

Short Communication

Preparative separation of higher fullerenes by high-performance liquid chromatography on a tetrachlorophthalimidopropyl-modified silica column

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ABSTRACT

The preparative chromatographic separation of buckminsterfullerene (C_{60}) and the larger, related carbon spheres C_{70} , C_{76} , C_{20} - and D_3 - C_{78} and C_{84} on a tetrachlorophthalimidopropyl-modified silica stationary phase was achieved and quantified. A 1-mg amount of a mixture of the higher fullerenes per injection can be separated on a 250 mm \times 20 mm I.D. column using dichloromethane–hexane (33:67, v/v) as the mobile phase and 1,2-dichlorobenzene as the sample solvent.

INTRODUCTION

The discovery of a gram-scale fullerene production process in 1990 made these interesting carbon allotropes more readily available for

investigation [1]. Since then, the techniques for separating and isolating C_{60} and C_{70} , a task not easy to perform on gram scale, have been constantly improved [2–6]. The separation and isolation of the higher fullerenes (C_n , $n > 70$) has proved to be even more difficult, making studies of these allotropic forms of carbon extremely tedious [2,7,8].

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One of the most common techniques for the separation of larger amounts of fullerenes from the crude soot extract is flash chromatography on alumina using hexane–toluene (95:5, v/v) as the mobile phase. Pure C_{60} , C_{70} and a fraction containing the higher fullerenes with residual C_{70} is obtained [2,3]. A recent paper described the medium-pressure LC separation of C_{60} and C_{70} , either on normal-phase silica gel with hexane or on C_{18} reversed-phase silica gel with toluene–acetonitrile (75:25, v/v) as the eluent [4].

Different HPLC procedures have been reported for the separation/isolation of C_{60} and C_{70} . Among the stationary phases that have been used are alkyl- (C_{18}) and phenylsiloxane-based materials [9–17], Pirkle-type phases [18–20] and charge-transfer phases with residues not containing amino acid building blocks, such as 2,4-dinitroanilinopropyl- (DNAP) [21,22] and a variety of dinitrophenyl-derivatized π -acidic and some π -basic phases [20]. The eluent most commonly used is *n*-hexane, either pure or in a combination with a more polar component such as dichloromethane, diethyl ether, tetrahydrofuran or an alcohol.

A major problem always encountered is the relative insolubility of all fullerenes in the mobile phase used, a fact that severely limits the amount of material that can be processed. The best solvents for fullerenes are carbon disulphide [13,14] and benzene and alkylated or halogenated derivatives of the latter. With these solvents, on the other hand, virtually no retention is observed on any of the stationary phases mentioned above.

It is only recently that separation techniques using pure toluene as the mobile phase have been described. Gel permeation chromatography using this eluent is reported to yield a C_{60} fraction (92–95% pure), an overlapping fraction (*ca.* 1:1 C_{60} – C_{70}) and a fraction enriched in C_{70} (24% C_{60} , 76% C_{70} , with several percent of higher fullerenes). Reinjection of the fractions obtained in this way leads to purer samples, but the method is not suitable for the separation of higher fullerenes [23–25].

A recent gram-scale C_{60} purification procedure uses a gravity column packed with a mixture of Norit A carbon and silica gel [6]. This method yields pure C_{60} and a mixture of C_{60} and C_{70} .

Most of the C_{70} and all the higher fullerenes, however, remain adsorbed on the stationary phase [26].

