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Synthesis and characteristics of [60]fullerene polysiloxane stationary phase for capillary gas chromatography

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Abstract

A new type of fullerene-containing polysiloxane was synthesized by reacting [60]fullerene with azidopropyl polysiloxane directly. The polysiloxanes have been used successfully as stationary phases for capillary gas chromatography. They displayed high column efficiency, wide operational temperature and high thermostability, and exhibited unique selectivity for many organic substances, such as alkanes, alcohols, ketones and aromatic compounds. The stationary phase was especially suitable for separation of high boiling-point compounds like polycyclic aromatic hydrocarbons and phthalic esters, etc. It was also found that some alcoholic or aromatic positional isomers could be well separated on the column. The influence of the fullerene content on the separation was also investigated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, GC; Fullerene; Polysiloxane

1. Introduction

Recently fullerene has been attracted much attention as stationary phase for chromatography due to its unique shape, conjugate three-dimensional π electric system and high thermostability. In fact, fullerene or various silica chemically bonded fullerene has been used as stationary phases for LC to separate polycyclic aromatic hydrocarbons (PAHs) [1–3], haloaromatics [4], cyclic oligomeric compounds like calixarene or cyclodextrins [5,6], C_{60}/C_{70} mixture [3,5], some helical shaped peptides [5] and nature occurring quinones [7]. Surface-linked $C_{60/70}$ polystyrene divinylbenzene beads was also reported as a chromatographic material for enrich-

ment of coplanar polychloro-biphenyls (PCBs) [8,9]. But these fullerene-modified polymers could not be used directly as stationary phases for gas chromatography.

Polysiloxanes are the most commonly used stationary phases in capillary column GC because of their good film-forming ability, wide operational temperature, high column efficiency and thermal stability. Fullerene also shows significant potential in gas chromatography, especially for rapid analysis of high boiling-point organic compounds [10]. The combination of fullerene and polysiloxane may create a novel type of stationary phases with unique properties. Great interest was thus currently focused on the challenge. In 1998, Glausch et al. first reported synthesis of a fullerene-containing polysiloxane by reacting 1,2-cyclohexylamino-carbonyl-(N) - succinimidylloxycarbonyl - 1,2 - dihydro[60]fullerene with aminopropylpolysiloxane [11]. The

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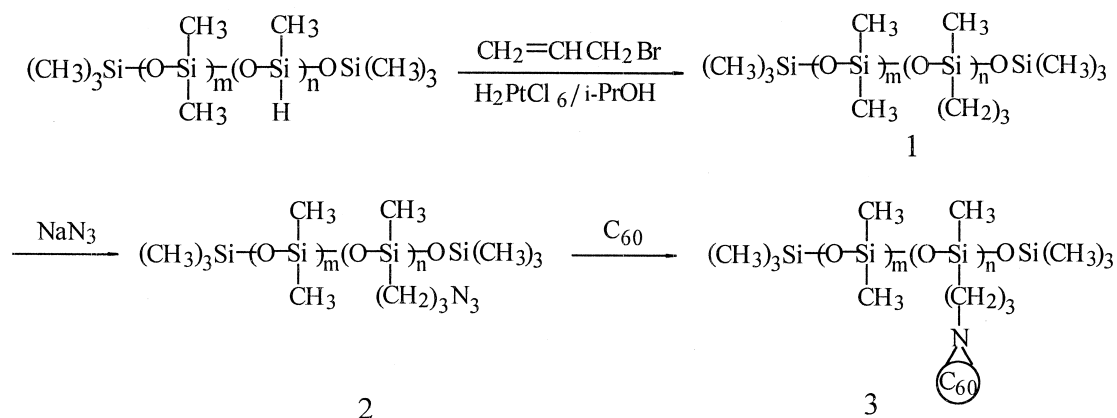


Fig. 1. Synthesis of [60]fullerene polysiloxane stationary phase.

stationary phase was applied in gas chromatography to the separation of polychlorinated biphenyl (PCB) isomers with different degrees of substitution in the ortho-position. In this study, we describe a kind of fullerene stationary phases which was conveniently prepared by directly reacting [60]fullerene with azidopropyl polysiloxane (Fig. 1). The phases exhibit good selectivity for alkanes, alcohols, ketones, anilines, aromatic substances, etc. They are especially suitable for separation of high boiling-point compounds, such as PAHs, fatty acid methyl ether. Some aromatic or alcohol positional isomers also can be efficiently separated on it. The influence of fullerene content on separation is also investigated.

