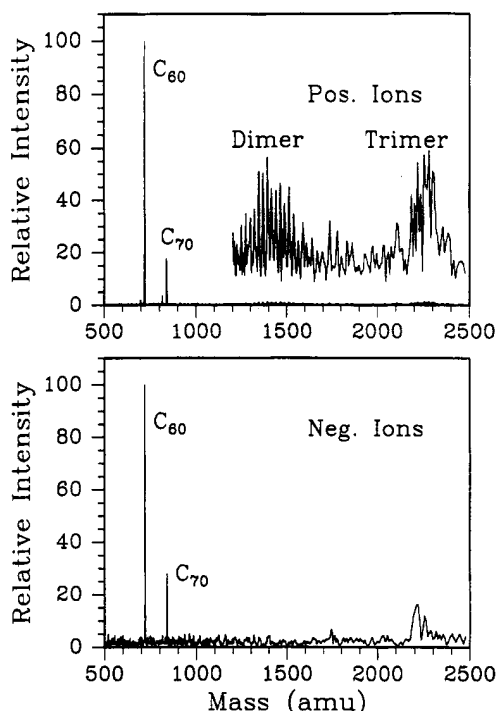


Figure 1. Positive and negative ion LDMS mass spectra (top and bottom panels, respectively) of C₆₀ and C₇₀ in toluene extract.

negative mass spectra. Neither spectrum shows a large amount of fragmentation of the C₆₀ or C₇₀, although weak fragment peaks for C₅₈ and C₆₈ are present in the positive ion spectrum. In fact, the amount of fragmentation is less than for a corresponding static SIMS spectrum.⁴ The positive spectrum also shows weak distributions of peaks roughly corresponding to the dimer and trimer masses of C₆₀, which were also observed in the SIMS spectrum.⁴ These groups are not observed in the negative ion spectrum. (The peak at 2200 amu in the negative spectrum is due to noise.) The dimer and trimer groups have been shown to form during the desorption and ionization of pure C₆₀ both for the SIMS spectra³⁰ and for laser desorption spectra,^{22,31} due to coalescence reactions of the desorbed fullerenes.

The negative ion spectrum has a significantly weaker signal than the positive ion spectrum, judging from the signal-to-noise ratio. Other studies have reported that negative ion spectra give signals that are as strong as the positive ion spectra.^{3,16} They have also reported that higher fullerenes can be detected in raw toluene extract with negative ion spectra.¹⁶ It is not clear at present why stronger signals or higher mass fullerenes are not observed in this case, although it may be a function of the laser wavelength, spot size, or substrate material, which could affect the production of electrons which are available for electron attachment. For the other extracts, there is also generally a weaker signal for negative ions.

For many of the extracts which were analyzed, the positive and negative ion mass spectra are in good agreement, which provides confirmation that higher mass fullerenes are present and can be extracted. Figure 2 shows the positive ion spectrum of extract in *o*-xylene at 300 °C. Fullerenes are observed up to about 2000 amu, corresponding to C₁₆₀. This distribution is somewhat lower than that reported by Lamb and co-workers.⁷

Figure 3 shows the negative ion mass spectra as a function of the number of laser pulses for the high-temperature *o*-xylene extraction. Comparison of Figures 2 and 3 shows that there is good agreement between the positive and negative ion large fullerene distributions. The spectra in Figure 3 also show an interesting fractionation effect for increasing numbers of laser pulses on a spot of the sample, which is very reproducible. For the first 20 laser pulses on a spot, large peaks for C₆₀, C₇₀, and

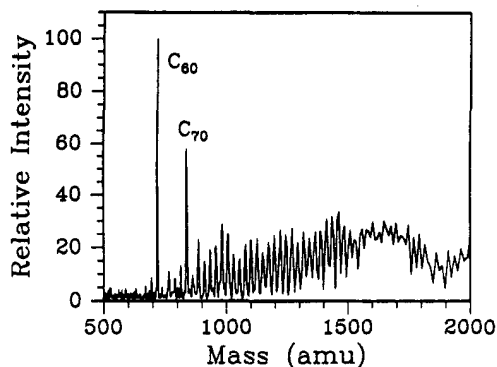


Figure 2. Positive ion LDMS mass spectrum of extract using 300 °C *o*-xylene in a closed vessel.

