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Separation of C₆₀ and C₇₀ on polystyrene gel with toluene as mobile phase

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ABSTRACT

The separation of C₆₀ and C₇₀ on polystyrene gel using toluene as mobile phase is described. A fully automated system was designed that permits the separation of 5–10 g of C₆₀–C₇₀ mixture within 24 h on a column of only 20 mm I.D. The purity of the isolated C₆₀ is greater than that achieved by standard procedures (separation on alumina) and the recovery is nearly 100%.

INTRODUCTION

Alkali-metal-doped C₆₀ is a molecular superconductor with by far the highest onset temperature of superconductivity, T_c [1], C₆₀-based material (charge-transfer complex) has the highest critical temperature, T_c , of any molecular organic ferromagnet [2,3] and buckminsterfullerene and its derivatives possess remarkable non-linear optical properties [4]. Owing to these outstanding properties and the resulting extensive research activity [5], there is an increasing need for an efficient separation of fullerenes. The isolation of pure C₆₀ is tedious and has proved to be the major constraint on the pace at which research can proceed.

In the last 2 years, several attempts at the separation of fullerenes have been published, *e.g.*, on C₁₈ reversed-phase [6], silica gel [7], alumina [8], graphite [9] and a π -acidic Pirkle phase [10]. Attempts to achieve the separation on a 10- μ m nitrophenyl phase (60 \times 25 mm I.D. column) with pure toluene as the mobile phase were unsuccessful because all fullerenes were eluted together. Mixtures

of hexane and toluene as mobile phases gave good separations but were not superior to the other reported methods.

All the methods described so far suffer from severe disadvantages: either the fullerenes are only slightly to moderately soluble in the mobile phase, which severely limits the amount of purifiable material, or the separation requires higher temperatures and is therefore not transferable to columns with larger inner diameter. Pure toluene, in which the fullerenes are more soluble (the solubility at room temperature is *ca.* 6 mg of fullerene mixture in 1 ml of toluene compared with about 0.4 mg/ml in hexane or 0.8 mg/ml in chloroform) is due to its greater elution power, generally not applicable to the above separation procedures. Thus, chromatography on alumina using pure toluene or even hexane with only 10% toluene leads to virtually no retention of the fullerenes. In summary, all the chromatographic methods applied so far are not suitable for the purification of larger amounts of C₆₀, because either the solvent consumption is very large (solvent mixtures are even not suitable for continuous recovery) or the efficiency, expressed in grams of raw material separated per day, is very low.

Owing to the size differences of C₆₀ and C₇₀ (7 Å spheres *versus* 7 \times 7 \times 9 Å ellipsoids) (Fig. 1), it

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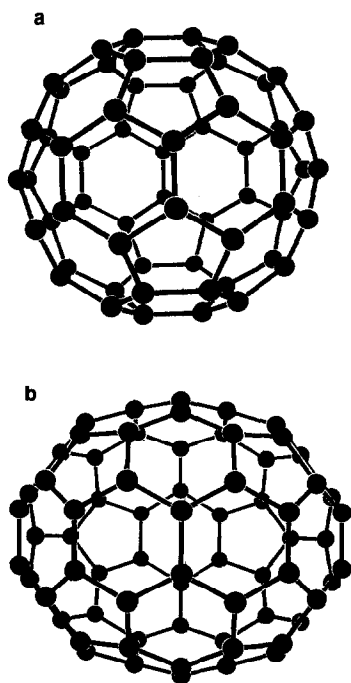


Fig. 1. (a) Structure of C_{60} ; (b) structure of C_{70} .

seemed appropriate to try to separate C_{60} and C_{70} by size-exclusion chromatography (SEC) on polystyrene gel [11,12]. In addition to the ability of SEC to separate compounds with a size difference of about 10%, this method possesses the following additional advantages over conventional chromatographic methods [13,14]: (1) compounds are eluted isocratically with a pure solvent so that equilibration after each run is not necessary, saving much time and solvent, and further the isocratic elution allows for immediate recycling of the mobile phase by distillation, permitting the design of a fully automated system; (2) the reproducibility of retention times is excellent, which makes unattended use of the apparatus possible; and (3) the lifetime of SEC columns is generally greater than that of conventional chromatographic columns.

