Separation of C_{60} and C_{70} fullerenes on silica modified with phthalocyanines

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A series of stationary phases have been prepared by attachment of different phthalocyanines (PcM) to γ-aminopropyl silica and tested for HPLC separation of C_{60} and C_{70} fullerenes; strong dependence of chromatographic properties on the central metal ion and substituents of attached complexes was found, and for the phase containing 3-(β-naphthyloxy)-substituted PcCo good results were achieved.

The growing interest in the preparation of fullerenes has created the need for an effective means of separating them by HPLC.[1,2] To date, the best phase for the separation of C_{60} and C_{70} fullerenes with a 'good' solvent such as pure toluene is tetraphenylporphyrin–silica gel stationary phase (selectivity factors $\alpha = k'C_{70}/k'C_{60},\ \alpha = 4.8$).[3]

In this article we report the preparation of new phases containing metal phthalocyanines (PcM) covalently attached to silica and the first results on the separation of C_{60} and C_{70} using these phases.

Our choice of PcM as a modifier of silica for fullerene separation arose from the following considerations: (*a*) the PcM molecular size corresponds well to the fullerene size; (*b*) the PcM π-system is larger than the porphyrin one; (*c*) PcMs are more readily synthetically available and allow a wide range of molecular design.

A series of phases **1**–**12** containing different PcMs attached to γ-aminopropyl silica *via* the sulfonamido group have been prepared. These phases can be divided into two groups — phases **1**–**5** prepared by the attachment of readily available PcM sulfochlorides,[4] and phases **6**–**12** prepared using recently synthesized by us 4-(chlorosulfonyl)phthalonitrile[5] *via* a well-known procedure of solid-phase synthesis.[6†] Both procedures were simpler to prepare than the tetraphenylporphyrin phases.[3]

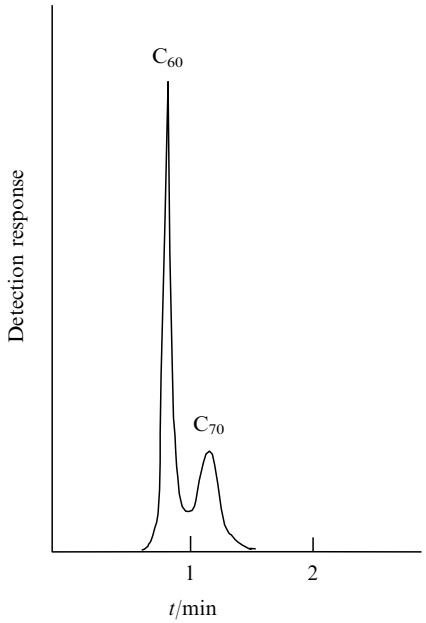


Figure 1 HPLC chromatogram of a mixture of C_{60} and C_{70} fullerenes: stationary phase **12**, mobile phase heptane–1-methylnaphthalene mixture (1:19), flow rate 0.2 ml min^{-1} in column 60 × 2 mm, detection 360 nm, injection 3 μl of 1.0 mg ml^{-1} fullerene solution in toluene.

Table 1 Capacity (k') and selectivity factors (α) for C_{60} and C_{70} fullerenes on PcM modified stationary phases.

Stationary phase	Mobile phase	k' (C_{60})	k' (C_{70})	α (C_{70}/C_{60})
1	pentane–toluene (1:1)	0.47	0.82	1.8
2	pentane–toluene (1:1)	0.53	0.97	1.8
3	pentane–toluene (1:1)	0.75	1.4	1.9
4	pentane–toluene (1:1)	0.97	1.8	1.9
5	pentane–toluene (1:1)	1.4	2.9	2.1
6	heptane–toluene (1:1)	0.68	1.4	2.0
7	pentane–toluene (1:1)	1.6	4.1	2.6
8	pentane–toluene (1:1)	2.1	4.7	2.2
	toluene	0.46	0.9	2.0
9	toluene	0.42	0.75	1.8
10	pentane–toluene (1:1)	4.5	10.1	2.4
	toluene	0.68	1.4	2.1
11	toluene	0.46	0.75	1.6
12	toluene	2.2	17.1	7.8
	o-xylene	1.4	8.5	6.0
	heptane–1-methylnaphthalene (1:1)	1.2	4.5	3.8
	heptane–1-methylnaphthalene (1:19)	0.20	0.68	3.4

