Improved Chromatographic Separation of C_{60} and C_{70}

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Column chromatography of fullerene-containing soot extract using Norit Elorit carbon as the stationary phase, with toluene followed by 1,2-dichlorobenzene, as eluants, gives pure C_{60} and up to 98% C_{70} in one pass; production of C_{60} is very rapid, and both simpler and less expensive than other methods.

Our original chromatographic method for isolating pure C_{60} and pure C_{70} from the soot extract produced by the arc discharge method, used neutral alumina as the stationary phase, and hexane as eluant.[1] Disadvantages of the method are: large amounts of expensive alumina and high purity hexane are required in order to process a small amount of material, the low bp of hexane results in substantial losses during solvent recovery, and it is labour intensive. On-column degradation of the fullerenes (especially C_{70}) can occur, particularly if anhydrous alumina is employed.[2] Two further re-passes of the C_{70}-rich fraction are needed to produce C_{70} of *ca.* 98% purity and this is accompanied by substantial losses.

Various modifications were subsequently introduced in order to overcome some of these deficiencies. These include (*i*) elution with hexane–toluene[3] (this gives a higher throughput, but introduces solvent recovery problems); (*ii*) deposition of the soot extract onto the stationary phase from a CS_2 solution[4] (the solvent eluant is better able to dissolve the fullerenes from the microcrystalline deposit produced, but it is essential to remove all traces of CS_2, otherwise the C_{60} produced is contaminated with sulfur[5]); (*iii*) use of a soxhlet-chromatography method in which hot solvent is continuously recycled thereby reducing solvent losses and labour.[6] A disadvantage of the latter method is that the low pressure differential in the column (it is surrounded by solvent) slows the process so increasing the on-column degradation of the fullerenes. We have carried out several quantitative tests of this method, involving a total of 7.58 g of soot extract which yielded 3.02 g of C_{60} (40%) and 1.0 g of C_{60}–C_{70} mixture (60–65% C_{70}, as determined by ^{13}C NMR spectroscopy), total recovery 53%. In our hands the other methods described give C_{70} of similar purity from a single pass.

Carbon columns have also been used for separation of fullerenes. Depending upon the carbon type and mesh size, carbon can absorb fullerenes either more or less strongly than alumina. In some cases, virtually irreversible absorption occurs, especially of C_{70}. Vassallo *et al.* described the use of a graphite column with hexane–toluene as eluant, but elution was slow and fullerene recovery was poor.[7] A Norit A/silica gel column (1:2 weight ratio) which permits elution with toluene (and was reported to give 63–67% recovery of C_{60}),[8] has been widely employed; the silica gel (which does not separate fullerenes on its own), reduces the absorption by the carbon, and both aids throughput and reduces cracking of the stationary phase. We find this method produces C_{60} of higher purity than use of alumina columns, but has the disadvantage of requiring pressure, and the recovery of C_{70} is unacceptably slow. Using this method we obtained 170 mg of C_{60} (38%) and 85 mg of C_{60}–C_{70} mixture (81% C_{70}) from 450 mg of soot extract (overall recovery 57%). We have found that by using a mixture of Norit A (1.5%) on neutral alumina, the performance with respect to throughput can be improved, no pressurisation of the column being necessary. A run involving 1 g of soot extract, packed at the top of a 90 mm i.d. × 400 mm column run under hot soxhlet conditions (toluene as eluant), yielded 636 mg of C_{60} within 2 h, 66 mg of mainly C_{60} admixed with some C_{70} during a further 1 h, and then 100 mg of 85% C_{70} during a further 15 h, overall recovery 80%. Unfortunately uniform packing of these columns is difficult, and both separation and yield are very sensitive to the amount of carbon in the mixture and the column length. For example, using 1.2% Norit A in alumina does not achieve separation, whilst a concentration of 1.8% leads to almost no recovery. An alternative method of overcoming the slow throughput of carbon-based columns, recently described, uses a very wide, short column packed with carbon/silica gel, operated under reduced pressure; this gave a 59% recovery of C_{60}.[9]

We now report a chromatographic method that is so advantageous that we have abandoned all other procedures. Norit 'Elorit' carbon (peat based) is used as the stationary phase and is seventy times less expensive than alumina for processing the same weight of soot extract. The fine granular material avoids the dust problems associated with other forms of graphite and alumina, and column packing is quick and easy.