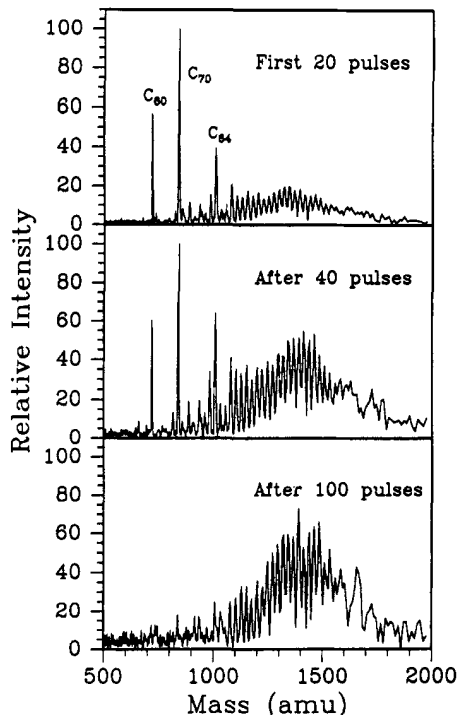


Figure 3. Negative ion LDMS mass spectra of extract using 300 °C *o*-xylene in a closed vessel: top panel, first 20 pulses on a spot of the sample; middle panel, 20 pulses after 40 pulses on the same spot; bottom panel, 20 pulses after 100 pulses on the same spot.

C_{84} are observed. During 100 laser pulses, these peaks gradually decrease so that only higher mass fullerenes are observed. This effect can be explained as preferential evaporation of more volatile, smaller fullerenes compared to the larger fullerenes. This provides additional evidence that the negative ion spectra are representative of species that are present on the surface. The positive ion spectra also show a fractionation effect, but it is not pronounced, and C_{60} can still be observed after 100 pulses.

Positive ion mass spectra taken with SIMS and LDMS were previously compared for solvent extractions using mixed xylenes, 1,3,5-trimethylbenzene, and 1,2,4-trichlorobenzene.⁴ The spectra agreed well for the extractions with xylenes and 1,3,5-trimethylbenzene. The positive and negative ion spectra taken with LDMS also agree well. The fullerene distributions for these solvents extend to about 1800 amu, with the extract from 1,3,5-trimethylbenzene having fullerenes with slightly higher relative intensity and higher mass range. The C_{60} peak is the largest peak in these spectra.

The extraction with 1-methylnaphthalene gives a high mass fullerene distribution. Figure 4 shows both the positive and negative ion LDMS spectra. Both fullerene distributions extend to about 2500 amu, in reasonable agreement with the positive ion

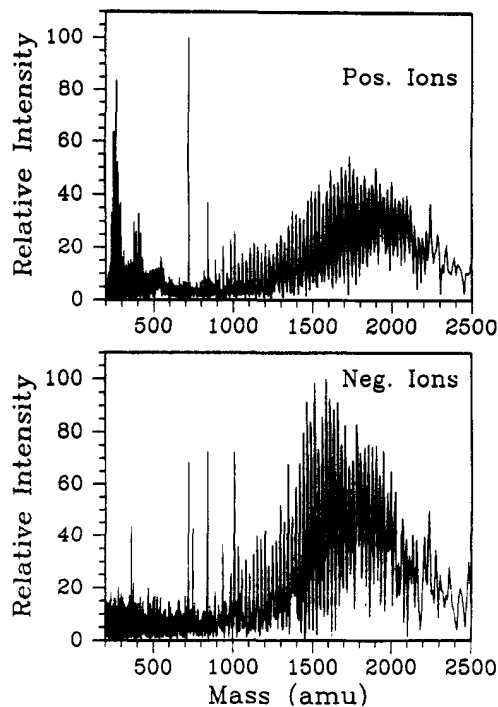


Figure 4. Positive (top panel) and negative (bottom panel) LDMS mass spectra of extract using 1-methylnaphthalene as a solvent. The low mass hydrocarbon peaks in the range 200–600 amu can be assigned to dimers, trimers, and tetramers of the 1-methylnaphthalene (MW 142 amu).

distribution published previously.⁴ The C_{60} peak is the largest peak in the positive ion spectrum, although it is smaller in intensity than the higher fullerenes in the negative ion spectrum. The observation of the highest mass distribution of fullerenes for this solvent is consistent with the fact that 1-methylnaphthalene has the highest boiling point (240 °C) of the solvents studied. The correlation of the solvent boiling point in refluxing with extraction efficiency has previously been noted.⁴

