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Extraction and Purification of Fullerenes: A Comprehensive Review

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REVIEW

Extraction and Purification of Fullerenes: A Comprehensive Review

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ABSTRACT

This review summarizes the advances of the last four years in the field of fullerenes purification. Purification involves extraction from soots, which may be considered as a prepurification step, and separation by liquid chromatography, where the different stationary phases tested are listed. We also describe other purification techniques, like elution on molecular sieves or activated charcoal, gel permeation, and supercritical fluids purification. Our purpose is to show the reader the general trends for obtaining pure C_{60} and C_{70}. We conclude that no technique is better than another, but that each purification method may offer its own qualities, depending on the application.

INTRODUCTION

The chemistry of fullerenes began in 1966 when David "Daedalus" Jones published the possibility of creating some kinds of graphite balloons similar to geodesic cages built from carbon atoms shaped in 12 pentagons and an unlimited number of hexagons. In 1970 and 1971, Osawa demonstrated that such molecules would be stable. The Hückel calculation of the C_{60} molecule was published in 1973 by Bochvar. In 1980 Davidson

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applied the general group theoretical technique to a range of fullerene-like molecules.

The first practical artificial fullerene synthesis was carried out in 1985 in Smalley's laboratory at Rice University (1) by vaporizing a graphite pellet with a laser beam. The detection by mass spectrometry of the species created in the plasma revealed a dominant peak that could correspond to a carbon cluster containing 60 carbon atoms. Smalley and Kroto formulated the hypothesis of a soccerball shape for this very stable molecule that was named "fullerene" in reference to Buckminster Fuller who developed a new architectural style drawn from these original geodesic forms.

In the following years no concrete evidence of the C_{60} structure was put forth, and work on fullerene molecules consisted essentially of formation schemes, endohedral adducts detection, and reactivity studies. Beyond these theoretical considerations, the possibility of the formation of fullerenes as by-products of soot formation was proposed.

The second major step in the study of fullerenes was the production in macroscopic amounts of these molecules in an electric arc plasma. In 1990 Krätschmer used this technique to produce some soots containing molecules (2) whose infrared (IR) analysis led to the detection of the characteristic absorption signal of C_{60} that had previously been determined by calculation, thus confirming the hollow cage structure prediction for C_{60} and the other fullerenes. Finally, a significant amount of a red-brown benzene solution containing principally C_{60} and C_{70} was extracted. X-ray analysis of the corresponding crystals showed the presence of arrays of spherical molecules, some with a diameter around 7 Å.

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The first separation of C_{60} and C_{70} was carried out by Taylor at the University of Sussex (3), which offered the possibility of obtaining the ^{13}C nuclear magnetic resonance (NMR) spectra of the purified species. The NMR analysis indubitably assigned the spherical shape to C_{60} by giving a singlet, meaning that all the carbon atoms were equivalent. The NMR analysis of C_{70}, which was also chromatographically separated, gave five peaks assigned to the five parallel planes in which the 70 carbon atoms are set.

The discovery of the macroscopic production method by electric arc discharge and the possibility to separate fullerenes led to intense research in this new field of carbon chemistry. Numerous laboratories throughout the world started to work on the subject, leading some people to compare fullerenes research to an epidemic (4)! The results were better knowledge of the various potentials of C_{60} and other fullerenes. The discovery of the very particular properties of C_{60} (geometry, physics, chemistry, electronics, superconductivity) led to hazardous speculation on the possible applications of C_{60} and higher fullerenes in many areas, among which were electrochemistry (batteries), chemistry (as reagents, catalysis supports, polymers), biology, and supraconductivity. Many applications and production methods have already been patented. Even the molecules themselves were the subject of patents, which led to the curious situation of people trying to patent molecules that exist in nature.

The possibility of industrial applications of C_{60} has redirected the research on fullerenes that was initially essentially fundamental to research on large-scale production methods and large-scale separation methods in order to obtain pure fullerenes. In 1987 German researchers invented a hydrocarbon flame combustion process (5) that offered the possibility of continuous production of fullerenes.

However, among different production methods, each has its own specificity, with its advantages and drawbacks:

- The combustion process is continuous, but polycyclic aromatic hydrocarbons (PAH) are cosynthetized in significant concentration,
- The electric arc process leads to good quality soots, but is not continuous.
- The laser ablation process is very expensive but would allow the production of doped fullerenes, starting from doped graphites or mesophases.

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We have attempted to develop a comprehensive review of the methods of extraction and separation of the fullerenes (mainly C_{60} and C_{70}) through the numerous techniques proposed in the literature. This paper highlights the progress that has occurred since the beginning of solvated fullerenes in 1990 and the problems of solvatation and affinity toward the classical chromatography stationary phases that make these molecules so hard to obtain as pure materials.

Whatever the synthesis method of fullerene crude mixtures, obtaining high purity products poses numerous problems:

- The presence of impurities, either other fullerenes (at low or very low percentages), residual solvents, molecules created during synthesis [i.e., polycyclic aromatic compounds (PAC)], or pollutants (such as greases from the vacuum group or particles desorbed from the synthesis cell surface).
- The formation of solvates that result from the strong interaction and affinity between fullerenes and the solvent molecules commonly used for the extraction and separation steps. These solvates have been identified as crystals by x-rays analysis.
- The formation of fullerene adducts, particularly with oxygen, but also with all kinds of metals or other species.

- The origin of the soots (starting carbon, production method). This influences the purification steps of fullerenes (extraction yields, nature of the fullerenes extracted).

In this paper we discuss the following topics:

1. Solubility of fullerenes
2. Extraction of fullerenes
3. Purification of fullerenes by chromatographic methods
4. Other purification methods

SOLUBILITY OF FULLERENES IN SOLVENTS

C_{60} solubilization is widely described in the literature. Other fullerenes are not taken into account due to the high cost of C_{70} and the unavailability of pure higher fullerenes. Experimental observations show that the higher the number of carbons in a fullerene, the lower is its solubility, whatever the solvent. Good knowledge of the solubility of fullerenes is nevertheless very important for optimal extraction, purification, and potential for use in organic chemistry.

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Solubility of C_{60} in Organic Solvents

The fullerenes have a rigid structure. Consequently, their solubility should be approached carefully. The following classical solvent parameters were taken into account for the prediction of fullerene solubility in any solvent (6):

Molecular surface area
Molecular volume
Polarizability
Polarity
Cohesive energy density

Experimental C_{60} solubilizations in many solvents have been carried out. In 1992 Mathews proposed a table of solubilities of C_{60} with 15 solvents (7). It showed toluene, benzene, and carbon disulfide to be good C_{60} solvents (3, 2, and 8 $g \cdot L^{-1}$, respectively).

Some authors tried to explain C_{60} solvation phenomena by taking into account other solvent parameters. In 1993 Ruoff and Malhotra led an extended experimental and theoretical study (8) (Table 1). They tried to find a C_{60} solubilization prediction method by calculating such solvent parameters as the index of refraction $[(n^2 - 1)/(n^2 + 2)]$, the dc dielectric constant $[(\epsilon - 1)/(\epsilon_{.} + 2)]$, the Hildebrand solubility parameter δ, and

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TABLE 1
Solubility of C_{60} in Various Solvents[a]

Solvent	$[C_{60}]$, mg/mL	Mole fraction ($\times 10^4$)	n	ϵ	v, $cm^3 \cdot mol^{-1}$	δ, $cal^{1/2} \cdot cm^{-3/2}$
Alkanes:						
n-Pentane	0.005	0.008	1.36	1.84	115	7.0
Cyclopentane	0.002	0.003	1.41	1.97	93	8.6
n-Hexane	0.043	0.073	1.38	1.89	131	7.3
Cyclohexane	0.036	0.059	1.43	2.02	108	8.2
n-Decane	0.071	0.19	1.41	1.99	195	8.0
Decalins:	4.6	9.8	1.48	2.20	154	8.8
cis-Decalin	2.2	4.6	1.48	—	154	8.8
trans-Decalin	1.3	2.9	1.47	—	158	8.6
Haloalkanes:						
Dichloromethane	0.26	0.27	1.42	9.08	60	9.7
Chloroform	0.16	0.22	1.45	4.81	86	9.3
Carbon tetrachloride	0.32	0.40	1.46	2.24	80	8.6
1,2-Dibromethane	0.50	0.60	1.54	4.79	72	10.4
Trichloroethylene	1.4	1.7	1.48	3.40	89	9.2
Tetrachloroethylene	1.2	1.7	1.51	2.46	102	9.3
Freon TF (dichlorodifluoroethane)	0.020	0.042	1.36	—	188	—
1,1,2-Trichlorotrifluoroethane	0.014	0.017	1.44	—	118	—
1,1,2,2-Tetrachloroethane	5.3	7.7	1.49	8.20	64	9.7
Polars:						
Methanol	0.000	0.000	1.33	33.62	41	14.5
Ethanol	0.001	0.001	1.36	24.30	59	12.7
Nitromethane	0.000	0.000	1.38	35.90	81	12.7
Nitroethane	0.002	0.002	1.39	28.00	105	11.1
Acetone	0.001	0.001	1.36	20.70	90	9.8
Acetonitrile	0.000	0.000	1.34	37.50	52	11.8
N-Methyl-2-pyrrolidone	0.89	1.2	1.47	—	96	11.3
Benzenes:						
Benzene	1.7	2.1	1.50	2.28	89	9.2
Toluene	2.8	4.0	1.50	2.44	106	8.9
Xylenes	5.2	8.9	1.50	2.40	123	8.8
Mesitylene	1.5	3.1	1.50	2.28	139	8.8
Tetralin	16	31	1.54	2.76	136	9.0
o-Cresol	0.014	0.029	1.54	11.50	103	10.7
Benzonitrile	0.41	0.71	1.53	25.60	97	8.4
Fluorobenzene	0.59	0.78	1.47	5.42	94	9.0
Nitrobenzene	0.80	1.1	1.56	35.74	103	10.0
Bromobenzene	3.3	4.8	1.56	5.40	105	9.5
Anisole	5.6	8.4	1.52	4.33	109	9.5
Chlorobenzene	7.0	9.9	1.52	5.71	102	9.2
1,2-Dichlorobenzene	27	53	1.55	9.93	113	10.0
1,2,4-Trichlorobenzene	8.5	15	1.57	3.95	125	9.3
Naphthalenes:						
1-Methylnaphthalene	33	68	1.62	2.92	142	9.9
Dimethylnaphthalenes	36	78	1.61	2.90	156	9.9
1-Phenylnaphthalene	50	131	1.67	2.50	155	10.0
1-Chloronaphthalene	51	97	1.63	5.00	136	9.8
Miscellaneous:						
Carbon disulfide	7.9	6.6	1.63	2.64	54	10.0
Tetrahydrofuran	0.000	0.000	1.41	7.60	81	9.1
Tetrahydrothiophene	0.030	0.036	1.50	2.28	88	9.5
2-Methylthiophene	6.8	9.1	1.52	2.26	96	9.6
Pyridine	0.89	0.99	1.51	12.30	80	10.7

