

Improved Chromatographic Separation and Purification of C₆₀ and C₇₀ Fullerenes

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Improved procedures for the chromatographic separation of fullerenes on alumina make essentially pure C₆₀ and C₇₀ available in amounts suitable for routine synthetic chemistry: ca. 600 and 100 mg, respectively on a per column, per day basis.

The perception that research into the reaction chemistry of C₆₀ and C₇₀ is a material-limited field is beginning to fade. The 1991 report of a simple benchtop reactor for the production of fullerene-containing soot from graphite rods¹ made the field widely accessible and a multi-rod version² allows accumulation of 'fullerite' soot at the rate of about 25 g per day. Extraction of this soot with toluene³ is straightforward and typically produces ca. 10% yield of fullerene extract. The limiting step in the production of pure fullerenes is the tedious chromatography of this extract. Of the reported preparative or potentially preparative scale adsorbents (silica gel,⁴ alumina,⁴⁻⁷ graphite⁸, coal⁹) alumina is clearly the material of choice^{6,7} but the reported yield of C₆₀ is limited to about 250 mg per column per day and in our experience can be much less because of crystallization at the top of the column. C₇₀ is produced in <50 mg quantities and is seriously contaminated with C₆₀. In this paper we describe procedures which consistently lead to approximately trebled yields of excellent and specified purity.

The fundamental problem with the chromatography is not

the separation but the loading. Even when as much as 100 g of alumina is used to pre-adsorb 300 mg of extract *via* evaporation of a toluene solution, microscopic inspection of the alumina reveals significant crystallites of fullerenes amongst the faintly brown-coloured alumina particles. Adsorption of C₆₀ onto the alumina surface is apparently intrinsically weak, as might be expected for non-polar molecules on a polar surface and, in addition, fullerenes are not very soluble. Paradoxically, however, the separation of C₆₀ and C₇₀ is remarkably effective once elution with hexanes-toluene is begun. We find that the chromatographically effective loading can be significantly increased by paying attention to procedures which favour adsorption over crystallization. These include (a) the use of extract that has not been recrystallized or vacuum dried. Traces of oily or waxy hydrocarbons probably slow down crystallization, making *impurity* a virtue. (b) The extract is significantly more soluble in carbon disulfide than toluene which, combined with greater volatility, speeds the process of pre-adsorption onto alumina. (c) By allowing alumina to soak up a near-saturated CS₂ solution of extract to no more than the consistency of wet sand, and by rapidly evaporating the solvent [10⁻³ Torr (1 Torr = 133.3 Pa) vacuum pump with liquid N₂ trap], the adsorption process is

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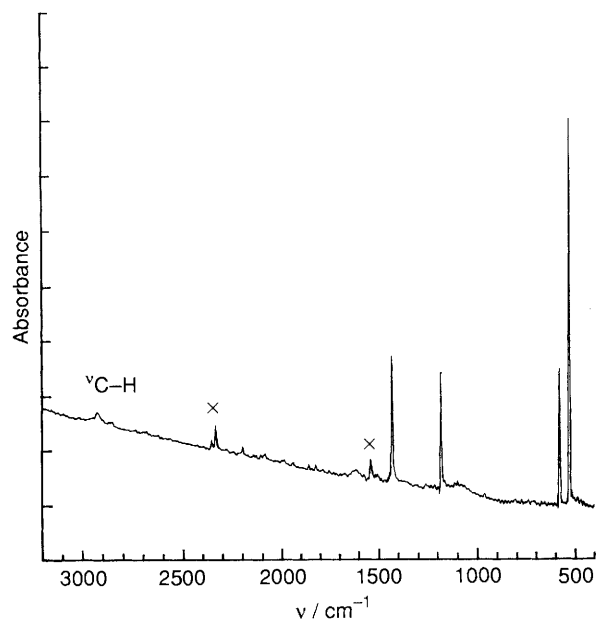


Fig. 1 FTIR spectrum (CsI disc) of final C_{60} product showing ν_{C-H} at 2950 and 2920 cm^{-1} . Product peaks are consistent with reported spectra.¹¹ Peaks marked with \times (2348, 2328 and 1538 cm^{-1}) are probably from CS_2 (2280, 2142 and 1540 cm^{-1}).

enhanced. After drying for a few hours microscopic examination reveals distinctly brown alumina particles with little or no fullerene crystallites.