However, 1-methylnaphthalene is not an ideal solvent for this work. The high boiling point makes it difficult to remove the solvent from the extract by evaporation, which complicates the measurement of the weight of extract. In addition, the positive ion spectrum in Figure 4 shows that some low mass hydrocarbons are present. These hydrocarbons are close in mass to dimers, trimers, and tetramers of the solvent. Malhotra³² has suggested that these *n*-mers are formed by hydrogen atom transfer reactions which involve the fullerenes. Clearly, additional purification of the extract is required to obtain pure fullerene samples, for example by liquid chromatography.

The extraction with 1,2,4-trichlorobenzene is unusual in several ways. It was previously shown that for this extraction the SIMS and LDMS spectra did not agree well.⁴ The SIMS fullerene distribution extended to about 2200 amu, but the peak of the distribution was only between 900 and 1000 amu. The positive ion LDMS spectrum, shown in the top panel of Figure 5, is quite different, with a distribution up to about 3300 amu which peaks at 2500 amu. There is also a very low relative abundance of C_{60} , unlike all the other extractions. The distribution is very reproducible and does not vary significantly as a function of laser power (within a relatively small range), number of pulses, or sample thickness.

In the negative ion mass spectrum, no fullerene ions are observed. Only low mass hydrocarbon ion species in the range 30–250 amu are seen, shown in the bottom panel of Figure 5. Little chloride ion signal is observed in the spectrum. This suggests that there is a minimal amount of residual solvent in the sample, since it is likely that chloride anion would be formed from ionization of the solvent. It also suggests that chloride is not

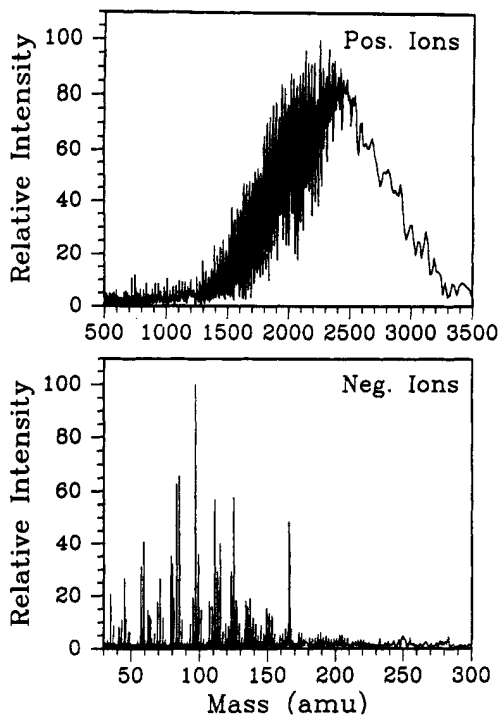


Figure 5. Positive (top panel) and negative (bottom panel) LDMS mass spectra of extract using 1,2,4-trichlorobenzene.

responsible for scavenging electrons in the desorption process, which could inhibit the formation of fullerene negative ions. This extraction will be discussed in more detail in the next section.

An extraction using α,α,α -trichlorotoluene demonstrates that residual solvent in the sample can affect the observed fullerene distribution. If a sample of extract is analyzed by LDMS soon after it is dried, a positive ion fullerene distribution is observed which extends to 3500 amu and includes a C_{60} peak. However, low mass positive ions are also observed, and the negative ion spectrum has a strong chloride signal and no fullerenes. If the sample is run again several months later, after it has thoroughly dried in air, the positive ion fullerene distribution extends only to 1800 amu, and the corresponding negative ion fullerene distribution appears which is very similar. For both spectra, the C_{60} peak is the most intense peak. The chloride signal is no longer present. This result implies that, immediately after drying, the extract has a considerable amount of solvent remaining in it, and the ablation of fullerenes and solvent forms a higher mass fullerene distribution. After thorough drying, a more representative fullerene distribution can be obtained in both the positive and negative ion spectra. Thus, residual solvent can affect the observed fullerene distribution.