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the molar volume v of a solvent. These parameters describe the solvent polarizability, the solvent polarity, the cohesive energy density, and the molecular size, respectively. The closer are solvent parameters values match those of C_{60}, the higher the C_{60} solubility would be. C_{60} solubilization was tested in 47 different solvents, and the experimental results were compared with theoretical predictions. No real correlation was found. The authors concluded that the solvent parameters n, ϵ, v and δ are closed to C_{60}'s in the case of relatively strong solvents. Each parameter gives information concerning C_{60} solubility, but no one can be considered as an "universal parameter." That illustrates the very particular physical and chemical behaviors of fullerenes.

The measured solubilities confirm that C_{60} is poorly soluble in polar and H-bonding solvents, and has low solubility in alkanes (the higher the number of carbons, the better the solubility), even though decaline solubilizes C_{60}. C_{60} is more soluble in halogenated derivatives than in analog alkanes. Aromatics are in general good solvents; increasing the number of rings increases the solubility. The very best solvent found to date is 1-chloronaphthalene (51 $g \cdot L^{-1}$ at room temperature).

Temperature Dependence

Although solubility in common organic solvents increases with temperature, Ruoff showed that C_{60} solubility versus temperature has a break at around 280 K (9). That feature was observed in hexane, toluene, and CS_2. Ruoff proposed phase changes in solid C_{60}. The difference between the crystalline phase transition sc-fcc determined at around 260 K and the observed transition temperature recorded for C_{60} solutions may be attributed to solvent effects which could modify the solid phase crystallinity (Fig. 1).

Considering H_A, H_B, and H_S respectively as the "low temperature phase," the "high temperature phase," and the solution enthalpies ($H_A < H_S < H_B$), the transition slope depends on the solvent. Plots can be modeled by the following equations:

$$k(T) = \exp\left(\frac{\Delta S_{AS}}{R} - \frac{\Delta H_{AS}}{RT}\right) \quad \text{for } T \leq 280 \text{ K}$$

$$= \exp\left(\frac{\Delta S_{BS}}{R} - \frac{\Delta H_{BS}}{RT}\right) \quad \text{for } T \geq 280 \text{ K}$$

The fit to experimental results gives:

$$T_P = 280 \pm 10\text{K}$$

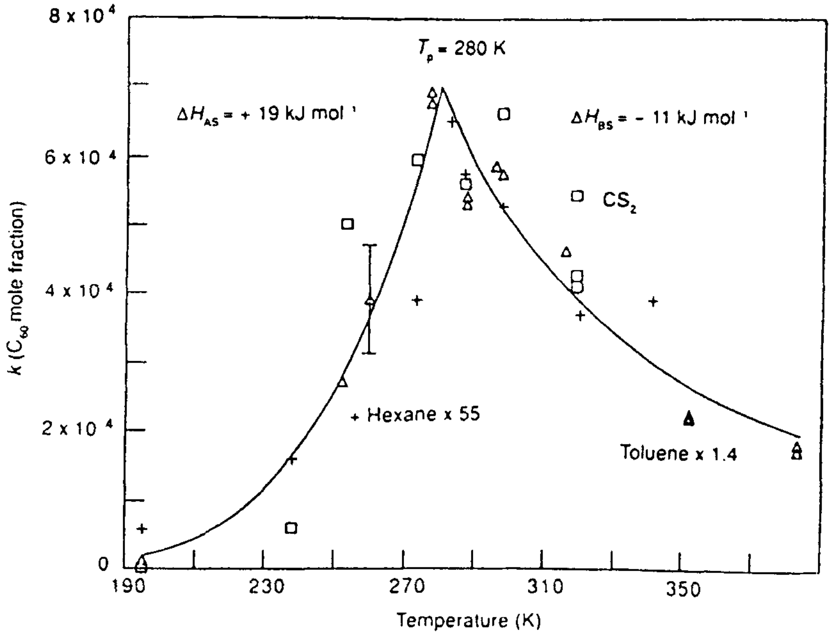

FIG. 1 Temperature-dependant solubility of C_{60} in hexane (+, ×55), toluene (Δ, ×1.4), and CS_2 (□). Reprinted from Ruoff et al. (9) with kind permission from *Nature*, copyright 1993, Macmillan Magazines Ltd.

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$$\Delta H_{AS} = 19 \pm 3\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_{BS} = -11 \pm 2\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_{AB} = 30 \pm 3\ \text{kJ}\cdot\text{mol}^{-1}$$

Conclusions

According to some authors, solid C_{60} solubility dependence versus temperature reveals the presence of two crystalline forms for the solute, leading to endothermic dissolution below 280 K and exothermic dissolution above it. This change at 280 K can be explained by a phase transition in solid C_{60} that could be close to the phase change observed in the absence of a solvent (10–12).

An evaluation of C_{60} solubility in various solvents was attempted with the use of solubility parameters. A C_{60} solubility evaluation based on calculations does not lead to reliable results. Theoretical predictions give rough trends, but they cannot be used for an accurate evaluation. No multicomponent study has been carried out, but a reliable theoretical method could be found in this way.

FULLERENES EXTRACTION

The relative proportions of fullerenes in a synthesis mixture of soots depend mainly on the production method. The synthesis conditions of electric arc discharge (ac or dc current), the combustion of aromatics, the laser ablation, and the high frequency inductive heating method lead to various fullerene weight distributions. Electric arc discharge and laser ablation favor the single products C_{60} and C_{70} with a very low concentration of other impurities, whereas combustion gives a statistical distribution (with C_{60} and C_{70} dominating) but also with a large proportion of polycyclic aromatic compounds and fullerene adducts.

On the other hand, the extraction step can be considered to be a prepurification step because the choice of the extracting solvent may be quite selective toward the extracted fullerenes. The reader must be aware that starting soots are a complex material, and the straightforward extraction by any solvent will not reveal the real distribution of fullerenes.

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Fast Characterization of Fullerenes Containing Soots Extracts

The material extracted from soots contains polycyclic aromatic compounds (PACs), fullerenes, and adducts. In order to evaluate and optimize the efficiency of the extraction method, a rapid characterization technique has to be employed. The most useful technique for the detection of the fullerenes in the extracted materials is mass spectrometry. The first fullerenes extracted from soots were analyzed by direct mass spectrometry (13). Classical fast atom bombardment mass spectrometry (FAB MS) and electron impact mass spectrometry (EI MS) are also used (14, 15), but laser desorption followed by postionization of neutral species is the most convenient method for fullerene detection in crude extracts. This last technique led to the discovery of fullerenes (1) and was used further for the routine characterization of fullerene-containing samples. Using laser desorption mass spectrometry (LD-MS) for both the formation and detection of the fullerenes may sound curious, considering that the same process is at the origin of the synthesis of fullerenes, even though the range of energetic conditions is dramatically different. It was also demonstrated by an isotope-scrambling experiment that the fullerenes detected by LD-MS exist in the original sample (16), but it was also shown that fullerenes may be formed during analysis, except if the analysis is carried out with carefully controlled conditions of laser desorption; that is, with very low laser fluences (17) (Fig. 2).

Extraction Method

The classical methods for extracting fullerenes from soots are stirring or rinsing the crude material at ambiant temperature or by hot solvent extraction under reflux or by Soxhlet extraction (18–25).

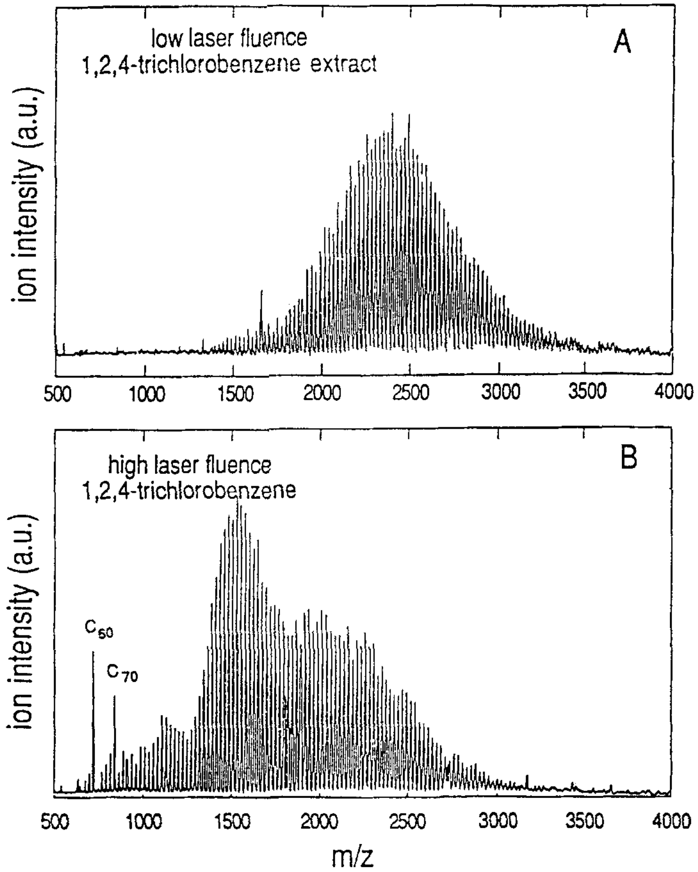

FIG. 2 Laser desorption FTMS spectra of 1,2,4-trichlorobenzene extract prepared by Soxhlet extraction of soot previously extracted in toluene to deplete the soot of C_{60} and C_{70}. Panel A depicts data collected with low laser fluence showing no C_{60} peak. Panel B shows data collected with high laser fluence, resulting in considerable fragmentation. Noise spikes have been removed from the spectrum. Reprinted from Parker et al. (25), copyright 1992, with kind permission from Elsevier Science Ltd.