EXPERIMENTAL

Equipment

For SEC, the pumps, manometer module, detector, printer and additional accessories were obtained from Abimed Analysen-Technik (Langen-

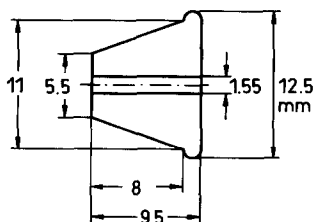


Fig. 2. Septum for leak-free connection of capillaries to the distillation flask.

feld, Germany), the motor valve and controller from Latek Labortechnik (Eppelheim, Germany), 500 Å columns from Polymer Standards Service (Mainz, Germany) and 50 Å columns from Showa Denko (Shodex, Japan). For HPLC, the column and stationary phase were obtained from Merck (Darmstadt, Germany), the elution pump from Spectra-Physics (Darmstadt, Germany) and the detector from Waters (Milford, MA, USA).

An M 305 master pump and an M 306 slave pump, both with 25 SC piston pump heads, an M 803 C manometer module with integrated pulse damper, a holochrome UV detector with a 0.3- μ l flow-through type cell (light path 0.1 mm) an HMV-6 motor valve (six-way valve) with a PT 810 S-controller and a BD-40 printer were used.

Two 600 \times 20 mm I.D. main columns (10 μ m, 500 Å) in series with a 60 \times 20 mm I.D. guard column (10 μ m, 500 Å) were used (two columns in series improve the resolution, allowing the amount of material that can be purified in a single injection to be increased or the purity of the fractions to be increased [11]; 10- μ m material was used because of the improved life time and flow compatibility compared with 5- μ m material). Capillaries were in front of the T connection (I.D. 1 mm) and behind the T connection (I.D. 0.5 mm to avoid a dead volume). Slip-on filters (10- μ m frit) were located in front of the pump heads and in-line membrane filters (0.5- μ m frit) behind the pump heads. For the distillation apparatus, all glassware was made of brown glass to avoid exposure of the fullerenes and the solvent to daylight [15–17]. The septa of the distillation flasks were conical and made of PTFE (Fig. 2). By tightening the G1 14 screw-caps the capillaries were clamped and sealed. The distillation head was heated by a heating tape to ensure rapid distillation of the solvent. The complete apparatus

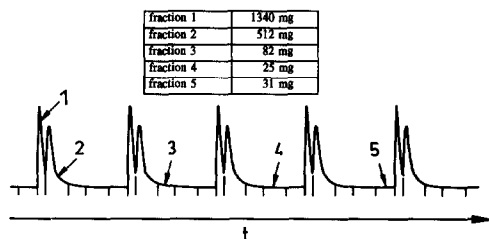


Fig. 3. Elution diagram showing the automatic separation of fullerene raw material obtained by Soxhlet extraction of carbon soot with hexane. The mass balance for the separation of about 2000 mg raw material is also shown. Injection frequency, 8 min; detection, UV at 350 nm; other conditions as in Fig. 4.

must be a closed system because the fullerenes are oxidized in refluxing, oxygen-containing toluene [15–17].

Procedure

Carbon soot, produced by evaporation of graphite rods in an arc reactor under a helium atmosphere [18,19], was Soxhlet extracted with hexane [20] for 48 h. After evaporation of the solvent, the residue was dissolved in toluene with the aid of ultrasound, filtered through a 0.25- μm PTFE membrane filter, injected by the M 306 pump into the elution stream at 8-min intervals and eluted with pure toluene. Hence there were always about three substance bands simultaneously on the column. Switching of the clute subsequently from one distillation flask to the other was achieved with the six-way valve (remote controlled by the time-programmable controller) (Fig. 3). The purity of fraction 1 (C_{60} fraction) was always >99.8% (determined by HPLC).

The conditions for HPLC were as follows: column and stationary phase, RP-18 (5 μm) cartridge (12.5 cm \times 8 mm I.D.); mobile phase, 2-propanol-toluene (60:40) at a flow-rate of 1 ml/min (Spectra-Physics gradient pump); injection, 10 μl of toluene eluate; detection, UV at 590 nm (Waters Model 281). At 590 nm the ratio of the molar absorptivities of C_{60} and C_{70} has been given as 1:1.2 [21]. However, the calculation of this C_{60} : C_{70} ratio of the used fullerene raw material using the published [21] molar absorptivity ratio gave 0.75, which is obviously not correct; therefore, the C_{60} / C_{70} ratios in Fig. 7b should be corrected to higher values.

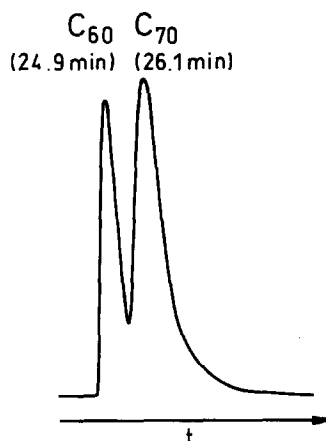


Fig. 4. Separation of fullerene raw material obtained by Soxhlet extraction of carbon soot with toluene. Two columns (600 \times 20 mm I.D.) in series + 60 \times 20 mm I.D. guard column; stationary phase, PSS-Gel (10 μm , 500 \AA); mobile phase, toluene at 15 ml/min; injection, 7.5 ml of a saturated solution of fullerene raw material in toluene (ca. 80% C_{60} , 18% C_{70} and 2% higher fullerenes); detection, UV at 380 nm.