It is worth analyzing the graphite arc soot using LDMS to see whether fullerenes can be detected directly, prior to extraction. Figure 6 shows the positive and negative LDMS spectra of soot which has been extracted with toluene. The positive ion mass spectrum shows a distribution of fullerenes. However, the negative distribution has no fullerenes but only low mass carbon clusters, C_n^- for $n = 6-13$. Similar positive and negative distributions have been observed for ablation of diamond-like carbon films, which do not contain fullerenes.^{10,18} Thus, the evidence that fullerenes are present in the soot is not conclusive from these spectra. Some fullerenes can be extracted by the solvents, so some quantity of them is present. However, LDMS is not an appropriate technique for determining the presence of extractable fullerenes prior to extraction.

Another extraction experiment showed that the solvent can react with the fullerenes or soot, if extreme conditions are used in the extraction. This effect was shown in a supercritical extraction using carbon tetrachloride.²⁹ This solvent was chosen

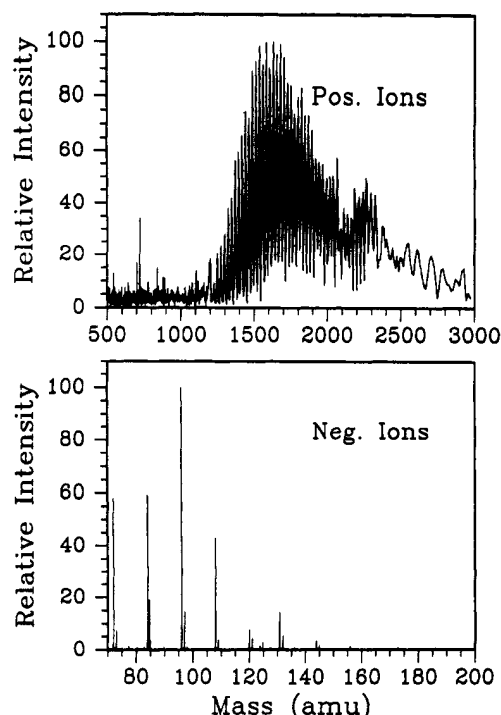


Figure 6. Positive (top panel) and negative (bottom panel) LDMS mass spectra from ablation of residual soot remaining after toluene extraction.

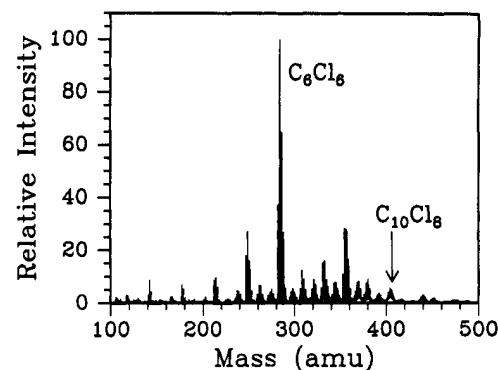


Figure 7. Positive ion electron impact mass spectrum of the volatile material from the extract using supercritical CCl_4 .

to avoid the possibility of solvent polymerization, which was observed for high temperatures with toluene and xylene.^{7,29} However, LDMS analysis of the extract with this solvent showed only a very weak positive ion fullerene spectrum even with very thick samples. However, some material in the extract was volatile, so a positive ion electron impact mass spectrum was obtained, which is shown in Figure 7. The spectrum shows that perchlorinated aromatic compounds are present, such as C_6Cl_6 , $C_{10}Cl_8$, and larger molecules. Due to the distribution of chlorine isotopes, the assignments can be made very confidently. The most likely source of these chlorinated aromatics seems to be from the reaction of fullerenes or soot with the CCl_4 under the high-temperature and high-pressure conditions of the extraction. This line of research was not pursued further, since it appeared to be an unpromising method of extraction. However, it indicates that extreme conditions can cause chemical reactions to occur which lead to undesirable byproducts, in addition to extraction. Further work may indicate the range of conditions under which these reactions can take place.

Discussion

These results indicate that extracts from graphite arc soot using several different solvents give LDMS mass spectra in which the

positive and negative ion fullerene distributions are similar. This information, in association with previous studies,²⁻⁸ gives good evidence that large fullerenes can be extracted from the soot. The results also show that under many conditions LDMS is a reasonable survey method for determining the relative abundance and molecular weight of fullerenes in the extract, as long as both positive and negative ion mass spectra are similar. If they are not similar, it is necessary to consider other effects that may change the molecular weight distributions.