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Because maximal C_{60} solubility is close to the ambient temperature (9), some extraction procedures deserve particular attention: extraction under reflux or by Soxhlet extraction, which nevertheless should involve cooling the main part of the extractor with a high yield cooling fluid exchanger in order to maintain the maximum solubility temperature range. Circulating solvent methods (Soxhlet or Kumagawa) are acceptable extraction methods.

Temperature plays a role in both solubility and extraction kinetics. Temperature and solubility should not be linked because most extraction methods do not work at saturation (Soxhlet, Kumagawa). In these cases, some physical chemical phenomena, such as diffusion into the soot and adsorption in pores, play a role.

A comparison of extracting solvents can be found in the literature, but no real evaluation of any technique has been done. The choice of extracting technique is guided by the application dedicated to the extracted species, e.g., extraction with hexane is chosen for the production of C_{60} and C_{70} because no higher fullerenes are extracted, thus simplifying separation. However, for the study of "rare" fullerenes, extraction with high boiling point solvents is preferable because it allows recovery of all the soluble species, "rare" included.

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Selective Extraction Methods

Many trials of extraction of depleted soots (residual soots from which C_{60} and C_{70} were previously extracted, commonly by toluene or by benzene) were performed with various solvents. The rough trend is: the higher boiling point solvent, the higher molecular weight fullerenes extracted.

The alkane series solvents were studied by Mathews on soots obtained by vaporization of graphite (19) and by Parker on soots obtained by vaporization of coal rods (25) from *n*-pentane to *n*-tetradecane. Unlike other solutes that become less and less insoluble with an increase in the alkane number of carbons, C_{60} solubility increases with long carbon chain solvents. This could be interpreted as a better accommodation of the fullerenes spheres between the chains, with fewer discontinuities of the intermolecular interactions between the solvent molecules and the fullerenes (Fig. 3).

Electric arc soots extracted with *n*-pentane, *n*-hexane, and *n*-heptane reveal no real presence of higher fullerenes. Small amounts of C_{78} and C_{84} can sometimes be detected when pentane and heptane are used, but hexane leads to quasi-pure $C_{60} + C_{70}$ mixtures. This observation conflicts with the general trend of fullerene solubility in alkanes, as mentioned above.

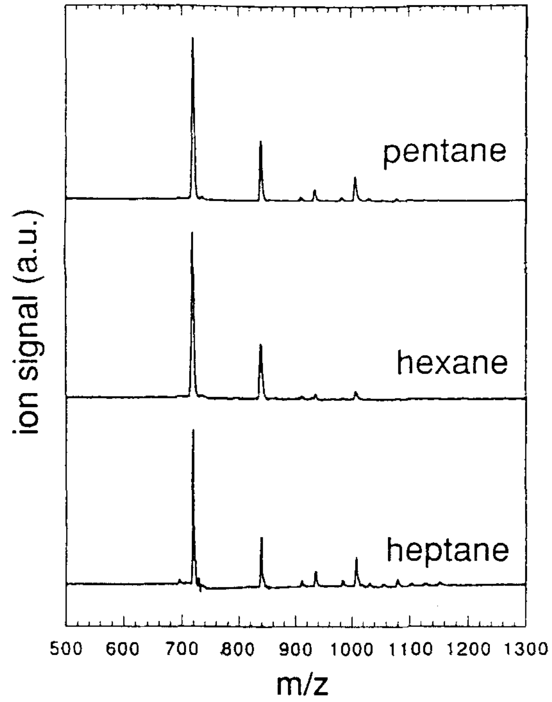

FIG. 3 Laser desorption TOF mass spectrum of pentane, hexane, and heptane extracts of raw soots. Reprinted from Parker et al. (25), copyright 1992, with kind permission from Elsevier Science Ltd.

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The aromatic solvents series was also tested with toluene, benzene, xylenes, 1,3,5-trimethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4-trichlorobenzene, and methyl-naphthalene. The role of the boiling point and the molecular weight of the solvent was also demonstrated (Fig. 4).

Soots may be extracted up to 30–40% of their original weight with some solvents (21, 22, 24, 25). Extraction higher than 90% with *N*-methyl pyrrolidinone (NMP) has been mentioned (25). It is reasonable to expect fullerenes to be the only soluble species in soots with small quantities of polycyclic aromatic compounds (PAC), but on no account do soluble amorphous carbon particles disturb the extraction yields.

NMP is commonly used in the field of coal and petrochemistry to dissolve carbonaceous materials, especially aromatics (13–15). The carbonaceous structure of the extracted material is penetrated deeply and swollen by NMP. A 94% solubility can be reached (25) due to systematic breakage

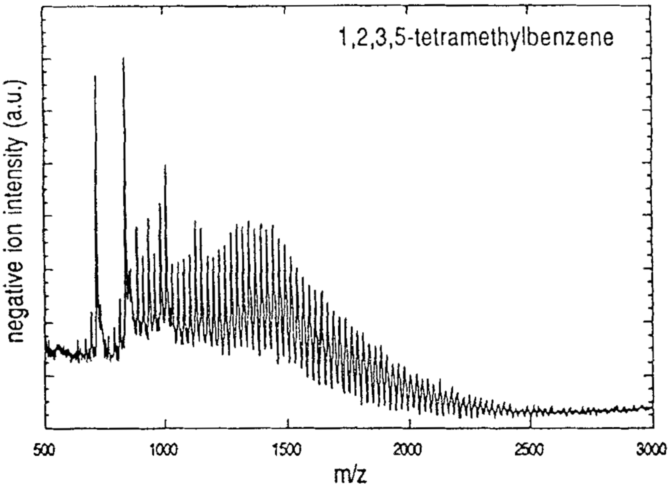

FIG. 4 Time-of-flight mass spectrum of fullerenes prepared by Soxhlet extraction in 1,2,3,5-tetramethylbenzene showing C_{60}, C_{70}, and large amounts of higher molecular weight fullerenes up to cluster size C_{200}. Reprinted from Parker et al. (25), copyright 1992, with kind permission from Elsevier Science Ltd.

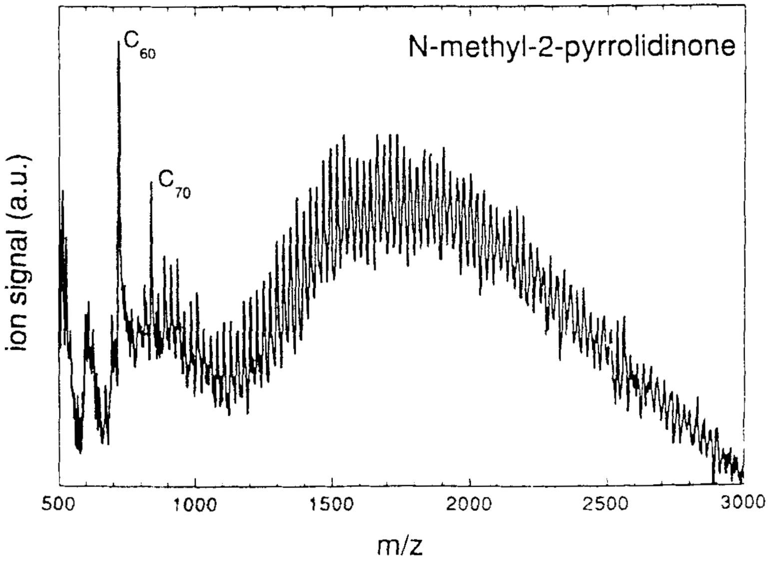

FIG. 5 Laser desorption TOF mass spectrum of raw soot extract prepared by Soxhlet extraction with *N*-methyl-2-pyrrolidinone. Reprinted from Parker et al. (25), copyright 1992, with kind permission from Elsevier Science Ltd.

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of the polarization forces between the fullerene molecules and the soot matrix, thus allowing solvent penetration in the pattern and proving the main molecular structure of soots (Fig. 5).

Conclusions

In some case, molecular weight fractions of fullerenes may be selected by extraction with the appropriate solvent. The Soxhlet extraction method is at least twice a efficient as solvent reflux because of the better solubility of fullerenes at lower temperatures.

It is possible to extract fullerenes up to C_{200} with 1,2,3,5-tetramethylbenzene, but also to limit the extraction to C_{60} and C_{70} (with a little C_{76}/C_{78} and C_{84}) with *n*-heptane.

These considerations make extraction a major step in fullerene purification, but the vast number of experiments carried out on different soots under different operating conditions makes any comparison of the techniques difficult and prevents the selection of a "best method."

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FULLERENES PURIFICATION BY LIQUID CHROMATOGRAPHY

Whatever the synthesis method, the soluble fraction extracted from crude fullerenes containing soot is a complex mixture, mainly composed of C_{60} and C_{70} (see extraction with *n*-heptane) but also involving higher clusters and fullerene derivatives (oxides, isomers, etc.).

Thus, even if the extraction step is considered to be a prepurification, further separation is necessary to obtain pure products.

Currently, liquid chromatography seems to be the appropriate technique for both the analysis and the separation of fullerenes. Many stationary phases have been tested, the objectives being an increase in selectivity between the differents components of a fullerene mixture, the productivity, and then the cost of separation. There are no miraculous conditions that lead to perfect separation by liquid chromatography, so other separation methods have been studied, including gel permeation chromatography (GPC), supercritical extraction or chromatography (SFE or SFC), sublimation, crystallization, etc.