2. Experimental

2.1. Materials

[60]Fullerene (99.9%) was obtained from Fullerene Institute of Wuhan University, P.R. China), Polymethylhydrosiloxane (active hydrogen content: 0.05%) was obtained from Xinghuo Chemical Factory (Jiangxi Province, P.R. China).

2.2. Synthesis of the [60]fullerene polysiloxane stationary phase

2.2.1. Synthesis of compound 1

A mixture of 5.0 g polymethylhydrosiloxane (active hydrogen content is 0.05%), 0.6 g of

allylbromide and 15 ml of benzene was stirred at 20°C for 1 h, then 0.1 ml of chloroplatinic acid solution (0.1 mol/l H_2PtCl_6 -i-PrOH) was added. After stirring for another 24 h at 60°C, the solvent and the excess allylbromide were removed under vacuum. The residue was dissolved in dichloromethane and washed with 50% aqueous methanol. The organic phase was dried over anhydrous MgSO_4 and filtrated. The solvent was distilled off. 5.25 g of a colorless viscous oil was obtained. FT-IR (KBr/ cm^{-1}): 2963, 2926, 2856, 1412, 1261, 1093, 1024, 860, 800, 702, 456.

2.2.2. Synthesis of compound 2

To a solution of 5 g of compound 1 in 15 ml of dichloromethane, a solution of 2 g of NaN_3 in 40 ml of dimethylsulfoxide was added. The mixture was stirred for 24 h at 70°C, poured into ice-water mixture after cooling, then extracted with CHCl_3 for three times. The organic phases were combined, dried with anhydrous Na_2SO_4 . After removal of the solvent, 4.68 g of product was obtained as colorless viscous oil. FT-IR (KBr/ cm^{-1}): 2963, 2927, 2856, 2097, 1412, 1260, 1093, 1022, 862, 800, 702.

2.2.3. Synthesis of compound 3

A mixture of 1 g of compound 2, 37 mg of C_{60} and 30 ml of chlorobenzene was refluxed for 24 h under argon atmosphere. No unreacted C_{60} was detected by TLC. Then 1 ml of cyclohexene was added in order to react with remaining active hydrogen of polymethylhydrosiloxane. The mixture was

stirred for another 10 h at 60°C. After evaporating off the solvent and excess cyclohexene, 1.033 g of fullerene-containing polymer PSO-C₆₀-1 was obtained as a brown gum. The fullerene content was 3% by weight, and the mole ratio of propylfullerene methyl vs. dimethyl side chain was 1:310.

PSO-C₆₀-2 was prepared similarly: A mixture of 1 g of compound **2**, 72 mg of C₆₀ and 50 ml of chlorobenzene was worked up as described above, 1.067 mg of brown gum was obtained. The fullerene content of PSO-C₆₀-2 was 6% by weight and the mole ratio of propylfullerene methyl vs. dimethyl side chain was 1:148.

The spectra of two kinds of fullerene-containing polysiloxanes were almost the same. UV-Vis (CH₂Cl₂): λ_{max} = 231, 258, 325 nm. FT-IR (KBr/cm⁻¹): 2963, 2925, 2854, 1412, 1261, 1093, 1024, 861, 801, 702. ¹³C-NMR (125 MHz, CDCl₃, 25°C): 150-135(br), 53.29, 33.82, 33.22, 32.74, 29.48, 29.36, 29.28, 28.69, 28.08, 22.86, 17.38, 1.67, 1.52, 1.32, 1.21, 0.92, 0.62, 0.45, 0.16.

