Improved Separation of Fullerene-60 and -70

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Separation of fullerenes by chromatography on graphite is shown to be a simple and effective method for their isolation in large amounts.

The production of fullerenes[1] (C_{60} and C_{70}) in macroscopic amounts has recently been demonstrated.[2–4] Toluene extraction of the soot so-produced yields a crude mixture of C_{60} and C_{70} in a ratio of approximately 10:1. Most attempts at the separation have used silica[5] or alumina[3] as the stationary phase and mixtures of hexane and benzene (or toluene) as the mobile phase. Fullerenes, however, have only limited solubility in hexane and adequate column separation is usually only achieved by limiting the amount of sample to a few milligrams. An improvement over the hexane–silica technique using phenylglycine based HPLC columns has also been described and appears to offer good separation[6] but only for sub-milligram amounts. An alternative separation technique is now described which allows much larger quantities of C_{60} to be purified.

The use of graphite as a stationary phase in liquid chromatography has recently been demonstrated[7–10] and it is thought that the retention mechanism for graphite interactions with solutes is related to its ability to act as an electron pair acceptor under non-polar conditions.[10] Fullerene-60 and

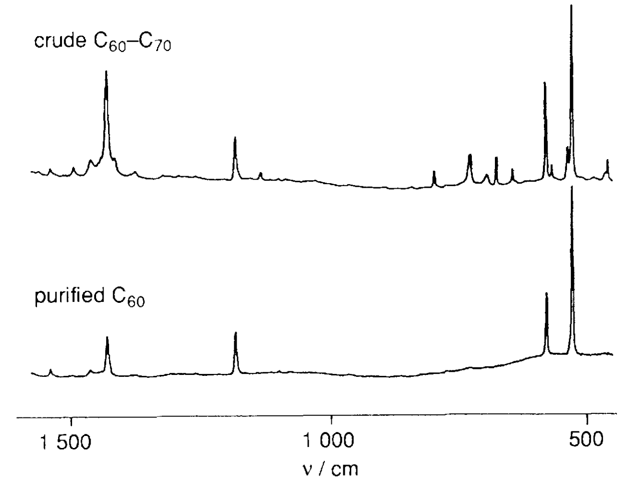

Fig. 1 IR spectra of crude fullerene and fullerene-60 separated on a graphite column. The spectra were obtained in the transmission mode using KBr pellets at a nominal resolution of 2 cm^{-1} and co-adding 64 scans. The spectra are offset for clarity. The weak band at 1 536 cm^{-1} in the spectrum of C_{60} is as yet unassigned.

-70 differ in their degree of electron delocalisation, such that C_{60} is much less diamagnetic than C_{70}.[11] Because of this dissimilarity, it is expected that these molecules will exhibit differing interactions with graphite, and so can be separated on this basis.

Crude fullerenes were produced using the technique of Haufler *et al.*[4] and isolated by toluene extraction. Additional crude fullerene-70 recovered from previous separations was added to the mix to provide a higher fullerene-70 content to determine the capacity of the support. Graphite powder (90 g, >99%, <100 μm, Carbon Products of Australia, Melbourne) was packed into a 60 × 3.5 cm column and *ca.* 100 mg of crude fullerene dissolved in 40 cm^3 toluene was added to the graphite. The column was eluted with hexane–toluene (90 : 10) at a flow rate of 1.4 cm^3 min^{-1}. Thirty two milligrams of fullerene-60 was recovered as a magenta solution after 925 cm^3 of solvent was eluted. Although fullerene-70 can be recovered by elution with pure toluene, we have found that it is preferable to recover fullerene-70 and any higher fullerenes by soxhlet extraction of the graphite with toluene. This overcomes tailing effects and the limited solubility of these fullerenes in toluene. The fullerene-70 fraction so isolated (*i.e.* soxhlet extracted, 70 mg) contains some contaminants and possibly higher fullerenes. The Fourier transform infrared (FTIR) spectra of the crude fullerene mix and the recovered fullerene-60 are shown in Fig. 1. The spectrum of fullerene-60 is essentially identical with that obtained from separation on silica.[12] The spectrum of the fullerene-70 fraction (not shown), contained small signals from residual fullerene-60 and an unidentified contaminant, in addition to absorptions from fullerene-70.

In view of the ease of separation on graphite of these fullerenes, HPLC on commercially available graphite columns (Hypercarb S, Shandon Scientific Ltd., Cheshire, England) was attempted. However, we were unable to effect a separation on this column using mixtures of hexane in toluene. Additional work is underway using other solvent mixtures. It is possible that the spherical particles used in these columns do not show the same affinity for fullerenes as the predominantly flaky graphite used above.

Finally, preliminary experiments on longer preparative columns have indicated that pure toluene may be used to separate these fullerenes, however, further work is required to determine the optimum conditions for separation.

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