Gas chromatography, which is a more efficient chromatographic method, cannot be applied to fullerenes because they are in the solid state up to 450°C.

Pure fullerenes are of first importance for research in this new variety of carbon. Physical and chemical properties, and thus applications, can only be precisely defined with pure separated materials. Therefore, progress in the fullerene chemistry depends on the development of improved chromatographic methods aimed at the best efficiency and the best productivity at the lowest cost.

The various chromatographic methods used for fullerene separation will be described below, including the stationary and mobile phases, the conditions of detection, the separation yields in some case, and a general discussion for each method.

Alumina (Table 2)

First, the most abundant fullerenes, C_{60} and C_{70}, were extracted with benzene or toluene, followed by column chromatography on alumina (14, 15, 26, 27). This is an efficient method for separating these fullerenes, but this technique is tedious, time-consuming, and not convenient due to the very large volumes of HPLC-grade solvent required for the ultrapurification of C_{60} and C_{70}

The yields obtained with this method are under 1 gram of extract a day in the best case when using preadsorption of fullerenes on alumina (28) or continuous column chromatography (29). The yields are commonly around 250 mg per column per day (see Table 2).

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Silica (Table 2)

The use of silica phases has been reported in the literature. Whatever the mobile phase employed, C_{60} and C_{70} retention factors are low, and the selectivity is poor (30). On the other hand, PAC that are cosynthetized during the production of the fullerene-containing soots may be well isolated on a silica column (31).

Reversed Phases (Table 3)

The main approach to fullerene separation is to use an octadecyl silica phase (ODS), monomeric or polymeric. *n*-Hexane is commonly used, but aromatic solvent-based eluents can be also used to increase the solubility of fullerenes in the mobile phase and thus increase the quantity injectable.

Separations with toluene/acetonitrile and toluene/methanol are advocated and compared in the literature (32) (Fig. 6), even though the behavior of the elution is not explained by the solvent strength rules on a typical reversed phase. Acetonitrile or methanol can be used as countersolvents; acetonitrile gives good separation of higher fullerenes and methanol gives a shorter cycle time. The ratio of acetonitrile or methanol in toluene will influence the selectivity and the duration of separation.

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TABLE 2
Separation Conditions on Alumina and Silica Phases

Ref.	Stationary phase	Eluent	Flow rate (mL/min)	Temperature (°C)	Detection (mm)	Selectivity (alpha C_{60}–C_{70}) (kC_{60}–kC_{70})	Column dimensions (diam/length)	Sample injected (μL)
				Alumina				
28	Alumina (Aldrich standard grade neutral ~150 mesh, Brockman I)	Toluene/hexane, 10/90, 5/95	15	Ambient	—	—	80 × 500	250
66	Neutral alumina	Hexane	—	—	—	—	—	—
14	Alumina	Hexane	—	—	—	—	—	—
				Silica				
62	Silica gel	Hexane/CH_2Cl_2 gradient	—	—	—	—	—	—
30	Lichrosorb Si60 silica (E. Merck, Darmstadt)		1	—	—	Low retention, poor selectivity	4.6 × 100	—
15	Econospher silica 5 μm (Alltech/Applied science)	Hexane	0.5	Ambient	UV 256	1.04 (6.93–6.64)	4.6 × 250	—

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TABLE 3
Separation Conditions of C_{18} Bonded Phases

Ref.	Stationary phase	Eluent	Flow rate (mL/min)	Temperature (°C)	Detection (mm)	Selectivity (alpha C_{60}–C_{70}) (kC_{60}–kC_{70})	Column dimensions (diam/length)	Sample injected (μL)
63	Develosil ODS-5 (monomeric)	*n*-Hexane	1	Ambient	UV 280	1.46	4.6 × 250	50 μg
		Toluene/methanol, 55/45	10	Ambient	UV 325	1.3	20 × 250	5
32	Develosil ODS-5 (monomeric)	Toluene/acetonitrile, 50/50	1	Ambient	UV 325	1.86 (9.37/17.41)	4.6 × 250	50
		Toluene/methanol, 50/50	1	Ambient	UV 325	1.31 (6.56/8.57)	4.6 × 250	50
		Toluene/acetonitrile, 45/55	1	Ambient	UV 325	1.65 (15.40/25.44)	4.6 × 250	50
	Wakosil II 5 C_{18} AR (polymeric)	Toluene/acetonitrile, 50/50	1	Ambient	UV 325	1.98 (6.96/13.79)	4.6 × 250	50
		Toluene/acetonitrile, 45/55	1	10	UV 325	—	4.6 × 250	50
				30		—		
				50		—		
				70		—		
	Wakosil II 5 C_{18} AR (monomeric)	Toluene/acetonitrile, 45/55	1	10	UV 325	—	4.6 × 250	50
				30		—		
				50		—		
				70		—		
69	Vydac 201 TP (polymeric ODS), bonded to 5 μm, 300 A silica 100 m²/g, 9% carbon loading	CH_2Cl_2/acetonitrile, 50/50, 100/0	0.2	Ambient	UV 368	2.10 (0.39–0.83)	2.1 × 250	—
	Hypersil ODS (monomeric), 5 μm, 120 A, 170 m²/g, 10% carbon	100/0	0.2	Ambient	UV 368	1.33 (0.59–0.78)	2.1 × 250	—
	Zorbax RX C_{18} (monomeric), 5 μm, 80 A, 200 m²/g, 12% carbon	100/0	0.2	Ambient	UV 368	1.28 (1.42–1.82)	2.1 × 150	—
30	IMPAQ RG 2010 C_{18} Silica, PQ, Conshohoken, PA, USA	Toluene/methanol, 80/20, 20/80	1	Ambient		4.6 × 250	—	
64	C_{18}-silica	Methanol/CH_2Cl_2	1	Ambient	UV 236–500	1.17 (9.37/10.98)	4.6 × 250	—
65	IMPAQ 2010 C_{18}	*n*-Heptane	1	Ambient	UV 260	1.46 (1.14/1.66)	4.6 × 250	7.5

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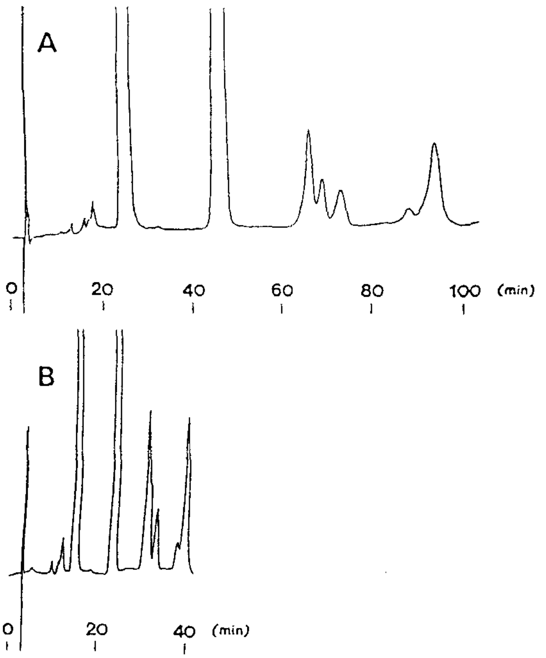

FIG. 6 Chromatograms of toluene extract from soot with toluene–acetonitrile and toluene–methanol mobile-phase systems: (A) toluene/acetonitrile = 50/50; (B) toluene/methanol = 50/50. Column, Develosil ODS-5; temperature, room temperature (ca. 15–20°C); mobile phase flow rate, 1 mL/min; detector, UV at 325 nm. Reprinted from Jinno et al. (32), copyright 1993, with kind permission from the American Chemical Society.

Monomeric and polymeric phases may be compared: the elution of C_{76} and C_{78} $2v'$ is reversed for the both phases. The peak attributed to C_{78} $D3$ can be observed on the polymeric ODS but not on the monomeric. A shoulder on the last peak of the polymeric is eluted as a single peak on the monomeric (Fig. 7).

These results show that the polymeric ODS column gives a different elution order than the monomeric column. Experiments with PAC (33–37) suggest that the polymeric phase has a higher capacity of "planarity" or "topological" recognition that could be extrapolated to a "bulky" recognition capability toward fullerenes. That would justify retention differences of fullerenes as a function of their sphere diameters and of their geometries in general.

Even if the polymeric ODS presents different elution orders because of this phenomenon of "bulky" recognition, some differences of elution

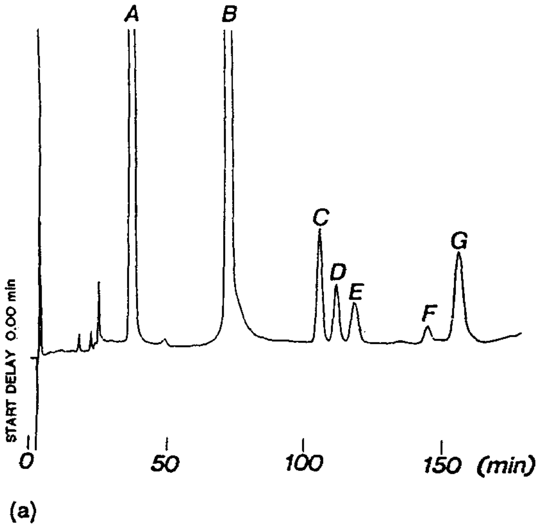

FIG. 7a Chromatogram of toluene extract from soot with the monomeric ODS: mobile phase, toluene/acetonitrile = 45/55; temperature, room temperature (ca. 15–20°C); mobile phase flow rate, 1 mL/min; detector, UV at 325 nm. Reprinted from Jinno et al. (32), copyright 1993, with kind permission from the American Chemical Society.