2.3. Capillary column preparation

2.3.1. Column PSO-C₆₀-1

Fused-silica capillary column (12 m×0.25 mm ID) (Yong Nan Optical Fibre Factory, Hebei, P. R. China) were rinsed with 10 ml of methanol and 10 ml of dichloromethane, then purged with nitrogen at 250°C for 2 h to remove acidic impurities. The columns were then statically coated with a solution of 0.5% (w/v) PSO-C₆₀-1 (or PSO-C₆₀-2) in dichloromethane. After the coating procedure the column was flushed with nitrogen for 2 h, then conditioned at 250°C for 4 h and 360°C for another 2 h.

2.3.2. Column PSO-C₆₀-2

Fused-silica capillary column (14 m×0.25 mm id)

was treated according to above procedure except for being coated with a solution of 0.5% (w/v) PSO-C₆₀-2 in dichloromethane.

2.4. Column evaluation

A Model SC-7 gas chromatograph (Sichuan Analytical Apparatus Plant, P.R. China) equipped with capillary split injection system and flame ionization detector was used throughout. Nitrogen was used as the carrier gas, at a linear velocity of 12–15 cm s⁻¹. Split ratio was 1/80, the injector and detector temperatures were maintained at 280–330°C and 300°C, respectively. The characteristics of the columns, such as column efficiency, glass transition temperature, polarity, selectivity of isomer separation were tested.

3. Results and discussion

3.1. Chromatographic properties

The efficiency of the column was evaluated by measuring the number of plates per meter for naphthalene at 120°C and the results were summarized in Table 1. The data indicated that the columns had efficiency above 3000 plates m⁻¹. The retention factor of PSO-C₆₀-2 was higher than that of PSO-C₆₀-1, but not the column efficiency. The peak asymmetry factors for 1-octanol on the fused-silica columns were close to 1.01~1.03, indicating that the fullerene phases had good film-forming ability.

The polarity and selectivity of the studied stationary phases were expressed by McReynolds constants, they also were measured at 120°C. Table 2 shows that the fullerene phases exhibited weak polarity. Their average polarity was higher than that of SE-30 (100% methylpolysiloxane) and similar with that of

Table 1
Characteristics of the fullerene-containing polysiloxane columns^a

Stationary phase	Column dimensions length (m)×I.D. (mm)	Retention factor (<i>k</i>) of naphthalene at 120°C	Film thickness <i>D_f</i> (μm)	Efficiency plates m ⁻¹
C ₆₀ -PSO-1	12×0.25	2.95	0.31	3450
C ₆₀ -PSO-2	14×0.25	3.03	0.31	3021

^a Conditions: The test temperature was 120°C.

Table 2
McReynolds constants and polarity of the investigated stationary phases^a

	X' (benzene)	Y' (1-butanol)	Z' (2-pentanone)	U' (nitropropane)	S' (pyridine)	Av. polarity
SE-30	15	53	44	64	41	43
C ₆₀ -PSO-1	23	78	44	78	183	79
C ₆₀ -PSO-2	34	83	56	86	207	93
OV-3	44	86	81	124	88	85

^a Conditions: The test temperature was 120°C.