Whereas most published work refers to the

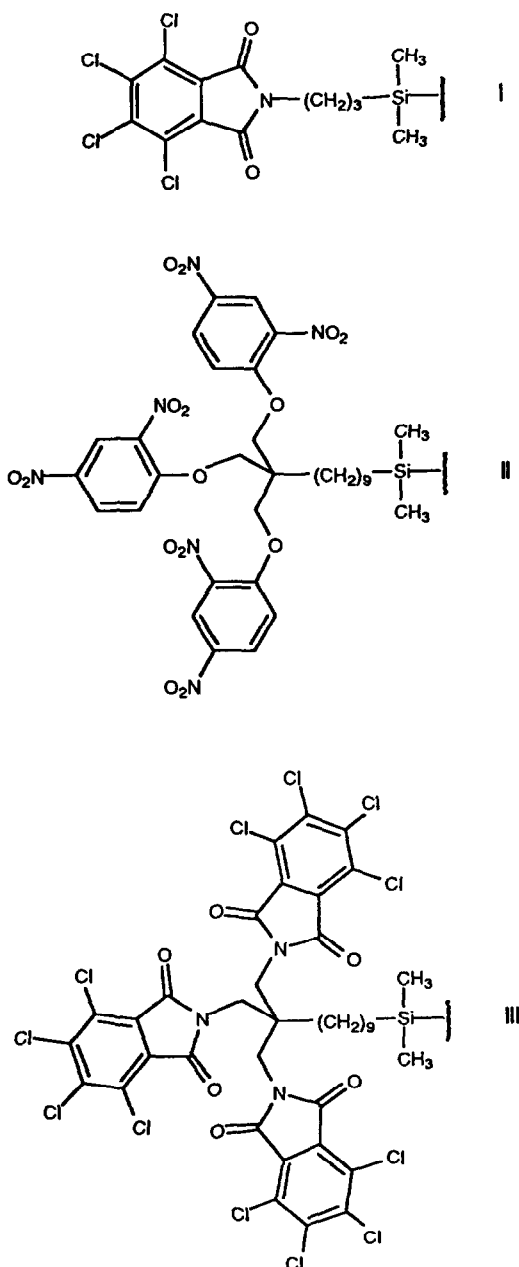


Fig. 1. Structures of stationary phases: I = tetrachlorophthalimidopropyl (TCPP) phase; II = tripodal dinitrophenyl ether phase of Welch and Pirkle [20]; III = hypothetical tripodal TCPP phase.

isolation of C_{60} and C_{70} only, a few small-scale preparative separations of higher fullerenes have been achieved by HPLC on alkylated silica [7,8,12–17]. Thus, repeated runs (2–3) on a Vydac 201 TP C_{18} phase using the unusual mixture acetonitrile–toluene (50:50, v/v) as the mobile phase yielded pure C_{76} , C_{2v} - C_{78} , D_3 - C_{78} and a mixture of D_2 - and D_{2d} - C_{84} [8,15–17]. An analytical separation of a different mixture of higher fullerenes on the same stationary phase with diethyl ether as the eluent has been described [10].

In this paper, we report on the efficient HPLC separation of C_{60} and especially the larger carbon spheres C_{70} , C_{76} , C_{2v} - C_{78} and D_3 - C_{78} and C_{84} on a tetrachlorophthalimidopropyl (TCPP)-modified silica stationary phase (Fig. 1, I). The mobile phase used was dichloromethane–hexane and the samples were injected as 1,2-dichlorobenzene solutions.

EXPERIMENTAL

Column

Separations were performed on Shandon (Runcorn, UK) PAH-2 (5 μ m) columns, 250 mm \times 20 mm I.D. (preparative) and 250 mm \times 4.6 mm I.D. (analytical). This stationary phase was TCPP-modified silica (Fig. 1, I).

Instrumentation

The following instruments were used: Merck–Hitachi LC 6200 HPLC pump, ERMA ERC 3511 solvent degasser, Negretti Model 190 sample injector, Kontron Uvicon LCD 725 detector (310 nm), Servograph rec 51 recorder and Hewlett-Packard HP 3396A integrator.

Fullerene production

The fullerene-containing carbon soot was produced through resistive heating of graphite under a helium atmosphere by methods described previously [1–3]. Soxhlet extraction of the soot with toluene gave an extract containing ca. 65% of C_{60} , 30% of C_{70} and 5% of higher-molecular-mass fullerenes consisting mainly of C_{76} , two C_{78} isomers and two C_{84} isomers [2,3,15–17]. The higher fullerene mixture was isolated by gravity chromatography on neutral alumina with hex-

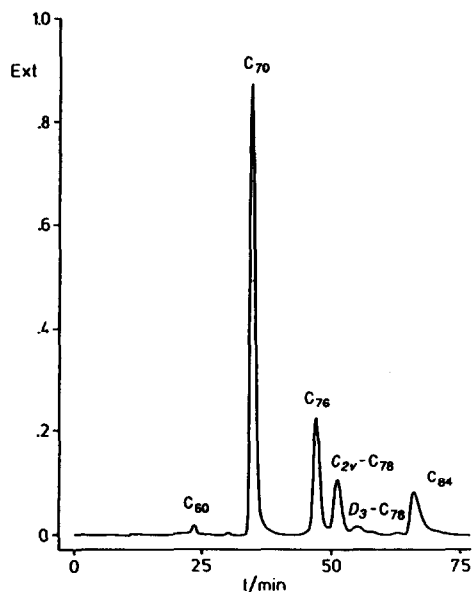


Fig. 2. Chromatogram of the separation of higher fullerenes plus C_{70} (plus traces of residual C_{60}) on a TCPP phase. Column, 250 mm \times 20 mm I.D.; injection, 100 μ l (1 mg) of a solution (10 mg/ml) in 1,2-dichlorobenzene; eluent, dichloromethane–hexane (33:67, v/v); flow-rate, 6.00 ml/min; temperature, ambient.

ane–toluene (95:5, v/v), yielding the fractions C_{60} , C_{70} and higher fullerenes with residual C_{70} .

Reagents

HPLC-grade dichloromethane and hexane were obtained from Romil Chemicals (Loughborough, UK) and 1,2-dichlorobenzene (analytical reagent grade) from Merck (Darmstadt, Germany).