Previous studies have indicated that about 40 wt % of soot can be extracted,^{3,4,8} with indications that up to 94 wt % can be extracted.⁸ This study agrees with previous evidence that solvents giving the highest weight of extracted fullerenes also tend to give the highest molecular weight distribution of fullerenes, implying that the extra weight is due to larger fullerenes along with some additional C₆₀. However, recent reports have indicated that only small amounts of fullerenes can be extracted from some soot samples.³² This result suggests that there may be considerable variation between the amounts of extractable large fullerenes in different soot samples, possibly depending on the arc conditions. Parker and co-workers⁸ suggest that the convection of vaporized material in the fullerene generator chamber is important in the formation of extractable material, due to the rate of cooling or annealing of the carbon vapor as it leaves the plasma. The rate of cooling has been shown to be important in the formation of C₆₀.³³ However, no systematic work has been done to optimize the total amount of extractable material (other than C₆₀) from the soot. LDMS will provide a useful method for comparing extracts of soots prepared under different conditions in order to accomplish this goal.

There are exceptions to the correlation of a larger weight of extracted material from soot, using different solvents, with a higher molecular weight distribution of fullerenes. The extraction with high-temperature, high-pressure solvents such as toluene has been reported to give only a few percent of extracted material, although the fullerenes are high in molecular weight.^{7,8} It is possible that this method is limited by the lack of agitation of the soot or of the flow of the solvent during the extraction or by the cooling of the solution in the presence of the soot prior to filtering. Further work may be necessary to optimize the procedure for this method, although autoclave extractions can minimize these problems.²⁹

The extraction with 1,2,4-trichlorobenzene has a number of exceptional features which are difficult to interpret at this point. Extraction with this solvent has been reported in three previous cases, and in all cases the LDMS positive ion mass spectra are in very good agreement with the spectrum in Figure 5.^{2,4,8} LDMS with two different laser wavelengths, 266 and 532 nm,⁸ gives similar mass spectra. These studies also agree that little C₆₀ is present in the extract. A FAB spectrum was also in agreement.² The SIMS results indicate a much lower molecular weight distribution,⁴ although it is possible that fragmentation is occurring in this case. Therefore, it seems likely that fullerenes are extracted by the solvent. However, it is also possible that the fullerene ion distribution observed by LDMS is not representative of the extracted material. The distribution of fullerenes in the positive ion spectrum is quite different from the other extracts in mass range and in the lack of smaller fullerenes. It is not clear why more C₆₀ is not detected in the extract by this particular solvent, since it is present in extracts by the other solvents. The negative ion spectrum in Figure 5 indicates that there is other material present, possibly polymer or impurity from the solvent. This contaminant may affect the desorption of the fullerenes and cause gas-phase growth to form larger fullerenes. The material is difficult to assign at present, although it does not seem to be chlorinated solvent. It is also possible that some unanticipated chemistry, such as reactions with the fullerenes, is occurring. Further analysis of this extract should be done, possibly by liquid chromatography, in order to confirm the mass spectrometry

results. In any case, extractions with this solvent are worth more study, since a large weight of extracted material has been found.⁴

More work is required to determine whether the fullerene distributions measured by LDMS are quantitative. As with all mass spectrometry of this type, it is not possible to determine quantitative abundances without known standard reference samples, which are not available for large fullerenes. Even though the fullerenes are similar in nature, it is possible that the ionization or electron attachment cross sections, as well as the volatility, are dependent on molecular weight. Such a dependence could skew the observed distribution. In electron attachment studies, the ratio of C₆₀ to C₇₀ is different for the positive and negative spectra.²⁶ A similar effect is observed here, for example between Figure 2 and Figure 3. McElvany and Callahan suggest that this effect is due to differences in the electron capture cross sections even for these similar species.²⁶ Similar differences in the ionization and electron attachment probability may occur across the distribution of higher fullerenes, although comparisons of the spectra indicate that the effects are less significant than the difference between C₆₀ and C₇₀. The sensitivity of the positive and negative ion spectra also needs further study, since it may be improved with different methods of sample preparation or different substrates.

