Purification of C60 Fullerene using Non-aqueous Reverse Phase with Redi*Sep* Rf Gold® Columns

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Abstract

The fullerene family, especially C60, has appealing photo, electrochemical, and physical properties which can be exploited in both medical and material science applications. Fullerenes are formed in soot produced in an inert atmosphere. This process results in a mixture of fullerenes which typically range in size from C20 through C70 and larger. Purification of fullerenes is hampered by solubility in most solvents. The use of non-aqueous reverse phase and adroit choice of solvents allow the isolation of C60 fullerene from soot with Redi*Sep* Rf Gold® C18 columns.

Experimental

Method development

Initial method development was performed with Redi*Sep*® TLC plates. Authentic samples of C60 and C70 were also run with the soot mixture. Various combinations of hexane/ toluene, and hexane/2-propanol, hexane/dichloromethane, and hexane/carbon disulfide were run with Redi*Sep*® Rf silica TLC plates (PN 69-2203-400), neutral Redi*Sep*® Rf alumina TLC plates (PN 69-2203-569), Redi*Sep* Rf Gold® amine TLC plates (PN 69-2203-573), and Redi*Sep* Rf Gold® diol TLC plates (PN 69-2203-574). Redi*Sep*® Rf C18 TLC plates (PN 69-2203-586) were run as non-aqueous reverse phase using 2-propanol/ethyl acetate, 2-propanol/dichloromethane, 2-propanol/toluene and toluene/carbon disulfide. Plates were visualized with 254nm UV light.

The Redi*Sep* Rf Gold diol plate developed with 90:10 hexanes: carbon disulfide exhibited retention and resolution with minimal tailing, but the solubility of fullerenes in this solvent system was low so that only a small sample load could be purified with any resolution. Redi*Sep* Rf C18 run with 2-propanol and toluene also showed retention with some resolution. The 2-propanol/toluene solvent system allowed a larger sample load to be run due to improved solubility of fullerenes in these solvents making it the preferred solvent system.

Purification

A soot sample (25 mg) was dissolved in 2.5 mL carbon disulfide and loaded onto a 5 g Redi*Sep*® Rf C18 solid load cartridge (PN 69-3873-237) A Redi*Sep* Gold® C18 column (30 g, PN 69-2203-335) was run with a 2-propanol/toluene gradient according to *Table 1*. Purification was run on a Combi*Flash*® Rf 200 with a UV-vis detector (PN 62-5230-008) at 310 nm.

Table 1: Gradient table used to purify C60 fullerene. Solvent A is 2-propanol; solvent B is toluene

Segment Duration (column volumes)	% B
Start	25
20	25
15	100
15	100
0	0
10	0

The Rf solvent system was determined via TLC using Redi*Sep* Rf TLC plates. Fraction purity was determined by TLC with Redi*Sep* diol TLC plates (10% carbon disulfide in hexanes). TLC was compared to authentic samples of C60 and C70 fullerenes.

Results and discussion

Method development

Redi*Sep* Rf silica TLC plates were initially tested because they work well for many situations; however, they tend to show poor retention with very non-polar samples such as fullerenes. Redi*Sep* Rf alumina TLC plates often work well with non-polar compounds, but failed to resolve the fullerenes with the solvents tested.

Redi*Sep* Rf Gold diol TLC plates and Redi*Sep* Rf amine TLC plates are less polar than Redi*Sep* Rf alumina and Redi*Sep* Rf silica TLC plates and also exhibit different selectivity. These media run as normal phase when developed with organic solvents[1,2]. While the amine plate failed to resolve the fullerenes, the Redi*Sep* Rf diol TLC plate did resolve C60 and C70 with a solution of 90:10 hexanes: carbon disulfide. Unfortunately, this solvent system has limited fullerene solubility which limits the amount of sample that could be loaded on a column. However, the diol plate allowed evaluation of fraction purity.

Redi*Sep* Rf C18 TLC plates run in 60:40 2-propanol: toluene also showed separation of the fullerenes, with

1. Silver, J.E.; Bellinghausen, P.; Fowler, N.; Pipes, R. Diol columns – pretend they're normal phase, presented at the American Chemical Society meeting Fall 2009
2. Silver, J.E.; Bellinghausen, P.; Fowler, N.; Pipes, R. Method Development Strategies for Amine Bonded Phase Columns for Medium Pressure Liquid Chromatography, presented at the American Chemical Society meeting Fall 2009

slightly reduced resolution compared to the diol plates. Fullerenes are more soluble in the Redi*Sep* Rf Gold C18 solvent system compared to the Redi*Sep* Rf diol TLC solvent system, so the fullerenes were purified on Redi*Sep* Rf Gold C18. A single run on a Redi*Sep* Rf Gold C18 column with a focusing gradient from 0 to 30% toluene in 2-propanol showed that 30% toluene would provide better resolution compared to 40% toluene.

The solvents chosen for the Redi*Sep* Rf TLC runs are not traditional flash solvents. The solvents were chosen on the basis of known fullerene solubility and availability. Although non-aqueous reverse phase is not a commonly employed technique, it is useful when purifying non-polar compounds.[3, 4]

Purification

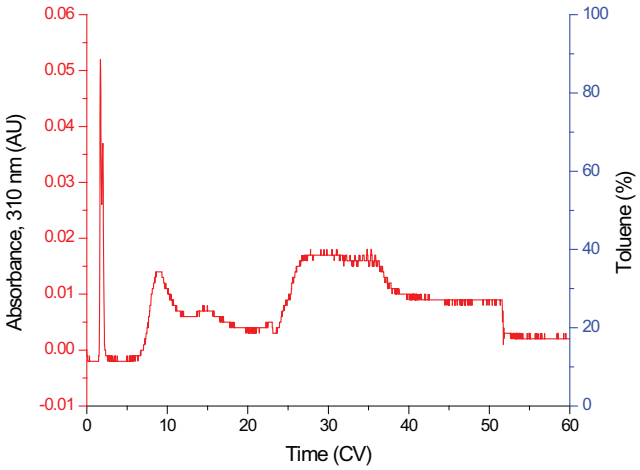

Figure 1: Purification of C60 using an Rf-200 flash system and Redi*Sep* Gold C18 column

The peak from 3-11 CV was combined and dried to give 9.6 mg of pure C60 (38%). Redi*Sep* Rf diol TLC showed C60 tailing into the gradient. The peak observed at ~15 CV contains C70. Peaks after the gradient begins are a mixture of other compounds in the soot, some C70 and C60, and a baseline change due to absorbance from the solvent.

Figure 2: Fractions on right exhibited the characteristic purple color of purified C_{60} fullerene

Conclusion

The Combi*Flash* Rf-200 and Redi*Sep* Rf Gold C18 columns allow for the flash purification of C60 fullerenes. Redi*Sep* TLC plates allow a large variety of solvent systems to be tested quickly with minimal sample usage. The major impediment to resolving fullerenes is solubility in solvent systems that provide good interaction of the fullerenes with the columns.

3. Snyder, L.R.; Kirkland, J.J.; Glajch, J.L.; *Practical HPLC Method Development*, 2nd Ed, John Wiley & Sons, 1997, p.264

4. Silver, J.E.; Bellinghausen, P.; Fowler, N.; Pipes, R. Facile Isolation of Carotenoid Antioxidants from *Solanum lycopersicum* using Flash Chromatography, presented at the American Chemical Society meeting Fall 2009

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