RESULTS AND DISCUSSION

It appears that neither the mobile phase nor the pore diameter of the polystyrene gel influences the separation. Both chloroform and toluene mobile phases on 50 or 500 \AA pore diameter polystyrene gel gave nearly identical chromatograms (see Fig. 4 for elution with toluene). The smaller C_{60} is eluted before C_{70} , followed by the higher fullerenes (C_{76} , C_{78} , C_{82} , C_{84}). All of them have an elution volume comparable to the column volume (column volume = 395.6 ml; elution volume of C_{60} \approx 370 ml).

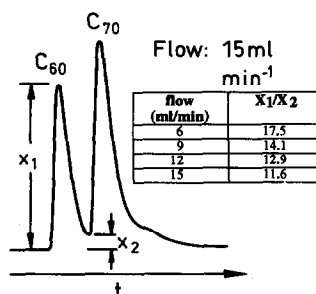


Fig. 5. Influence of the toluene mobile phase flow-rate on resolution. Injection volume, 1.5 ml; other conditions as in Fig. 4.

TABLE I
INFLUENCE OF INJECTION VOLUME ON RESOLUTION

Conditions as in Fig. 4.

Injection volume (ml)	X_1/X_2^a	Injection volume (ml)	X_1/X_2^a
1.5	11.6	7.5	3.9
3.0	10.0	9.0	2.9
4.5	7.7	10.5	2.2
6.0	5.6	12.0	1.7

^a See Fig. 5.

Hence it is obvious that the compounds are not separated by a true size-selective filtration. The greater contact area of C_{70} vs. C_{60} assuming that the adsorption face of the solute is the maximum available may explain the different elution behaviours of C_{60} and C_{70} on polystyrene gel.

Toluene was used for further separations owing to the higher solubility of the fullerenes. Optimum conditions for the separation were found by first increasing the mobile phase flow-rate at constant injection volumes (1.5 ml of saturated fullerene so-

lution) (Fig. 5) and then increasing the amount of sample injected at a flow-rate that still gave a nearly baseline separation of C_{60} and C_{70} at an injection volume of 1.5 ml (Table I and Fig. 6). Up to a mobile phase flow-rate of 15 ml/min and an injection volume of 12 ml no distortion of the C_{60} peak shape was observed, suggesting that the stationary phase has not been overloaded. Nevertheless, we observe that with increasing injection volume the C_{70} peak becomes more and more symmetrical, which may be attributed to the complete occupation of "active centres" by C_{60} at larger injection volumes, resulting in the "normal" elution of C_{70} . Further, we observe that C_{70} and the higher fullerenes (C_{76} , C_{78} , C_{82} and C_{84}) elute together at an injection volume of 7.5 ml. The optimum separation conditions were determined to be a flow-rate of 15 ml/min mobile phase and an injection volume of 7.5 ml. The best fraction cut points (Fig. 7a) were found by analysis of certain subfractions by HPLC on a reversed-phase column (Fig. 7b). The vertical dashed line in Fig. 7a indicates the change from the violet colour of C_{60} to the red-brown colour of C_{70} in the elute. The injection interval was determined by switching the detector to higher sensitivity (Fig. 8). Fullerene raw material, which was obtained by Soxhlet extraction of soot with toluene, showed marked tailing, resulting in the elution of fullerenes over 9 min,