In spite of the limitations of LDMS due to growth and fragmentation processes, there is no other method that is currently available that is significantly more reliable for measuring the molecular weight distributions of the extracted fullerenes. Static SIMS methods show significant fragmentation of C₆₀, as well as the formation of dimers and trimers from coalescence reactions in the gas phase.⁴ Thermal desorption methods are promising, since fullerenes up to C₁₂₄⁻ (1500 amu in mass) have been observed by thermal desorption/electron attachment mass spectroscopy.^{26,34} However, they may be limited for the largest fullerenes by low volatility and possible thermal decomposition. Chromatography methods will ultimately provide the best hope for quantitative analysis, but further work is necessary to optimize this technique for large fullerenes. Therefore, LDMS will be useful for analysis of relative fullerene molecular weight distributions and for optimizing the methods for preparing large fullerenes.

Conclusions

The negative ion LDMS spectra are generally reliable for determining the qualitative fullerene distribution, especially when compared to the positive ion spectra. In some cases, fullerenes may be present in the sample but are not observed in the negative ion spectra, possibly due to low formation probability of negative ions. A large amount of chlorinated solvent, in particular, can interfere with negative ion formation, due to preferential formation of chloride ions. The positive ion spectra, on the other hand, can be deceptive in that fullerenes can be formed in the gas phase which are not present on the surface, due to formation or growth during the ablation process. Positive ion spectra can also be affected by the presence of solvent or polymer in the sample.

From the comparisons of these extractions of soot, it is found that fullerenes up to 2500 amu can be extracted from the present lot of soot. Further work is necessary to determine the optimal conditions for forming soot with the greatest amount of extractable material. From the current results, the most promising methods for high mass fullerene extraction are using high-temperature toluene or xylene, if polymerization is avoided and if the yield can be optimized, or with methylnaphthalene, although the solvent is difficult to remove.

Most of the extracts in this study were confirmed to contain fullerenes. These results provide additional confirmation to the previous studies that high mass fullerenes can be obtained in quantity from graphite arc soot. However, caution must be used in interpreting LDMS mass spectra. The LDMS spectra of extract with 1,2,4-trichlorobenzene give equivocal evidence of

the fullerene distribution, and the extract may contain a contaminant or polymer which causes the fullerenes to grow during the ablation. The extraction with supercritical CCl_4 suggests that the fullerenes or the soot can be attacked, degraded, and chlorinated under the extreme extraction conditions.

Note Added in Proof. K. R. Lykke has repeated our measurement of both the positive and negative ion mass spectra of the solvent extract using 1,2,4-trichlorobenzene. He finds that the positive and negative ion spectra are similar and both resemble the fullerene spectrum in Figure 5.³⁵ His sample was dried at higher temperature than our sample, suggesting that our sample had residual solvent or contaminant that interfered with the negative ion spectrum. This result provides good evidence that the unusual fullerene spectra from this and previous studies correspond to the actual distribution of fullerenes in the extract. The solvent 1,2,4-trichlorobenzene is very promising for extraction of giant fullerenes.

A study by Wood and co-workers³⁶ has been submitted which compares positive and negative laser desorption and SIMS, using different experimental methods from those presented here. Their results are consistent with those reported here.

Acknowledgment. The authors thank C. Smart and N. Rivera, T. J. Watson Research Center, for solvent extractions, and T. Randolph, Yale University, for autoclave extractions. The authors thank R. Malhotra and D. Lorents for stimulating discussions.

References and Notes

- (1) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.
- (2) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, *252*, 548.
- (3) Parker, D. H.; Wurz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 7499.
- (4) Smart, C.; Eldridge, B.; Reuter, W.; Zimmerman, J. A.; Creasy, W. R.; Rivera, N.; Ruoff, R. S. *Chem. Phys. Lett.* **1992**, *188*, 171.
- (5) Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Honda, M.; Matsumiya, H.; Moriwaki, T.; Suzuki, S.; Shiromaru, H.; Saito, K.; Yamauchi, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1992**, *188*, 177.
- (6) Shinohara, H.; Sato, H.; Saito, Y.; Takayama, M.; Izuoka, A.; Sugawara, T. *J. Phys. Chem.* **1991**, *95*, 8449.