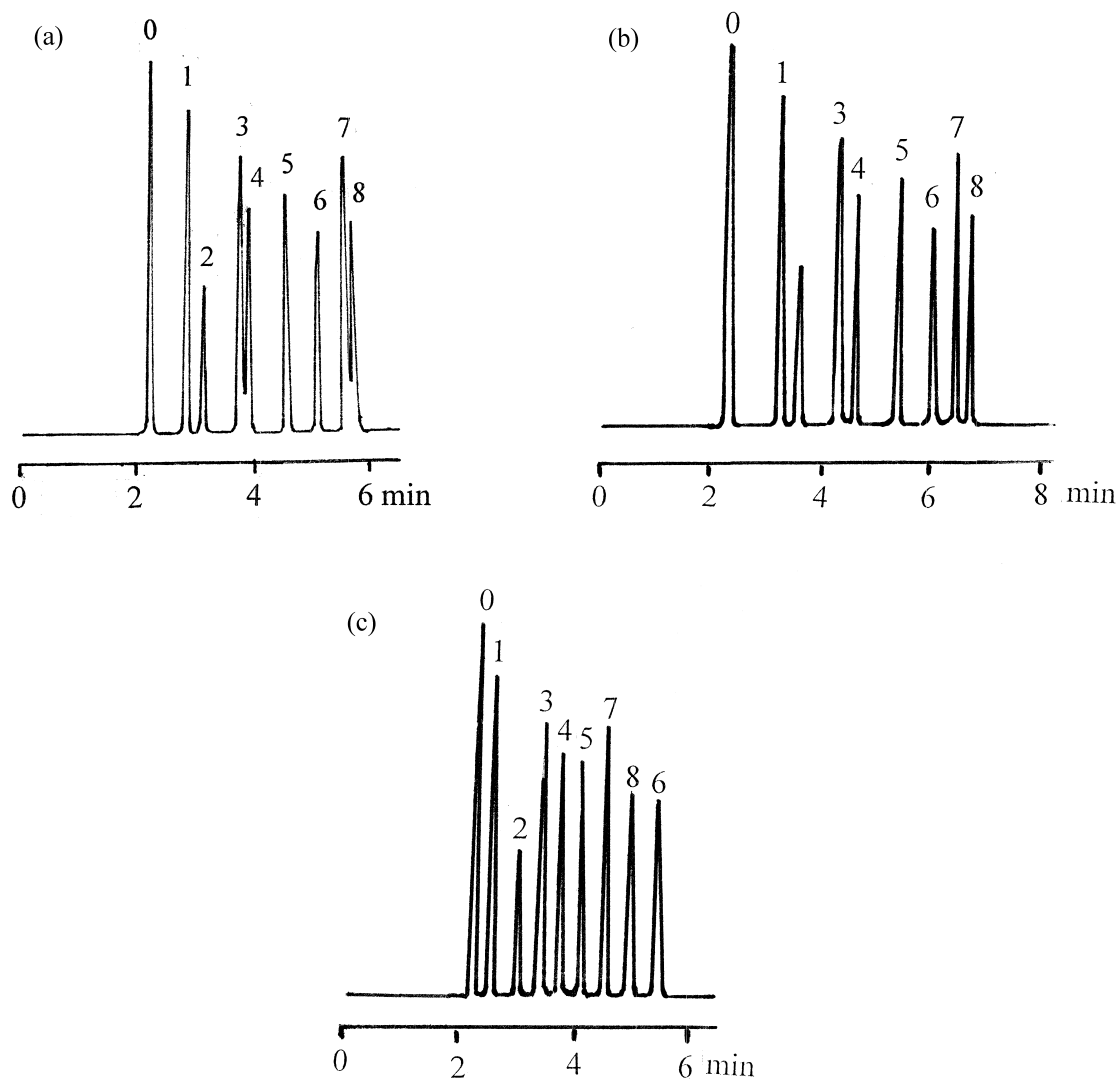


Fig. 2. Chromatogram of Grob test mixtures on the C₆₀-PSO column and OV-1 column a. C₆₀-PSO-1 column; b. C₆₀-PSO-2 column; c. OV-1 column. Column temperature: 140°C. Peak identification: 0=solvent; 1=1,3-butanediol; 2=*n*-decane; 3=1-octanol; 4=*n*-undecane; 5=2,6-dimethylphenol; 6=*n*-dodecane; 7=2,6-dimethylaniline; 8=naphthalene.

OV-3 (10% phenyl, 90% methylpolysiloxane). However, the value of S' of PSO-C₆₀ was much higher than that of SE-30 or OV-3, indicating that fullerene was a strong electron acceptor (EA). Known from Table 2, the polarity of PSO-C₆₀-2 was higher than that of PSO-C₆₀-1.