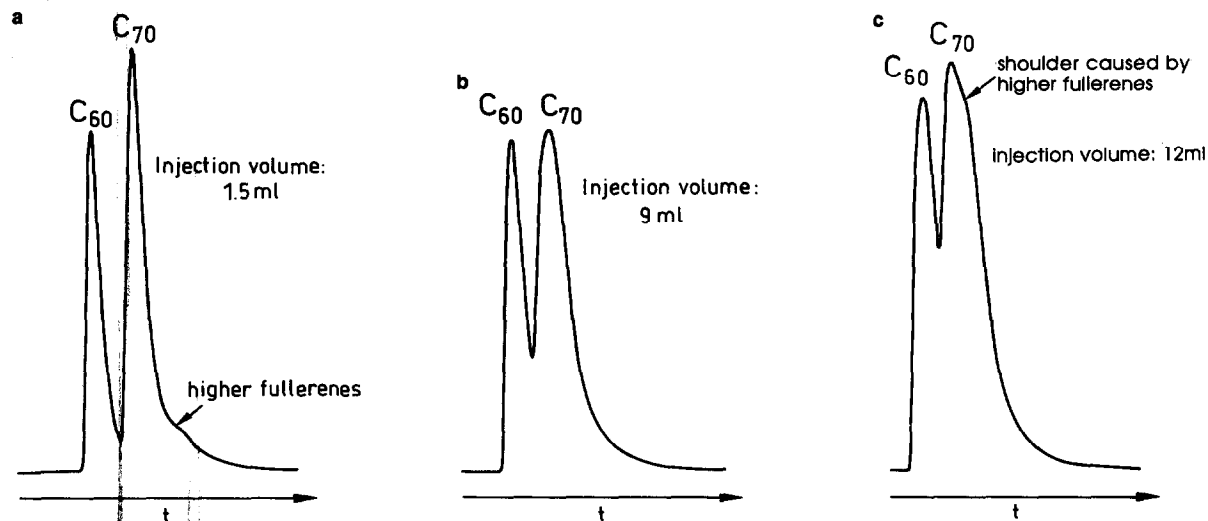


Fig. 6. Effect of injection volume: (a) 1.5; (b) 9; (c) 12 ml. Conditions as in Fig. 4.

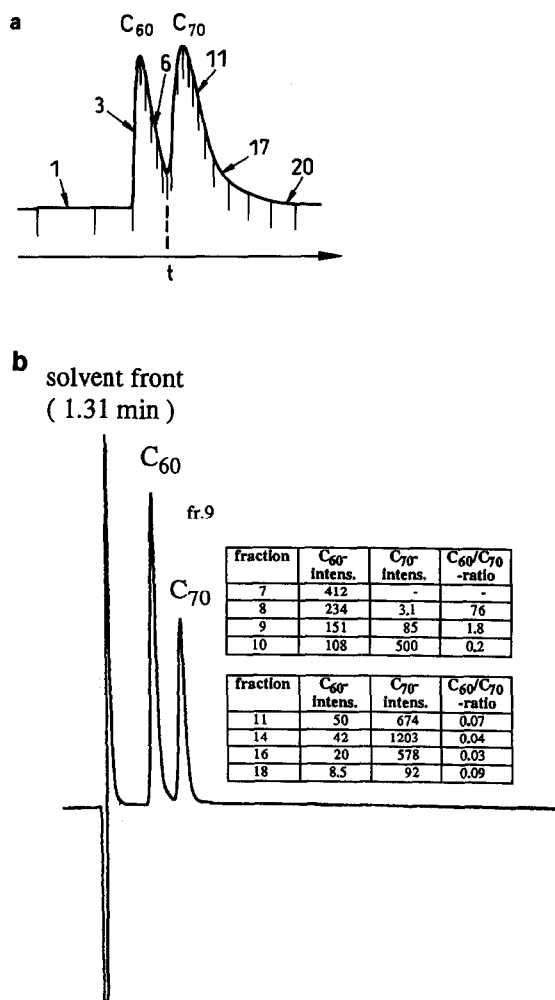


Fig. 7. (a) Separation of fullerene raw material obtained by Soxhlet extraction of carbon soot with toluene, with cut points for fractions 1–20. Conditions as in Fig. 4. (b) HPLC of fraction 9 and C₆₀/C₇₀ content of certain fractions determined by HPLC.

whereas the material obtained by Soxhlet extraction with hexane showed minor tailing, allowing the injection frequency to be increased to 8 min (Soxhlet extraction with hexane yields predominantly C₆₀ and C₇₀ and only traces of higher fullerenes, whereas Soxhlet extraction with toluene yields more of the higher fullerenes) [20].

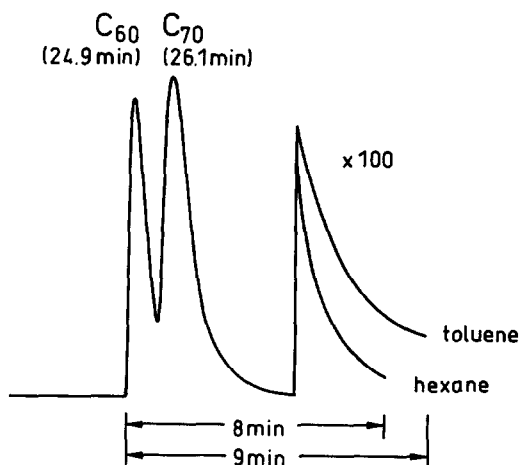


Fig. 8. Chromatogram of fullerene raw material obtained by Soxhlet extraction of carbon soot with toluene and hexane. Conditions as in Fig. 4.