- (7) Lamb, L. D.; Huffman, D. R.; Workman, R. K.; Howells, S.; Chen, T.; Sarid, D.; Ziolo, R. F. *Science* **1992**, *255*, 1413.
- (8) Parker, D. H.; Chatterjee, K.; Wurz, P.; Lykke, K. R.; Pellin, M. J.; Stock, L. M.; Hemminger, J. C. *Carbon*, submitted for publication.
- (9) Creasy, W. R.; Brenna, J. T. *Chem. Phys.* **1988**, *126*, 453.
- (10) Creasy, W. R.; Brenna, J. T. *J. Chem. Phys.* **1990**, *92*, 2269.
- (11) Brown, C. E.; Kovacic, P.; Wilkie, C. A.; Cody, R. B.; Hein, R. E.; Kinsinger, J. A. *Synth. Met.* **1986**, *15*, 265.
- (12) Lineman, D. N.; Somayajula, K. V.; Sharkey, A. G.; Hercules, D. M. *J. Phys. Chem.* **1989**, *93*, 5025.
- (13) O'Keefe, A.; Ross, M. M.; Baronavski, A. P. *Chem. Phys. Lett.* **1986**, *130*, 17.
- (14) McElvany, S. W.; Nelson, H. H.; Baronavski, A. P.; Watson, C. H.; Eyley, J. R. *Chem. Phys. Lett.* **1987**, *134*, 214.
- (15) Creasy, W. R. *J. Chem. Phys.* **1990**, *92*, 7223.
- (16) Lykke, K. R.; Pellin, M. J.; Wurz, P.; Gruen, D. M.; Hunt, J. E.; Wasielewski, M. R. *Mater. Res. Soc. Symp. Proc.* **1991**, *206*, 679.
- (17) Creasy, W. R.; Brenna, J. T. In *Polyimides: Materials, Chemistry, and Characterization*; Feger, C., Khojasteh, M. M., McGrath, J. E., Eds.; Elsevier: Amsterdam, 1989; p 635.
- (18) Siperko, L. M.; Brenna, J. T.; Creasy, W. R. *J. Vac. Sci. Technol. A* **1990**, *A8*, 1533.
- (19) Greenwood, P. F.; Strachan, M. G.; El-Nakat, H. J.; Willett, G. D.; Wilson, M. A.; Attalla, M. I. *Fuel* **1990**, *69*, 257.
- (20) Rubin, Y.; Kahr, M.; Knobler, C. B.; Diederich, F.; Wilkins, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 495.
- (21) Feld, H.; Zurmühlen, R.; Leute, A.; Benninghoven, A. *J. Phys. Chem.* **1990**, *94*, 4595.
- (22) Yerezian, C.; Hansen, K.; Diederich, F.; Whetten, R. L. *Nature* **1992**, *359*, 44.
- (23) Bunshah, R. F.; Jou, S.; Prakash, S.; Doerr, H. J.; Isaacs, L.; Wehrsig, A.; Yerezian, C.; Cynn, H.; Diederich, F. *J. Phys. Chem.* **1992**, *96*, 6866.
- (24) Yang, S. H.; Pettiette, C. L.; Conceicao, J.; Cheshnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1987**, *139*, 233.
- (25) Radi, P. P.; Hsu, M.-T.; Rincon, M. E.; Kemper, P. R.; Bowers, M. T. *Chem. Phys. Lett.* **1990**, *174*, 223.
- (26) McElvany, S. W.; Callahan, J. H. *J. Phys. Chem.* **1991**, *95*, 6186.
- (27) Brenna, J. T.; Creasy, W. R.; McBain, W.; Soria, C. *Rev. Sci. Instrum.* **1988**, *59*, 873.
- (28) Millipore-Extrel, Madison, WI.
- (29) Randolph, T.; Ruoff, R. S. Unpublished results.
- (30) Eldridge, B.; Ruoff, R. S. Unpublished results.
- (31) McElvany, S. W.; Ross, M. M. *J. Am. Soc. Mass. Spectrom.* **1992**, *3*, 268.
- (32) Malhotra, R. Presented at the Electrochemical Society Meeting, St. Louis, MO, May 18-22, 1992.
- (33) Smalley, R. E. *Acc. Chem. Res.* **1992**, *25*, 98.
- (34) Ben-Amotz, D.; Cooks, R. G.; Dejarne, L.; Gunderson, J. C.; Hoke, S. H., II; Kahr, B.; Payne, G. L.; Wood, J. M. *Chem. Phys. Lett.* **1991**, *183*, 149.
- (35) Lykke, K. R. Private communication.
- (36) Wood, T. D.; Van Cleef, G. W.; Mearini, M. A.; Coe, J. V.; Marshall, A. G.; Zimmerman, P. A.; Hercules, D. M. *J. Phys. Chem.*, submitted.