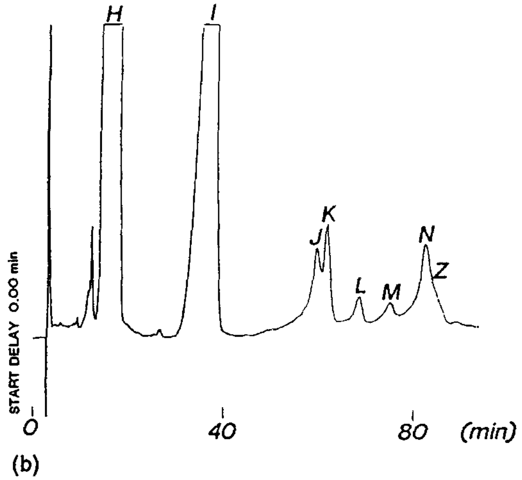

FIG. 7b Chromatogram of toluene extract from soot with the polymeric ODS: mobile phase, toluene/acetonitrile = 45/55; temperature, room temperature (ca. 15–20°C); mobile phase flow rate, 1 mL/min; detector, UV at 325 nm. Reprinted from Jinno et al. (32), copyright 1993, with kind permission from the American Chemical Society.

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or resolution, such as the nondetection of the *D*3 isomer of C_{78} with the monomeric, cannot be explained by planarity (or bulky) recognition. Other reasons have to be invoked.

Temperature Dependence. Temperature has classically had a significant influence on fullerenes separation. In this case, monomeric and polymeric must be separated as well.

Trials from 10 to 70°C were carried out (32) on a C_{18} reversed phase (Wakosil II 5 C_{18} AR, monomeric). High temperature does not give acceptable separations; decreasing the temperature increases the resolution. The same observations can be made for polymeric column. Operation at 10°C gives the best results because the rigidity of the alkyl chains improves the molecular planarity recognition capability. Moreover, the solubility of fullerenes has been proven to be the best near 280 K in many eluents (9), which explains the better results obtained in this range of temperatures (Fig. 8).

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Electron Donor/Acceptor Phases (Table 4)

DNAP-Type Columns. Good separation was achieved with a dinitroanilinopropyl silica (DNAP) column (38). The retention behavior of C_{60} on such a phase is close to that of triphenylene (a C_{18} planar polycyclic aromatic hydrocarbon), while that of C_{70} lies between a 5-ring (benzo[*a*]-pyrene) and a 6-ring (coronene) PAC. It was suggested that the retention of planar PAC on a DNAP phase can be described in terms of the electronic character of the molecule (39); that is, the difference between the highest occupied molecular orbital (HOMO) of the molecule and that of a reference compound such as naphthalene (Fig. 9).

Pirkle-Type Columns. Many Pirkle-type phases were synthetized and tested, with either π-donor or π-acceptor functional groups (40).

Tetrachlorophthalimidopropyl (TCPP) modified silica is one of the best (41), and thus will be the subject of this discussion. The separation of a C_{60} + C_{70} mixture can be carried out at ambient temperature by using a dichloromethane/hexane-based eluent. The TCPP phase presents great selectivity for C_{60} and C_{70} ($\alpha = 2.75$ in the best case), and the higher fullerenes C_{76}, C_{78} 2*v*, C_{78} *D*3, and C_{84} are also separated with a baseline resolution (Fig. 10).

TCPP is a π-acidic groups phase which is currently used for π-electron-rich polycyclic aromatic compounds (42). Even if PAC and fullerenes have dramatically different geometric shapes, this phase was expected to be able to separate the fullerenes (38, 40, 43–45).

Better separation results can be obtained with a tripodal dinitrophenylether phase (41). The capacity of this phase to separate C_{60} and C_{70} seems

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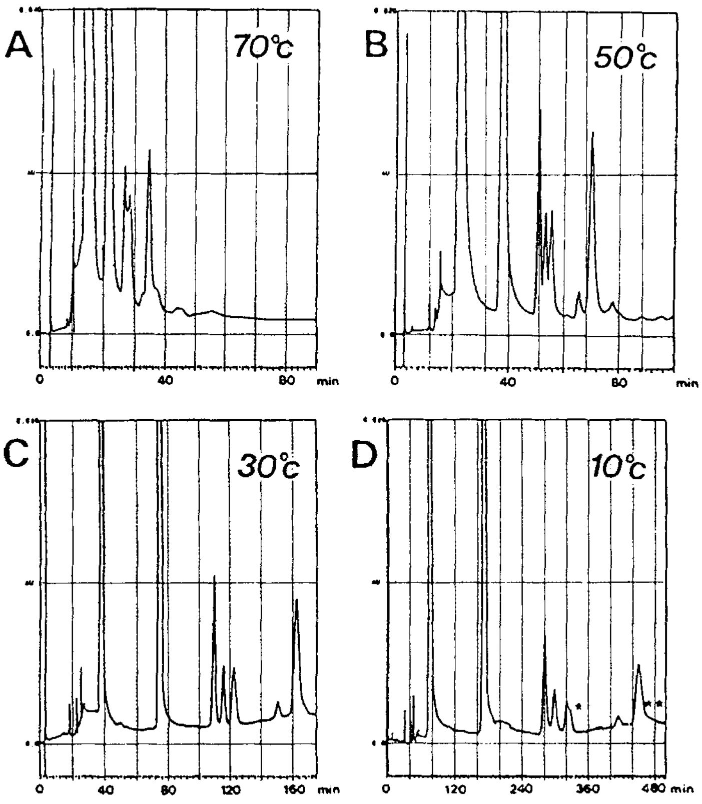

(a)

FIG. 8a Chromatograms of toluene extract from soot with the monomeric ODS at different temperatures: (A) 70, (B) 50, (C) 30, and (D) 10°C. Mobile phase, toluene/acetonitrile = 45/55; mobile phase flow rate, 1 mL/min; detector, UV at 325 nm. Reprinted from Jinno et al. (32), copyright 1993, with kind permission from the American Chemical Society.

to be due both to the interactions with π-acidic dinitrophenyl groups and to a steric effect created by a cone-shape arrangement of the dinitrophenyl group, leading to a kind of "cavity" similar to the γ-cyclodextrine effect which induce multipoint interactions with fullerenes.

γ-Cyclodextrine (Table 5)

γ-Cyclodextrine has been used as a complexing agent for C_{60} to giving a water-soluble complex (46). γ-Cyclodextrines are cyclic oligosaccharides,

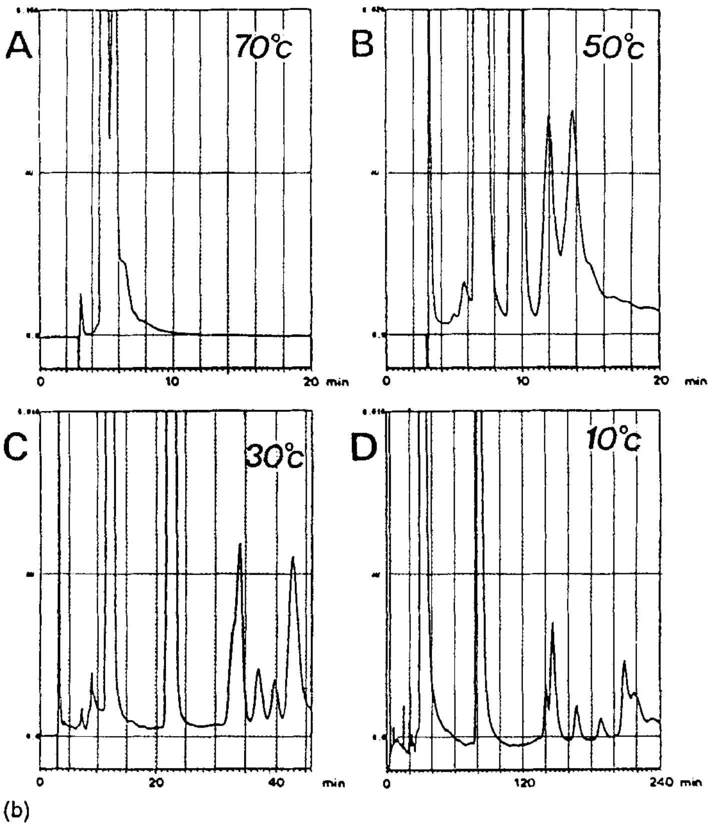

FIG. 8b Chromatograms of toluene extract from soot with the polymeric ODS at different temperatures: (A) 70, (B) 50, (C) 30, and (D) 10°C. Mobile phase, toluene/acetonitrile = 45/55; mobile phase flow rate, 1 mL/min; detector, UV at 325 nm. Reprinted from Jinno et al. (32), copyright 1993, with kind permission from the American Chemical Society.

known for their ability to form inclusion complexes with different substrates (47). This material was bonded to silica as a stationary phase for HPLC applications.

A C_{60} + C_{70} mixture can be injected and eluted with *n*-hexane (48). Greater retention is observed for C_{70}, meaning that the interaction of C_{70} with γ-cyclodextrine bonded silica is stronger (Fig. 11).

Using an unmodified silica in the same conditions gives absolutely no separation of C_{60} and C_{70}, which shows that the γ-cyclodextrine functional group is entirely responsible for the separation.