Grob test mixtures were used to evaluate the overall chromatographic properties of the capillary columns. Fig. 2 gives the chromatogram of Grob test mixtures on fullerene columns and OV-1 (100% methylpolysiloxane). The mixtures were well separated and gave symmetrical peaks. It was found that the elution order on column PSO-C₆₀ was different from that on column OV-1. 2,6-Dimethylaniline and naphthalene tailed in fullerene-containing polysiloxanes. The result indicated that the bonded [60]fullerene played an important role in chromatographic separation. It also could be seen that the selectivity of column C₆₀-PSO-2 was superior to that of column C₆₀-PSO-1.

The operating temperature range was determined by measuring the glass transition temperature and column bleeding. The glass transition temperature was obtained from the plot of log k of naphthalene versus reciprocal absolute temperature for the two fullerene columns. The changes in slope at 100°C and 110°C corresponded to glass transition points for column C₆₀-PSO-1 and column C₆₀-PSO-2 respectively. The results also corresponded to the glass transition temperature determined by differential scanning calorimetry (DSC). The column bleeding was measured by programming columns from 200°C to 360°C at 4°C min⁻¹. The results showed that both columns began to bleed at 300°C, and base line shift at 360°C of 3.2×10^{-14} Å and 4.0×10^{-14} Å was observed respectively. This indicated that the allowable operating temperature ranges of the two columns were from 110°C (100°C) to 360°C.

3.2. Separation of substrates

The two [60]fullerene polysiloxane phases possessed excellent selectivity for the separation of many organic compounds. Table 2 gives separation factors (α) and retention factors (k) for some alcohols, ketones, anilines and aromatic hydrocarbons being investigated. Fig. 3 shows a chromatogram of *n*-alkanes (C₁₂~C₃₂) with symmetrical peaks and

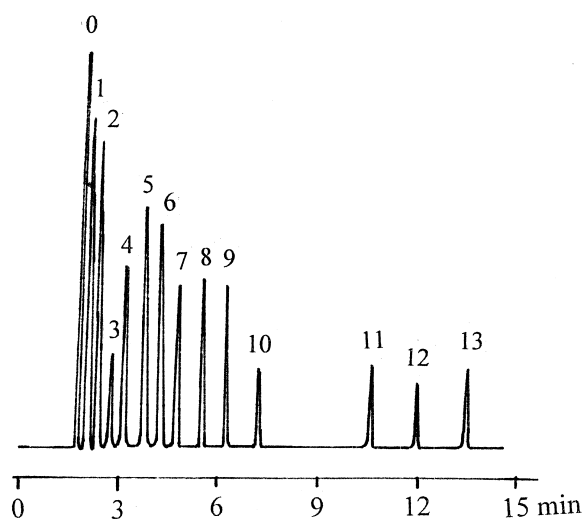


Fig. 3. Chromatogram of *n*-alkane mixtures on the C₆₀-PSO-1 column. Conditions: Temperature programmed from 250°C to 350°C at 4°C/min. Peak identification: 0=solvent; 1=*n*-dodecane; 2=*n*-tetradecane; 3=*n*-hexadecane; 4=*n*-eicosane; 5=*n*-docosane; 6=*n*-tricosane; 7=*n*-tetracosane; 8=*n*-pentacosane; 9=*n*-hexacosane; 10=*n*-heptacosane; 11=*n*-triacontane; 12=*n*-hentriacontane; 13=*n*-dotriacontane.

very small baseline drift on column 1 while programmed from 250°C to 350°C.