RESULTS

C_{60} – C_{70}

The separations were performed at ambient temperature using the preparative column and dichloromethane–hexane as the mobile phase at a flow-rate of 6 ml/min. The fullerene mixture was injected as a concentrated 1,2-dichlorobenzene solution (10 mg/ml). The capacity factors (k') and the separation factor (α) for these two fullerenes show a close dependence on the solvent mixture. With dichloromethane–hexane (33:67, v/v) as the eluent, the values were $k'(C_{60}) = 0.93$, $k'(C_{70}) = 1.88$ and $\alpha = 2.1$.

Changing the solvent to dichloromethane–hexane (5:95, v/v) gave $k'(C_{60}) = 5.11$, $k'(C_{70}) = 14.04$ and $\alpha = 2.75$. Injection of 0.5 ml of the fullerene solution (5 mg) resulted in the baseline separation of C_{60} and C_{70} with the 33:67 solvent mixture.

Higher fullerenes

The TCPP phase shows excellent selectivity for the higher fullerenes (Fig. 2). Baseline separation of C_{70} , C_{76} , C_{2v} - C_{78} , D_3 - C_{78} and C_{84} was obtained with a 100- μ l injection containing 1 mg of these fullerenes, using dichloromethane–hexane (33:67, v/v) as the mobile phase. The purity of the collected fractions was determined by analytical HPLC (injection of 50 μ l of a 1,2-dichlorobenzene solution containing 10 mg/ml of material; percentages refer to integrated peak areas and are not exactly equivalent to mass-% because of the slightly different molar absorptivities of the different fullerenes at 310 nm): C_{70} , 100%; C_{76} , 98.5% (1.5% C_{70}); C_{2v} - C_{78} , 97.5% (1.1% C_{70} , 1.4% C_{76}); D_3 - C_{78} , 45% (30% C_{70} , 15% C_{76} , 10% C_{2v} - C_{78}); C_{84} , 99.5%.

DISCUSSION

TCPP-modified silica belongs to the family of π -acidic phases which have been used for the separation of π -electron-rich polycyclic aromatic hydrocarbons (PAHs) for some time [27]. Their efficiency in separating C_{60} from C_{70} [18–22] therefore was not surprising, although there is an important difference in shape between the mostly flat PAHs and the curved fullerenes.

Recently, Welch and Pirkle [20] reported an extensive C_{60} – C_{70} separation study with ten different charge-transfer stationary phases, all of which showed retention and separation for these carbon spheres. They achieved capacity factors and separation factors even higher than those described here with a tripodal dinitrophenyl ether phase (Fig. 1, II) using dichloromethane–hexane (5:95, v/v) as the eluent (Table I). However, they did not investigate the separation of higher fullerenes.

The efficiency of the tripodal dinitrophenyl ether phase in the separation of C_{60} and C_{70} seems to be due at least in part to the cooperative effect of three π -acidic dinitrophenyl groups that adopt a cone-shaped arrangement, thus creating a “cavity” well suited for simultaneous multi-point interactions with the “buckyballs”. If this assumption is correct, it would certainly be interesting to study the effect of a similar arrangement of three tetrachlorophthalimido residues in the hypothetical phase III (Fig. 1).

For PAHs, on the other hand, the TCPP phase exhibits much higher capacity factors than the phases described by Welch and Pirkle (Table I). This may be due to the enhanced planarity and active surface area of the π -acidic tetrachlorophthalimido residue compared with the dinitrophenyl group. Interestingly, the elution order of phenanthrene and anthracene is inverted on transition from the tripodal dinitrophenyl ether to the TCPP phase.

The separation of higher fullerenes on charge-transfer phases was not investigated by Welch and Pirkle, or, apparently, by other workers. In

TABLE I
CAPACITY FACTORS FOR FIVE DIFFERENT ANALYTES

Naph = Naphthalene; Anth = anthracene; Phen = phenanthrene; C_{60} and C_{70} = fullerenes. Conditions: analytical TCPP column (250 mm \times 4.6 mm I.D.), eluent, dichloromethane–hexane (5:95, v/v); flow-rate, 2.00 ml/min; temperature, ambient. $\alpha_{60/70}$ = Separation factor for C_{60} and C_{70} .

Stationary phase	Analyte					$\alpha_{60/70}$
	Naph	Anth	Phen	C_{60}	C_{70}	
Tripodal DNPE [20]	0.58	1.28	1.41	6.59	20.77	3.15
TCPP	2.49	19.12	17.24	5.11	14.04	2.75

our study, we found that the TCPP phase allows the separation of the carbon spheres C_{76} , C_{2v} - C_{78} , D_3 - C_{78} and C_{84} and possibly even other very minor species, with excellent resolution and peak shape. In addition to the good separation quality, the TCPP phase also provides a considerable quantitative improvement (1 mg of material per run compared with ca. 0.05 mg per run on a 250 mm \times 20 mm I.D. preparative column [8]) so that higher fullerenes should soon become available in amounts large enough to study their exciting physical and chemical properties in greater detail.

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