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TABLE 4
Separation Conditions on DNAP and Pirkle Phases

Ref.	Stationary phase	Eluent	Flow rate (mL/min)	Temperature (°C)	Detection (nm)	Selectivity (alpha C_{60}–C_{70}) (kC_{60}–kC_{70})	Column dimensions (diam/length)	Sample injected (μL)
				DNAP				
38	Dinitroanilinopropyl (DNAP) silica, 5 μm, 300 A	Hexane/CH_2Cl_2, 100/0, 50/50	1.5	Ambient	DAD 330–384	—	—	—
				Pirkle				
40	Pirkle phases (not available on the market)	Hexane/CH_2Cl_2, 95/5	2	Ambient	—	—	—	—
41	Tetrachlorophtalimidopropyl (TCPP) (Shandon, Runcorn, UK), PAH-2 (5 μm)	Hexane/CH_2Cl_2, 67/33 95/5	6	—	UV 310	2.1 (0.93–1.88)	20 × 250	—
						2.75	20 × 250	—
44	1A ionically bonded phenylglycine (Regis Chemical Co., Morton Grove, IL, USA)	Hexane	5	Ambient	UV 280	2.25 (12.2–23.5)	10 × 250	2 mg/h
30	DNBPG (J. T. Baker, Phillipburg, NJ, USA)	Toluene/heptane, 50/50	1	—	DAD	1.35 (0.26–0.35)	4.6 × 250	—
	GCB (Shandon Scientific, Runcorn, UK)	Pure toluene, pure $CHCl_3$	1	—	DAD	Irreversible adsorption	4.6 × 100	—
			1					
	TAPA, homemade	Toluene/heptane, 50/50	1	—	DAD	2 (1.71–3.43)	4.6 × 100	—

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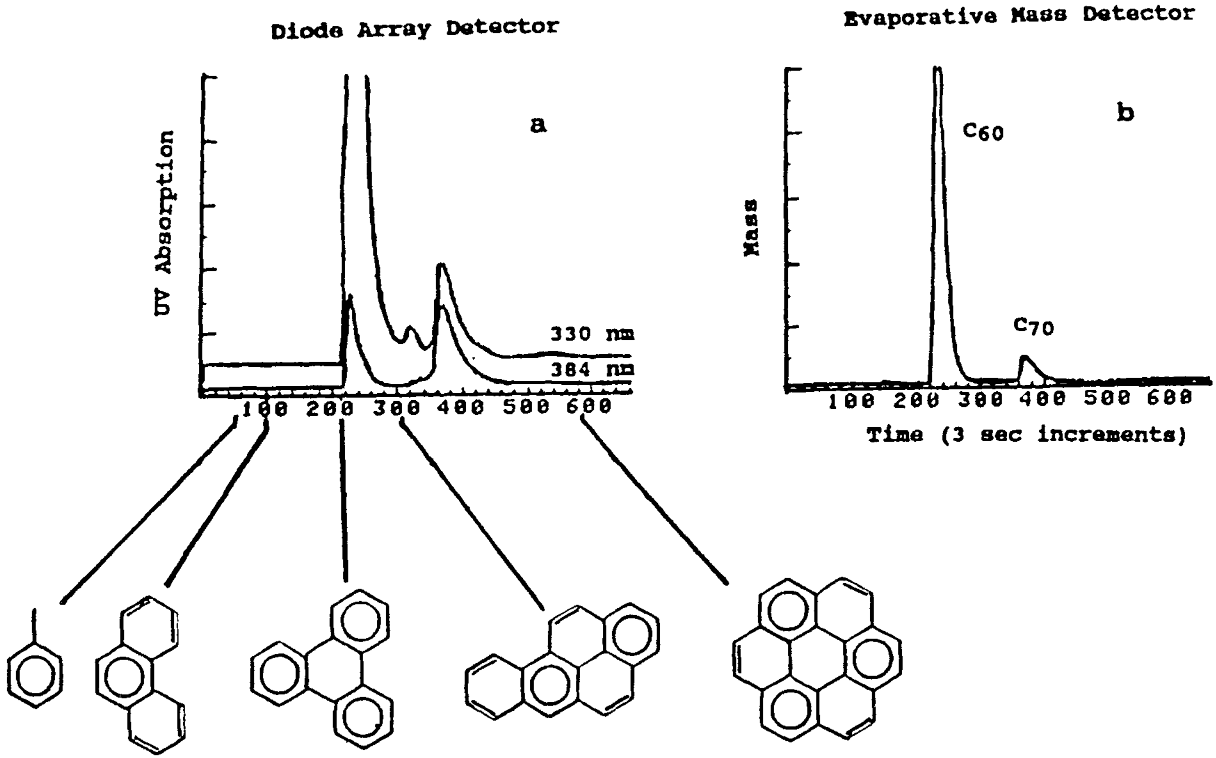

FIG. 9 HPLC chromatograms of C_{60} and C_{70} on dinitroanilinopropyl silica with linear gradient at 1.5 mL/min from 100% *n*-hexane at 50% CH_2Cl_2 over 35 minutes: (a) DAD response at 330 nm (upper trace) and 384 nm (lower trace); (b) evaporative mass detector. For comparison, retention times for different planar molecules (toluene, phenanthrene, triphenylene, benzo[*a*]pyrene, and coronene) on this column are also illustrated. Reprinted from Cox et al. (38), copyright 1993, with kind permission from the American Chemical Society.

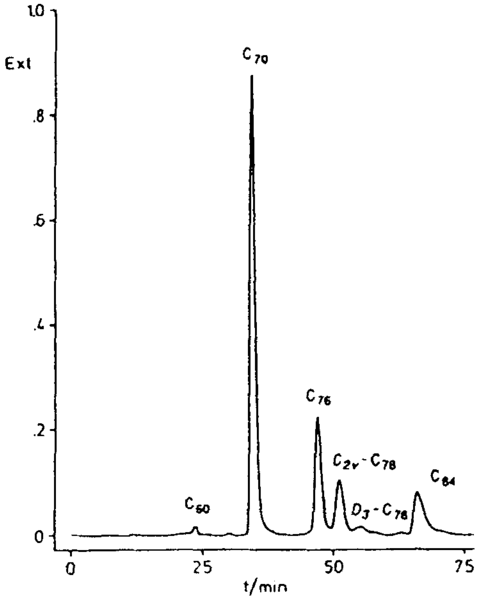

FIG. 10 Chromatogram of the separation of higher fullerenes plus C_{70} (plus traces of residual C_{60}) on a TCPP phase. Column 250 × 20 mm i.d.; injection, 100 μL (1 mg) of a solution (10 mg/mL) in 1,2-dichlorobenzene; eluent, dichloromethane/hexane (33:67, v/v); flow rate, 6 mL/min; temperature, ambient. Reprinted from Herren et al. (41), copyright 1993, with kind permission from Elsevier Science Ltd.

TABLE 5
Separation Conditions on γ-Cyclodextrines and Gel Permeation Columns

Ref.	Stationary phase	Eluent	Flow rate (mL/min)	Temperature (°C)	Detection (nm)	Selectivity (alpha C_{60}–C_{70}) (kC_{60}–kC_{70})	Column dimensions (diam/length)	Sample injected (μL)
				γ-Cyclodextrines				
48	Chemically bonded cyclodextrines, Chiradex gamma Merck 5 μm	*n*-Hexane	2	30	UV 298	—	4 × 250	—
		Hexane/ toluene, 70/30	1	Ambient	UV 334	—		—
				Gel permeation				
53	500 A ultrastyren, Waters	Toluene	5	Ambient	UV 600	1.1 (16.4–17.5)	19 × 300	—
55	PL Gel 500 Å 10 μm	Toluene	7	Ambient	UV 329	—	20 × 600	—
54	500 Å ultrastyren, Waters	Toluene	1	95	UV 500	1.1 (49.6–53)	4 × 7.8 × 300	—

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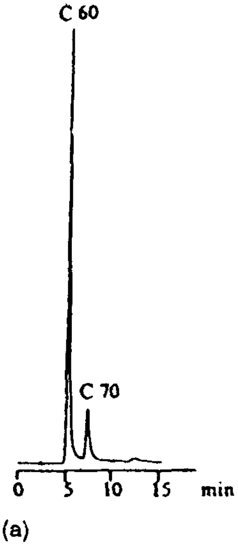

FIG. 11a Separation of C_{60} and C_{70} on ChiraDex-GAMMA. Chromatographic conditions: mobile phase, *n*-hexane; flow rate, 2 mL/min; temperature, 30°C; detection, UV at 298 nm; injection volume, 10 mg C_{60}–C_{70} (ca. 10:1) dissolved in 10 mL toluene. Reprinted from Cabrera et al. (48), copyright 1993, with kind permission from Elsevier Science Ltd.

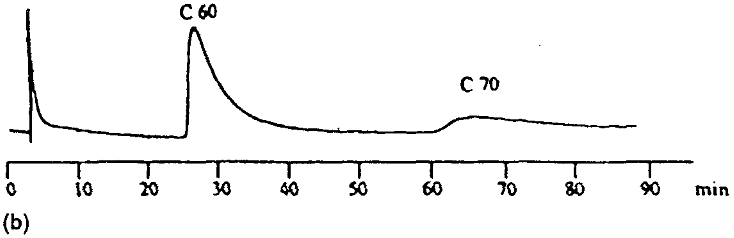

FIG. 11b Separation of C_{60} and C_{70} on ChiraDex-GAMMA. Chromatographic conditions: mobile phase, *n*-hexane/toluene (70:30, v/v); flow rate, 1 mL/min; temperature, room temperature; detection, UV at 334 nm; injection volume, 10 mg C_{60}–C_{70} (ca. 10:1) dissolved in toluene. Reprinted from Cabrera et al. (48), copyright 1993, with kind permission from Elsevier Science Ltd.

Unfortunately, the very low solubility of fullerenes under these chromatographic conditions has led to no other expectations beyond analytical applications. The addition of toluene up to 30% in order to increase the charge capacity of the column was studied. It led to interesting results and opened the possibility of prep-scale use.

The mechanism of interaction between γ-cyclodextrine groups and fullerenes can be interpreted as an inclusion (or a partial inclusion) of fullerene spheres in the cavity (47). The lower retention of fullerenes when toluene is used can be explained by a competition between the fullerene molecules and the solvent molecules for the inclusion. The higher retention of C_{70} compared to C_{60} is probably due to a C_{70} geometry more favorable for interaction with the γ-cyclodextrine molecule.

Conclusion

The separation of C_{60} and C_{70} by liquid chromatography is challenging research, even though analytical methods provide great selectivity. Low retention times and poor selectivity are obtained on silica columns. On the other hand, fullerenes can be separated on reversed phase columns, polymeric or monomeric, which is promising for further preparative applications. The importance of eluent constitution and the temperature dependence were shown with ODS phases: acceptable solubilities can be obtained with aromatic solvent-based eluents, and selectivity is increased at low temperatures.