In a typical run, soot extract (950 mg, Dynamic Enterprises Ltd.) dissolved in toluene (1 l) was poured onto a column of 31 mm i.d. and 300 mm length, packed with Elorit carbon (60 g). Elution with toluene (1 l) then yielded 380 mg of pure C_{60} within 20 min. Toluene was then eluted through the column during 20 h using the hot soxhlet procedure and this yielded a further 170 mg of C_{60}, overall recovery 58%. (Elution by the hot soxhlet method is slower than the conventional way but has the advantage of requiring no attention.) Since toluene alone is used as eluant, recovery by rotary evaporation is effectively quantitative, thereby minimising costs. The column is then flushed with 1,2-dichlorobenzene (250 ml) which removes toluene together with some residual C_{60} and some C_{70} (70 mg); recovery of the solvents from this fraction using a rotavap is easy because of the large difference in bps. Two different strategies were then employed: in the first, 1,2-dichlorobenzene was cycled through the column using the hot Soxhlet method under partial vacuum (to lower the bp so that the solvent could reach the top of the column). Two extraction periods of 16 h each yielded 79 mg of 85% C_{70} followed by 53 mg of 98% C_{70}. Alternatively (and more conveniently if vacuum is not readily available), the column packing may be transferred into a standard Soxhlet thimble (the granular nature of Norit carbon makes this easy) and the C_{70} recovered with 1,2-dichlorobenzene. Typically, 48 h extraction yielded 100 mg of 85% C_{70}. The overall recoveries are usually in the range 70–80% (in one run 92%). The rapid throughput using Elorit carbon suggests that a column of the dimensions given in the original hot-Soxhlet chromatography work[6] will permit

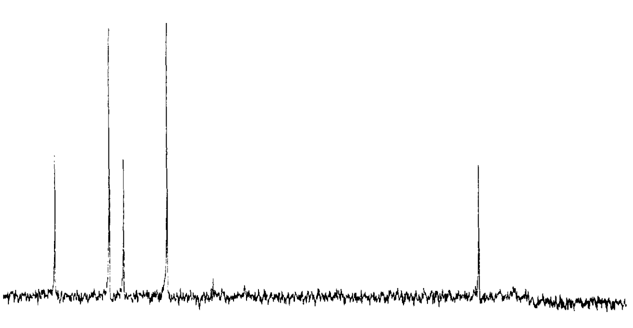

Fig. 1 ^{13}C NMR spectrum of 98% pure C_{70} obtained as described in the text

purification of soot extract in 7 g batches, yielding realistic outputs of grams of pure C_{60} per day, with almost total recovery of solvents. We believe that the purification of C_{60} is now no longer the cost-limiting factor[10] in its production.

The purity of the C_{70} may be increased by recycling. However, this leads to losses, especially since C_{70} is strongly absorbed on carbon columns. An alternative procedure is to prepare a saturated solution of C_{70} in benzene, and concentrate this very slowly to *ca.* half volume using a rotary evaporator, and then allow the solution to stand. The supernatant solution, carefully removed by pipette, contains a higher proportion of C_{60} than does the starting material, and likewise the deposited solid contains more C_{70}. The results depend on the initial fullerene ratio, and the extent and speed of concentration of the solution. The potential of the method is indicated by a solution containing 60% C_{70} being concentrated to 95% C_{70} in three cycles; the process is especially suitable for large scale production, and there are no losses of C_{70}.

C_{70} purity was determined by ^{13}C NMR analysis only. During chromatography, C_{60} continues to tail invisibly after the visible magenta solution has eluted, and does so into the orange–red C_{70} band. This can be misleading, giving the impression that pure C_{70} is being obtained. Note that a solution of C_{60} containing as little as 30% C_{70} is not visibly distinguishable from pure C_{70} (due to the higher extinction coefficient of C_{70}). HPLC assessment of purity can also be unreliable, because C_{60} tails undetectably into the C_{70} band, a problem compounded by the markedly lower extinction coefficient of C_{60} in the UV, and the dependence of the analysis upon the wavelength of the UV detector used. The SALI mass spectrometric technique is apparently also a reliable method for assessing C_{70} purity.[4]

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