New sorbents based on tetraphenylporphyrin bound to silica gel for the separation of C_{60} and C_{70} fullerenes

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Sorbents prepared by reactions of chloromethyl- and chlorosulfo-derivatives of tetraphenylporphyrin (H_2TPP) with γ-aminopropyl-silica gel (γ-APS) exhibit good chromatographic characteristics in the separation of C_{60} and C_{70} fullerenes; the sorbent based on Al(X) tetraphenylporphyrin sorbed on hydroxydimethylsilyl-silica gel [TPPAl(X)] is suitable for the large-scale separation of C_{60} and C_{70} fullerenes.

Since the discovery of C_{60} and C_{70} fullerenes, efforts have been made to develop new procedures for the separation of these compounds, in particular, using liquid chromatography. Asymmetrical cobalt 3-β-naphthoxyphthalocyanine[1] and tetraphenylmonocarboxyporphyrin[2,3] bound to silica gel are the best sorbents for the separation of C_{60} and C_{70}. Despite the fact that these sorbents are fairly selective in the separation of C_{60} and C_{70}, their capacities regarding the amount of the mixture of fullerenes being separated are low. In addition, wide use of these sorbents is held up by the complexity of their synthesis. In this study, we report on the synthesis of three new sorbents based on H_2TPP, an accessible compound for which methods of synthesis and chemical modifications have already been well documented.[4] Tetrachloromethyl-H_2TPP and tetrachlorosulfo-H_2TPP were prepared from H_2TPP by known chloromethylation[5] and sulfochlorination[6] procedures.[†]

The subsequent reactions with γ-APS yielded sorbents that contained H_2TPP bound by covalent bonds and were suitable for the separation of C_{60} and C_{70} (Table 1). Silica gels with various average pore diameters were used. It was found that sorbents based on narrow-pore silica gels contain low proportions of porphyrin and possess extremely low capacities with respect to C_{60} and C_{70}. Markedly better results were achieved when wide-pore silica gel Lichrosphere Si 300 Amin was used (Table 1); apparently this is due to the fact that its surface is more accessible to both H_2TPP derivatives and to the molecules of the fullerenes being separated. It can be seen from Table 1 that the chromatographic characteristics of the resulting sorbents – retention factors (*k*) and selectivities (α) – are approximately equal to those reported previously.[2,3] However, the capacities of these sorbents with respect to C_{60} and C_{70} are low; therefore they cannot be used for preparative separation. No data on the sorbent capacities were presented in the papers cited.[2,3] Our sorbent based on TPPAl(X) grafted onto hydroxydimethylsilyl-silica gel exhibited very good chromatographic characteristics (*k*), which differed markedly from those presented above, even in the first tests on the separation of C_{60} and C_{70} and, more importantly, high capacity. In fact, a relatively small 150×3 mm column permits full separation of 2 mg of a mixture of C_{60} and C_{70} fullerenes (Figure 1); moreover, the stationary phase is barely eluted from the column and can be easily separated from the eluent and from the fullerenes by passing them through a column with pure silica gel. The high chromatographic characteristics of the sorbent can be explained by the large proportion of TPPAl(X) on the surface of the support and by the favourable conditions for intermolecular interactions between porphyrin molecules and the fullerenes and for interactions of Al(X) (where, most likely, X = OH) with silanol groups on the silica gel surface. In our opinion, sorbents of this type based on TPPAl(X) can be

Table 1 Retention factors and selectivities of sorbents based on tetraphenylporphyrin for separation of C_{60} and C_{70} fullerenes in toluene.

Stationary phase	Retention factors		Selectivity α	Note
	k (C_{60})	*k* (C_{70})		
Carboxy-H_2TPP	1.7	8.1	4.8	Ref. 2
Tetrachloromethyl-H_2TPP	2.1	7.2	3.4	low capacity
Tetrachlorosulfo-H_2TPP	1.8	5.4	3.0	low capacity
TPPAl(X)	7.2	25.1	3.5	high capacity

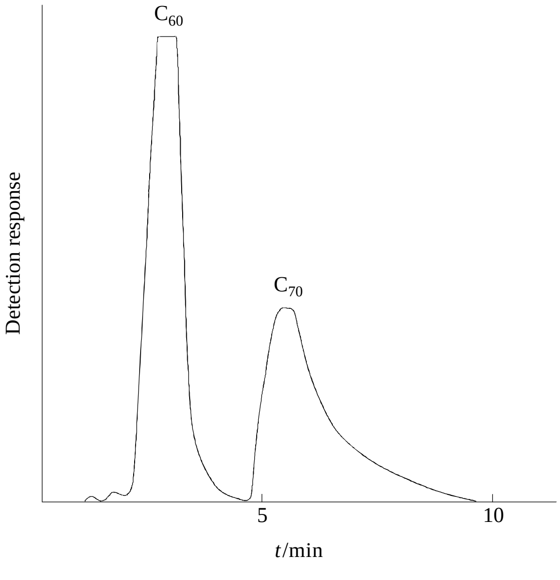

Figure 1 HPLC separation of a mixture of C_{60} and C_{70} fullerenes: TPPAl(X) as the stationary phase, 7 μm in a 150×3 mm column, toluene as eluent, flow rate 2.0 ml min^{-1}, UV detector (365 nm); 2 mg sample of a mixture containing C_{60} and C_{70} in 0.5 ml of xylene.

[†] *Synthesis of the sorbent based on tetrachloromethyl-H_2TPP.* Tetrachloromethyl-H_2TPP (300 mg) was dissolved in dry CH_2Cl_2, dry silica gel Lichrosphere Si 300 Amin (1.2 g) was added, and the mixture was stirred for 24 h at 20 °C. The sorbent was then washed on a filter with CH_2Cl_2, THF and water, dried, suspended in 50 ml of acetone and packed into a 150×3 mm glass column at a pressure of 30 MPa.

Synthesis of the sorbent based on tetrachlorosulfo-H_2TPP. Tetrachlorosulfo-H_2TPP (300 mg) was dissolved in dry THF, dry silica gel Lichrosphere Si 300 Amin (1.2 g) was added and the mixture was stirred for 24 h. The sorbent was then washed with aqueous THF and put into a column as described above.

Preparation of the sorbent based on TPPAl(X). Hydroxydimethylsilyl-silica gel was prepared by treatment of dry silica gel Silasorb 600 (7μ) with dimethyldichlorosilane at 20 °C for 1 h; excess dimethyldichlorosilane was removed *in vacuo* at 60 °C, and the sorbent was washed on a filter with water and dried *in vacuo* at 110 °C for 5 h.

TPPAl(X) was synthesized by refluxing H_2TPP in a solution of $AlCl_3$ in pyridine for 1 h, then the porphyrin was precipitated with water, filtered off and dissolved in toluene. A weighed portion of hydroxydimethylsilyl-silica gel was treated with the solution thus obtained, and the resulting sorbent was washed with toluene to remove excess porphyrin and dried *in vacuo*. The proportion of the modifier on silica gel was 10–12%.

HPLC was carried out on a GPC chromatograph with an UV detector (365 nm).

used in large-scale systems for preparative separation of fullerenes.

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