Many charge transfer (Pirkle-type) adsorbents were tested with various mobile phases. Separation are better than those obtained with classical columns. Elution at high temperatures seems preferable.

The best selectivity was obtained with a chiral stationary phase, a multileg phenyl-bonded phase, which gave the strongest electron acceptor behavior and led to better differentiation of the fullerenes in a mixture.

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OTHER PURIFICATION TECHNIQUES

Molecular Sieves

The adsorption of C_{60} on activated molecular sieve 13X (cage aperture size 10 Å) was revealed in 1991 by EPR detection (49). On examining the activated molecular sieve after exposure with C_{60} heated at 425°C, a powerful signal with an isotropic g of 1.9995 that was not present in the starting molecular sieve could be detected, showing the capture of C_{60} molecules. The same experiment was carried out with a 4 Å molecular sieve, but no modification of the EPR spectrum appeared, showing the specificity of the 13X molecular sieve.

Molecular sieve filtration can be also used for the separation of fullerenes and PAC (50). In the case of fullerene synthesis by combustion, which is known to produce a significant concentration of PAC, the molecular sieve could take the place of PAH removal by polar solvent rinsing. Trials were performed with 5A and 13X molecular sieves from Grace (cage aperture size of 5 and 10 Å, respectively). The greater affinity of both molecular sieves toward PAC was clearly shown, allowing for prepurification of fullerenes. Nevertheless, no real difference in the affinities of both molecular sieves toward C_{60} and C_{70} was revealed.

Activated Charcoal

The possibility of separating C_{60} and C_{70} with activated charcoal, even on a preparative scale, was studied (51). The activated charcoal most employed was Norit A. Activated carbon has been used extensively as a stationary phase for molecular size selection-based chromatography, and so it was logical to test fullerene separation on this kind of support.

Norit A tends to adsorb fullerenes irreversibly. By using the right amount (determined by experience) of charcoal mixed with silica gel, the adsorption forces were decreased and allowed for separation. However, part of C_{60} was still irreversibly adsorbed (around 20% of the initial concentration) as was around 50% C_{70}, which is retained more than is C_{60} (Fig. 12).

The properties of activated carbon depend on its origin and its specific area. Modification of the charcoal characteristics influences the retention

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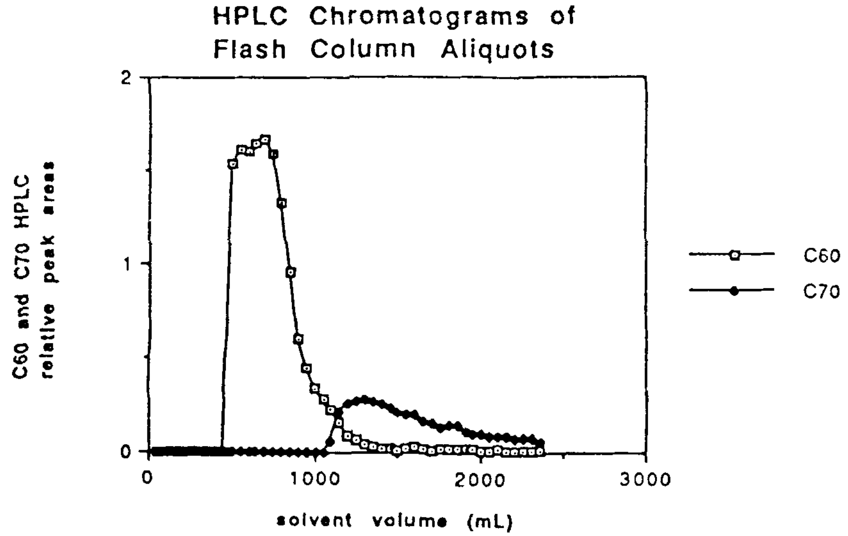

FIG. 12 Flash column aliquots analyzed by HPLC. Reprinted from Scrivens et al., *J. Org. Chem.*, *57*, 6932–6936 (1992), copyright 1992, with kind permission from the American Chemical Society.

times of the fullerenes, the peak widths, and the purities of the eluted products. Increasing the proportion of hydrophilic groups by oxidation decreases the amount of fullerenes adsorbed on the phase and thus increases the separation yield.

Gel Permeation (Table 5)

Owing to differences in the geometry and size of fullerenes C_{60} and C_{70}, it seemed appropriate to separate them by size exclusion (52–57). Unlike other separation methods for which the very low solubility of fullerenes leads to very low productivity, the separation of C_{60} and C_{70} on polystyrene gel offers the perspective of rather large-scale production. Pure toluene can be used as the mobile phase (Fig. 13).

Compared to classical chromatographic methods, gel permeation presents the following advantages when applied to the purification of fullerenes.

- Fullerenes can be eluted with an isocratic eluent (toluene is recommanded), allowing less constraint for solvent recycling.
- The lifetime of the gel for permeation is greater than that of conventional stationary phases for liquid chromatography.

The fact that C_{60}, the smaller of the fullerenes to be separated, is eluted before C_{70} and higher fullerenes, even with different mobile phases (toluene and chloroform) and different pore diameter polystyrene gels (50 and 500 Å), led Gügel and Müllen (52) to conclude that neither the mobile phase nor the pore diameter plays a role in fullerenes separation, and that solutes are not separated by a true size-selective filtration. No mechanism is proposed to explain the reasons why C_{60}, C_{70}, and higher fullerenes are separated on polystyrene gels. However, Meyer and Selegue (53) feel that hydrophobic interactions could be at the origin of the discrimination.

Supercritical Fluids Extraction and Chromatography

Although classical liquid chromatography separations are tedious, time and solvent consuming, and environmentally wasteful, the supercritical fluids techniques obviously contribute to the development of the fullerenes purification methods, offering a more simple, cleaner, cheaper, and convenient process.

Unfortunately, fullerenes are not soluble in pure CO_2 (58). Solubilizing solvents like hexane or toluene must be added as a cosolvent, allowing the solvation of fullerenes, but decreasing the advantages of the technique.

Subcritical Fluids Extraction. Jinno et al. used toluene and CO_2 in a 1:1 ratio as a subcritical fluid to extract soluble fullerenes from crude

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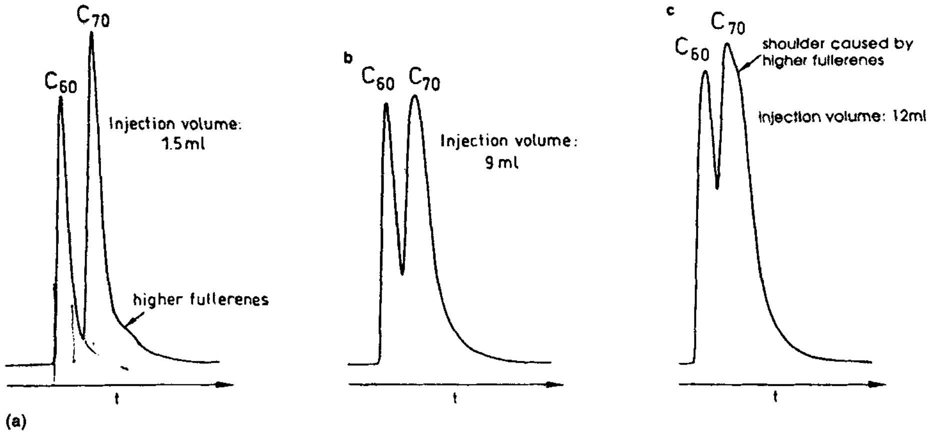

FIG. 13a Effect of injection volume: (a) 1.5, (b) 9, (c) 12 mL. Conditions: two columns (600 × 20 mm i.d.) in series + 60 × 20 i.d. guard column; stationary phase, PSS-Gel (10 μm, 500 Å); mobile phase, toluene at 15 mL/min; injection, 7.5 mL of a saturated solution of fullerene raw material in toluene; detection, UV at 380 nm. Reprinted from Gügel et al. (52), copyright 1993, with kind permission from Elsevier Science Ltd.

FIG. 13b Elution diagram showing the automatic separation of fullerene raw material obtained by Soxhlet extraction of carbon soots with hexane. Injection frequency, 8 min; detection, UV at 350 nm. Conditions: two columns (600 × 20 mm i.d.) in series + 60 × 20 i.d. guard column; stationary phase, PSS-Gel (10 μm, 500 Å); mobile phase, toluene at 15 mL/min; injection, 7.5 mL of a saturated solution of fullerene raw material in toluene. Reprinted from Gügel et al. (52), copyright 1993, with kind permission from Elsevier Science Ltd.

soots (59). Their experiments revealed a strong soot matrix effect on the extraction process: only the surface of the soot is extracted, not the bulk. In fact, the smaller the particle size of the soot, the higher the extraction yield will be.

Jinno et al. succeeded in extracting fullerenes by rinsing a toluene solution of soots with bubbling CO_2. The fullerenes in the soots were dissolved

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by toluene and entrained by the CO_2, giving higher extraction yields in a classical extraction with premixed toluene and CO_2.

Supercritical Fluids Chromatography. Trials were carried out at various backpressures (from 175 to 275 bar), but with constant supercritical fluid (toluene/CO_2 = 0.75) and temperature (150°C).

C_{60} and C_{70} are very well separated on silica with a selectivity of α = 1.12. The fact that higher fullerenes are not detected may be attributed either to the nonextraction of these fullerenes during the SFE step or to the failure of the SFC conditions used. The last supposition appears to be more probable (Fig. 14).

Conclusion. Using such a technique has the following advantages:

- Recovery of fullerene samples in pure toluene.
- Selective extraction of fullerenes by changing the temperature, the pressure, and the toluene/CO_2 ratio.

