Separation and Identification of Higher Fullerenes, Using HPLC/MS

Fullerenes larger than C70 are difficult to separate in a single HPLC analysis, because there can be many homologs and many isomers of each homolog. A SUPELCOSIL LC-PAH column and electrospray ionization mass spectrometry have allowed separation and identification of fullerenes up to C98. Fullerenes extracted from carbon soot were separated by molecular mass on a monomeric octadecyl silica column, then the fraction containing higher fullerenes was analyzed on the SUPELCOSIL column. The polymeric octadecylsilyl bonded phase recognizes molecular planarity and separates the fullerenes according to shape and structure, allowing identification of many higher fullerene isomers. Column temperatures below 15°C enhance the molecular planarity recognition of the column and improve separations.

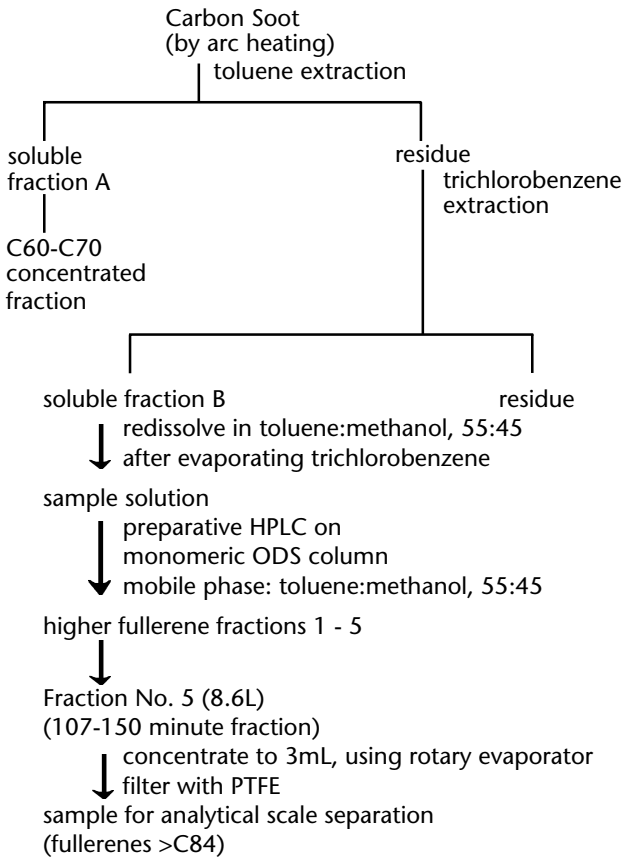
Key Words:
- fullerenes • higher fullerenes
- electrospray ionization mass spectrometry

Because of their unique structures and potentials for various uses, fullerenes have been attractive compounds to analysts in many fields. C60 and C70 fullerenes are the major components in carbon soot produced by an arc discharge of graphite, and these molecules have been well characterized. However, carbon soot also contains smaller amounts of higher fullerenes, some of which can encapsulate one or more metal atoms within their cages. Although separation and isolation of these molecules is the first step in understanding their properties, it has been very difficult to separate higher fullerene series in a single chromatographic analysis, because there can be many homologs and many isomers of each homolog.

Using a SUPELCOSIL™ LC-PAH HPLC column coupled with electrospray ionization mass spectrometry, a team of investigators has separated and identified fullerenes larger than C84 (1). After extraction from carbon soot, the fullerenes first were separated on a preparative scale column packed with monomeric octadecyl silica, then pooled material containing the higher fullerenes was analyzed on a SUPELCOSIL LC-PAH polymeric octadecylsilyl (ODS) column.

The carbon soot was produced by an arc discharge in an inert environment (Figure A). The soot was extracted with toluene to reduce the C60 and C70 fullerene content, then the residue was extracted with 1,2,4-trichlorobenzene to concentrate the fullerenes

Figure A. Sample Preparation: Fullerenes >C84



larger than C70. The trichlorobenzene solution was filtered through a 1µm porous PTFE membrane, then evaporated to dryness. The residue was redissolved in toluene:methanol (55:45) for preparative scale separation on the monomeric octadecyl silica column, from which the fullerenes elute primarily by relative molecular mass. Five fractions (48-59 min, 66-78 min, 78-93 min, 93-107 min, 107-150 min) were obtained. A total of 8.6 liters of fraction 5 was collected from 5 preparative analyses, concentrated to 3mL, and used for the analytical scale separation. A polymeric ODS bonded phase was used to separate the sample because these phases recognize molecular planarity, and thus can separate the higher fullerene isomers according to shape and