In a typical chromatography, a CS_2 solution of 1 g of extract (ca. 300 ml) is pre-adsorbed onto 375 g of alumina (Aldrich standard grade, neutral, ~150 mesh, Brockmann I) via the above mentioned procedures and loaded as a slurry in toluene-hexanes (5% toluene v/v) onto a 8×50 cm column of alumina (1.5 kg) in 5% toluene in hexanes. Elution is begun with 10% toluene in hexanes to quickly move the fullerenes onto the column. This helps prevent crystallization at the top of the column. The separation is achieved by switching the eluent to 5% toluene in hexanes once the fullerenes have left the loading fraction (2–3 h). A reasonable flow rate (15 ml min^{-1}) allows collection of the purple C_{60} fraction during a further 3–4 h period. Evaporation of the solvent gives 550–630 mg of product. Recrystallization from CS_2 -cyclohexane and vacuum drying at room temperature yields 520–600 mg of product. IR spectroscopy indicates significant solvent retention (ν_{C-H} 2950, 2920; ν_{C-S} 1538 cm^{-1}) as expected from solvate studies.¹⁰ Vacuum drying at 275 $^{\circ}\text{C}$, 10^{-3} Torr for 48 h produces a 2% weight loss. IR spectroscopy of this product still shows retention of solvents (see Fig. 1) and this may be unavoidable in liquid-phase isolation procedures which use high solubility solvents. However, given the problems of redissolution of purified fullerenes⁷ the solvated materials are more desirable for synthetic applications.[‡] Continued elution of the column with 20% toluene in hexanes yields ca. 130 mg of C_{70} that is contaminated with ca. 10–14% C_{60} [see ^{13}C NMR spectrum (a) in Figure 2]. This was rechromatographed on a scaled-down ($\times 2$) column. The pre-adsorption of 130 mg of C_{70} on 24 g of alumina was achieved by the above-mentioned procedures in 20 ml of CS_2 . This led to 105 mg of recrystallized C_{70} judged by ^{13}C NMR to contain no more than 2% C_{60} [see spectrum (b) in Fig. 2].§

Improvements in the scale and purity of fullerene production have now brought C_{60} and C_{70} firmly into the realm of

‡ Note added in proof: if desired, the purity of C_{60} can be enhanced by washing the crystalline product with diethyl ether or acetone followed by benzene recrystallization and vacuum drying at elevated temperatures (R. Taylor, personal communication).

§ Note added in proof: C_{70} purity is estimated to be 99.1% by SALI MS using 118 nm radiation (R. Ruoff, personal communication).

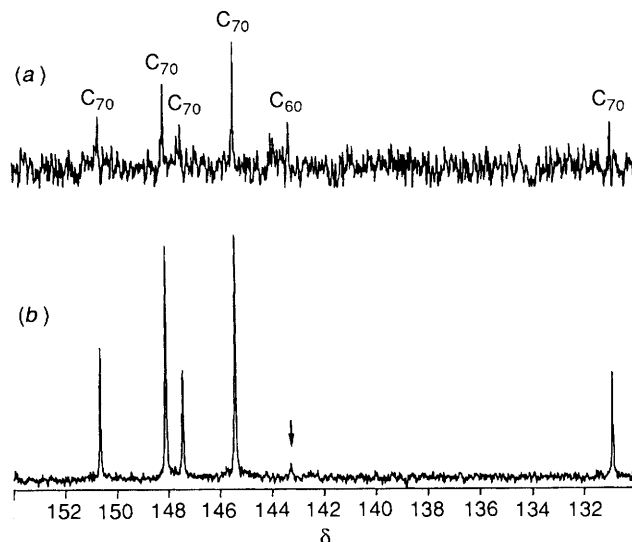


Fig. 2 ^{13}C NMR spectra of C_{70} in CS_2 : (a) from the original column and (b) after rechromatography. The arrow in (b) marks the resonance from remaining traces of C_{60} (δ 143.2). Signal to noise in the latter spectrum was improved by adding toluene to improve re-dissolution and by the use of $\text{Cr}(\text{acac})_3$ (Hacac = pentane-2,4-dione) as a relaxant. Peaks are consistent with reported spectra.^{4,5}

typical inorganic and organic synthetic chemistry. Wudl *et al.*¹² have very recently developed a solvent recycling chromatographic procedure based on the Soxhlet principle which reduces the tedium and the solvent expense of traditional column chromatography. A combination of this technology with the present loading methodology may lead to even further improvements.

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