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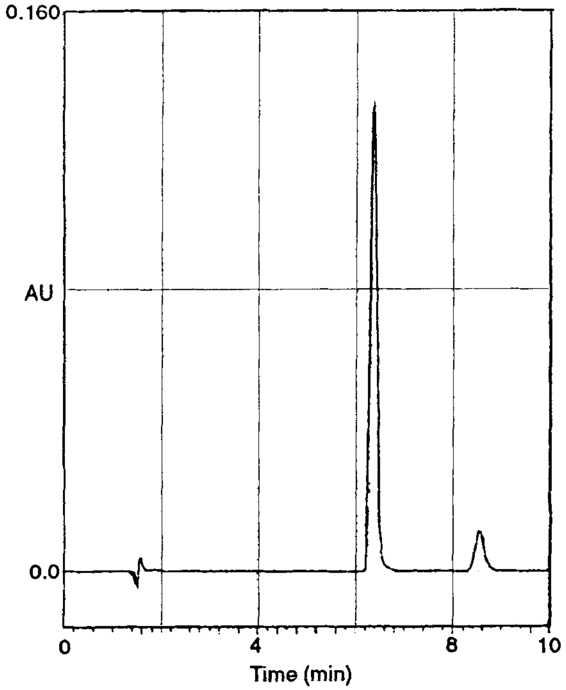

FIG. 14 SFC chromatogram of the extract C_{60}/C_{70}. SFC conditions: column JASCO Fine-PakSIL Silica (250 × 4.6 mm i.d.); mobile phase, CO_2 (1 mL/min) + toluene (0.75 mL/min); temperature, 150°C; pressure, 225 bar. Reprinted from Jinno et al., *Fresenius J. Anal. Chem.*, *344*, 435–441 (1992), copyright 1992, with kind permission from the American Chemical Society.

- The possibility to scale up to the preparative scale.

Sublimation

Sublimation can be considered a successful technique for partial fullerenes purification by heating crude soots at 1050°C (60). This original technique avoided the tedious classical chromatographic methods. A temperature gradient applied on a mixture of fullerenes leads to rough separation. The disadvantage of this method is the degree of purity of the separated species (not given in the literature). Moreover, the scale-up to kilograms of material does not seem to be realistic (Fig. 15).

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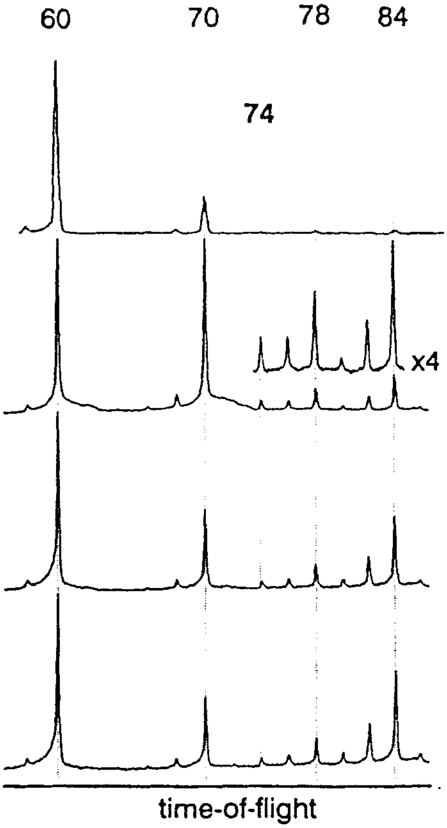

FIG. 15 Positive sensitive LDMS (positive ion mode, ArF/193 nm, ~1.5 mJ/cm^2) of the approximately 30-mm-long sublimed deposit along the temperature gradient of the fullerene-containing raw soot. Reprinted from Yeretzian et al. (60), copyright 1993, with kind permission of the American Chemical Society.

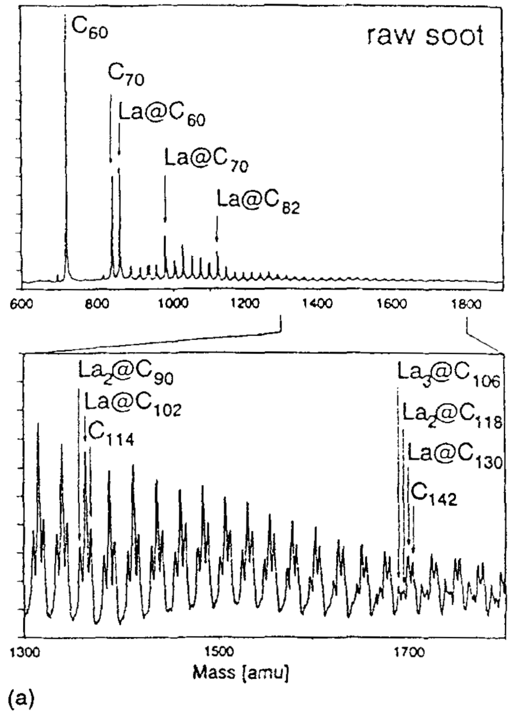

FIG. 16a Positive ion laser desorption time-of-flight mass spectrum of soot-containing lanthanum-fullerenes, using an ArF/193 nm laser line at a fluence of ~1 mJ/cm^2. Reprinted from Yeretzian et al. (60), copyright 1993, with kind permission of the American Chemical Society.

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However, sublimation offers a method for the purification of metallofullerenes that cannot be actually separated by liquid chromatography because they are not soluble in common chromatographic solvents (Fig. 16).

Crystallization

It was reported in the literature that a C_{60} of 98% purity as determined by HPLC can be obtained without chromatography by controlling the process of Soxhlet extraction of soots with hot toluene (61). After around 10 hours of extraction, one-third of the starting volume of toluene remained in the flask. The dark solution was filtered, giving a deposit containing 98% C_{60}. A second recrystallization by the same process gave 99.5% C_{60}.

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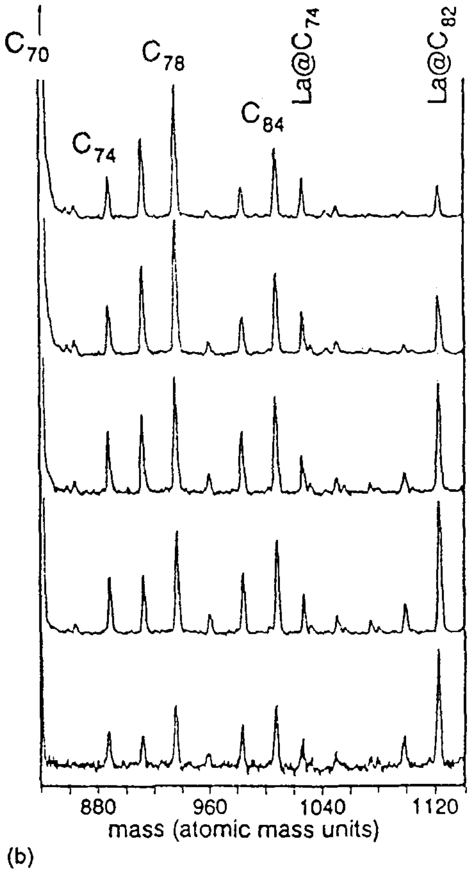

FIG. 16b Positive sensitive LDMS of Lax@Cy-containing soot (positive ion mode, ArF/193 nm, ~1 mJ/cm^2) of the approximately 30-mm-long sublimed deposit along the temperature gradient of the fullerene-containing raw soot. Reprinted from Yeretzian et al. (60), copyright 1993, with kind permission of the American Chemical Society.

PREPARATIVE SCALE

Separating fullerenes on a large scale (kilogram scale) is the challenge of the future for this new field of organic chemistry. Most of the separation techniques reported in this review are limited to laboratory analyses (gram scale).

The production of pure fullerenes on an industrial scale is more realistic by liquid chromatography. The aim of research to find a production method is guided by:

- The cost of investment for the separation process, the stationary phase, the solvents, and the recycling eluent system.
- The cost of functioning, which includes the loss of solvent during recycling, the cost of energy, and the manpower cost.

Reducing the cycle time and increasing the quantity of the fullerene mixture injected for each run will reduce the production cost of fullerenes, which is the condition for further industrial applications.

GENERAL CONCLUSIONS

The most studied fullerenes, C_{60} and C_{70}, were first extracted with benzene, toluene, or CS_2 and then separated on an alumina chromatographic column. The need to obtain pure C_{60} and C_{70} on the one hand and to separate larger fullerenes on the other hand led to the development of extraction and separation techniques.

The extraction of the fullerenes contained in raw soots is essentially guided by the problems of solubility of this new form of organic carbon. Extraction is the first important step in obtaining fullerenes and may be considered to be a prepurification stage: various fullerene sizes may be isolated by varying the nature of the extracting solvent. The use of *n*-hexane leads to the extraction of C_{60} and C_{70} from a crude mixture of fullerenes, although high boiling point solvents such as NMP and quinoline allow for the extraction of high molecular weight fullerenes among certain other high molecular mass products.

Today, liquid chromatography is the method of choice for the separation of fullerenes. The most used stationary phases (neutral alumina, silica, or C_{18} reversed phases) are not sufficiently selective; thus, more specific columns have been designed and checked. The retention processes of these columns are essentially based on π-electron charge transfers.

Unfortunately, these efficient columns can't be used on a preparative scale for reasons of cost and availability. Large-scale separations have been tested with more current phases such as silica or C_{18} reversed silica, but the selectivity in these cases is too low. Other parallel techniques have been checked, the more promising of which are carbon-composed stationary phases, even if the separation yield is not quite satisfactory; some C_{60}, C_{70}, and, above all, higher fullerenes are irreversibly retained on the column.

Having pure C_{60} and C_{70} is a challenge for fullerenes chemistry. Two kinds of separation methods must be available for progress to be made:

- A precise method to obtain pure fullerenes or adducts of pure fullerenes, necessary for physical and chemical studies.

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- A large-scale method for the production of huge quantities of fullerenes for industrial applications.

The future is in the hands of chromatographers and process engineers!

Be aware this review will soon be dated due to the epidemical spread of fullerene studies.

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