Figure B. Higher Fullerenes on a SUPELCOSIL LC-PAH Column

Column: **SUPELCOSIL LC-PAH, 25cm x 4.6mm ID, 5µm particles**
Cat. No. **58229**
Mobile Phase: toluene:acetonitrile, 50:50
Flow Rate: 1.0mL/min
Det: UV, 325nm
Inj.: 10µL fraction no. 5 from sample preparation scheme (fullerenes >C82)

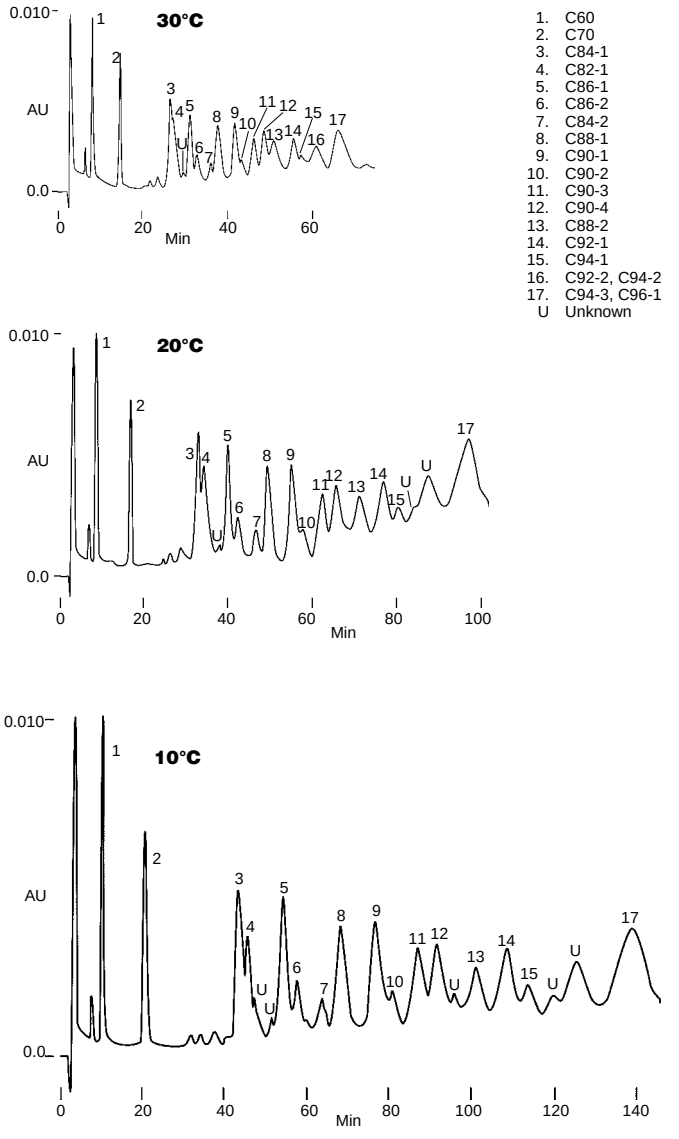


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Table 1. Higher Fullerene Isomers in Soot Extracts

Fullerene	Mass No.	Minimal No. Isomers
C82	984	2
C84	1008	5
C86	1032	2
C88	1056	3
C90	1080	6
C92	1104	9
C94	1128	8
C96	1152	3
C98	1176	2

structure. The original column was replaced with a SUPELCOSIL LC-PAH column, improving the separations and allowing identification of many higher fullerene isomers (Figure B). The existence of fullerenes up to C98 was confirmed by HPLC/ESI-MS (Table 1).

The effect of temperature on separation of fullerenes also was examined. Column temperatures below 15°C enhanced the molecular planarity recognition of the polymeric ODS column and improved isomer separations. According to the investigators, a 25cm x 4.6mm ID SUPELCOSIL LC-PAH column packed with 5µm particles provided excellent separations of the higher fullerenes (2).

Ordering Information:

Description	Cat. No.
SUPELCOSIL LC-PAH HPLC Column	
25cm 4.6mm, 5µm particles	**58229**

Columns of other dimensions are available – please inquire.

References

1. Jinno, K., Y. Sato, H. Nagashima, and K. Itoh, *Separation and Identification of Higher Fullerenes by High Performance Liquid Chromatography Coupled with Electrospray Ionization Mass Specrometry* (in press, *J. Microcolumn Separations*).
2. Jinno, K., personal communication.

References not available from Supelco.

Acknowledgment

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