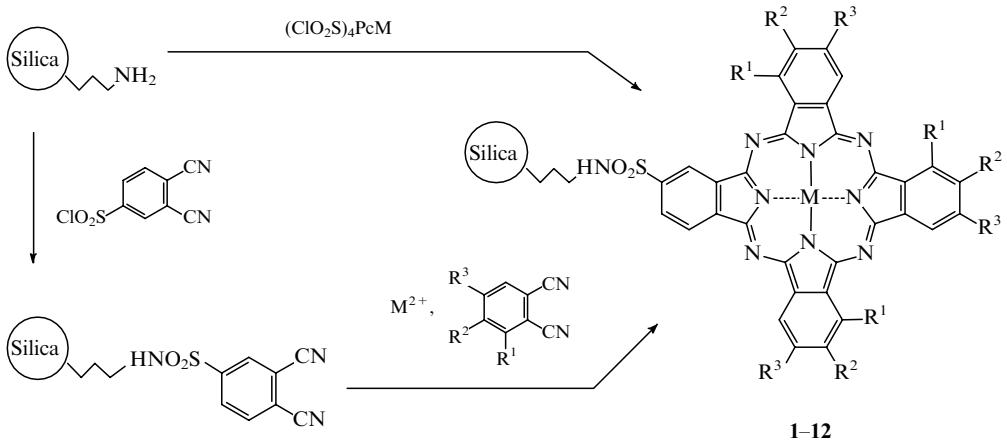
The examination of phases **1**–**5** demonstrated the remarkable influence of the PcM central metal ion on the retention (k') of C_{60} and C_{70}, accompanied by rather high

† 'Silasorb NH_2 10μ' was used as γ-aminopropyl silica. Chlorosulfonyl-substituted phthalocyanines were prepared as described[4] as well as 3,5-dinitro-, 4-chlorosulfonyl- and 4-*tert*-butyl-substituted phthalonitriles.[5,7,8] 3-(1-Naphthyloxy)- and 3-(2-naphthyloxy)-substituted phthalonitriles were synthesized from 3-nitrophthalonitrile by analogy with 3-phenoxyphthalonitrile.[9]

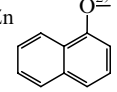
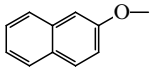
General method of phase **1**–**5** *preparation.* The appropriate chlorosulfonyl-substituted phthalocyanine (50 mg) and γ-aminopropyl silica (200 mg) were added to a mixture of 5 ml dry tetrahydrofuran and 1 ml pyridine with subsequent reflux during 2 h. Sorbents were then filtered off and washed with acetone and water, slurried in 10 ml acetone and packed into a HPLC column at ~ 30 MPa.

Phthalonitrile-modified silica. 4-Chlorosulfonylphthalonitrile (300 mg) and triethylamine (0.5 ml) were added to a suspension of 2.5 g γ-aminopropyl silica in 20 ml acetone and stirred for 5 h. Modified silica was filtered off, washed with acetone and dried.

General method of phase **6**–**12** *preparation.* A mixture of 300 mg phthalonitrile-modified silica, 300 mg of the appropriate substituted phthalonitrile, 85 mg of the appropriate metal acetate and 5 mg ammonium molybdate was heated for 2 h at 215–230 °C. Sorbents were then washed with hot water, dimethylformamide and acetone up to a colourless solvent and packed by analogy with phases **1**–**5**.



1–5 $R^1 = SO_2Cl$, $R^2 = R^3 = H$ **1** M = H_2, **2** M = Cu, **3** M = Zn, **4** M = VO, **5** M = Co
6 $R^1 = R^3 = NO_2$, $R^2 = H$, M = Co **7,8** $R^1 = R^3 = H$, $R^2 = Bu^t$ **7** M = Cu, **8** M = Zn

9 $R^1 =$, $R^2 = R^3 = H$, M = Zn **10–12** $R^1 =$, $R^2 = R^3 = H$ **10** M = Cu, **11** M = Zn, **12** M = VO

selectivity (Table 1) unlike the porphyrin phases.[3] In this first series PcH_2 modified silica has the weakest fullerene retention while the PcCo modified silica has the strongest retention suggesting significant participation of d-π interaction between PcM and fullerenes.

In the second group of phases **6–12** the influence of substituents in the PcM macrocycle on the separation of C_{60} and C_{70} was investigated. It was found that strong electron-withdrawing nitro groups in the macrocycle decrease the chromatographic properties of PcM phases whereas electron-donating substituents (*tert*-butyl and naphthyloxy groups) enhance both retention and selectivity (Table 1). Phase **12**, possessing optimal structural factors — cobalt as central ion and β-naphthyloxy groups as substituents — provides high chromatographic properties using toluene as a mobile phase ($\alpha = 7.8$). Moreover, good results were also obtained for other solvents such as *o*-xylene and heptane–1-methylnaphthalene mixtures (Figure 1). These are very important for the preparative separation of fullerenes because their solubilities in these solvents are much higher than in toluene (according to our data, the solubility of a C_{60}, C_{70} mixture in 1-methylnaphthalene is $\sim 10\%$ and in toluene $\sim 0.5\%$). However, it is necessary to increase sorbent capacity in order to use them for the separation of larger quantities of fullerene mixtures. These investigations are currently in progress.

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Received: Moscow, 25th October 1995
Cambridge, 7th November 1995; Com. 5/07155K