CONCLUSIONS

The major advantage of the described procedure is the use of pure toluene as eluent. In addition to the improved efficiency compared with literature methods, this solvent allows an automatic apparatus to be set up, which redistils the elute continuously (Figs. 9 and 10). Using this technique it is possible to separate 5–10 g of fullerene raw material per day without any solvent consumption. Moreover, the method can be easily scaled up by using columns of larger inner diameter. Two points are worth mentioning. Owing to the exceptionally long retention time of C₆₀ and the other fullerenes (“normal” compounds are eluted much earlier) the method is suitable for the detection of very small amounts of fullerenes in complex matrices (e.g., engine exhaust deposits or reaction mixtures). The interruption of buckminsterfullerene’s conjugation by functionalization leads to dramatically reduced retention times, permitting the separation of fullerenes from their reaction products: Diels–Alder addition products of C₇₀ with diphenylisobenzofuran are easily separated from the educts, which also applies to fragmentation and other addition products of C₆₀ and C₇₀. Additional work using other stationary phases (polystyrene gel for reversed-phase

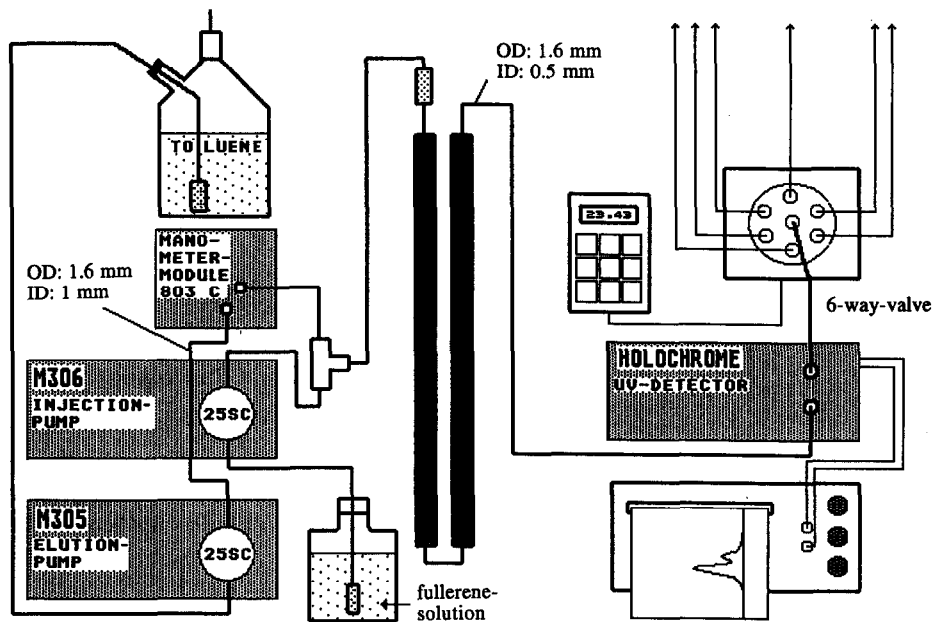


Fig. 9. Apparatus for automated separation of fullerene raw material.

chromatography, C_{18} -modified polystyrene gel, π -basic stationary phases which possibly separate the fullerenes by intermediary formation of charge-transfer complexes) and other solvents is in progress. Because the column is probably only volume overloaded at large injection volumes, replacement of toluene with a better solvent for fullerenes will dramatically enhance the productivity. Work is in

progress using *m*-xylene as solvent (the solubility amounts is *ca.* 8 mg of fullerene raw material in 1 ml of *m*-xylene) and working at higher temperatures with alkylated and halogenated aromatics and tetrachloroethane, which are excellent solvents for fullerenes under these conditions.

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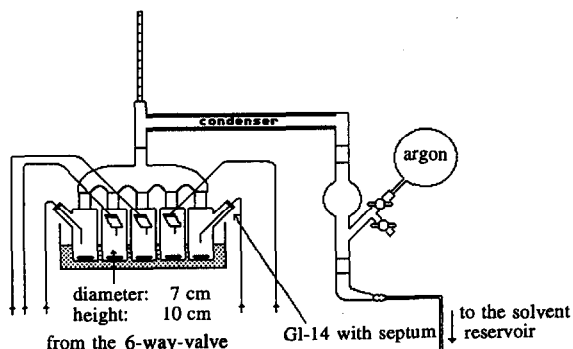


Fig. 10. Distillation apparatus for continuous recovery of the mobile phase.

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