The phase was very suitable to separate high boiling-point organic compounds. Fig. 4 shows excellent separation of polycyclic aromatic hydrocarbons. These compounds eluted in the order of their increasing dispersion force. Fig. 5 gives a chromatogram of long-chain fatty acid methyl esters. As could be seen from the figure, the methyl esters of the unsaturated acids were eluted after the corresponding esters of saturated acids due to π - π interaction of fullerene with the double bond of methyl ester of the unsaturated acid. Fig. 6 shows the separation of the C₁~C₁₀ phthalic esters. Polycyclic aromatic hydrocarbons and phthalic esters were pollutants. So the fullerene phases have significant potential application in the environment analysis.

The separation of some alcoholic or aromatic positional isomers was also studied (Figs. 7 and 8). All these compounds could form strong donor-acceptor interactions with fullerene. Table 4 shows retention factors (k) and separation factors (α) of the positional isomers being investigated. It could be seen that the isomers were separated effectively on

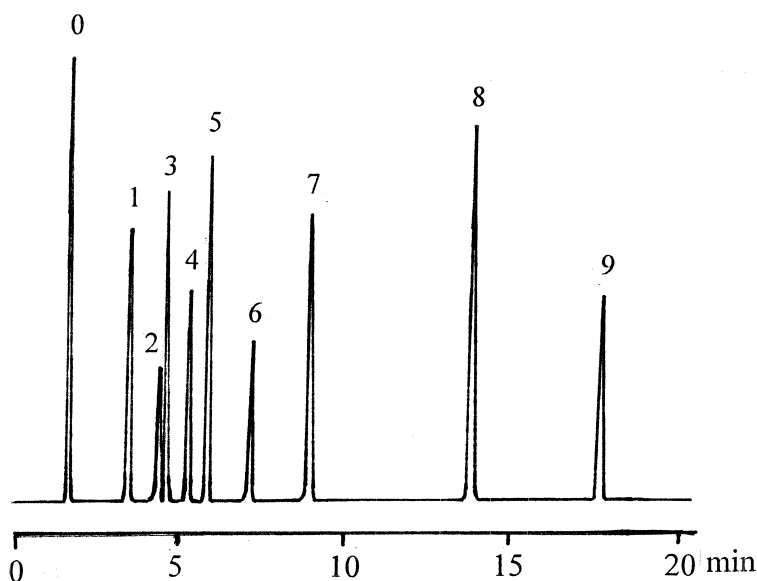


Fig. 4. Chromatogram of polycyclic aromatic hydrocarbons on the C_{60} -PSO-1 column. Conditions: Temperature programmed from 150°C to 210°C at 4°C/min. Peak identification: 0=solvent; 1=naphthalene; 2=2-methylnaphthalene; 3=1-methyl naphthalene; 4=biphenyl; 5=diphenylmethane; 6=acenaphthylene; 7=fluorene; 8=phenanthrene; 9=triphenylmethane.

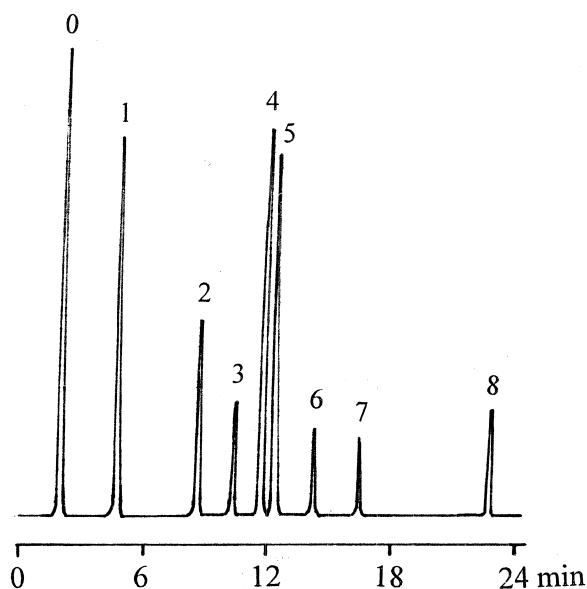


Fig. 5. Chromatogram of a fatty acid methyl ester mixtures on the C_{60} -PSO-1 column. Conditions: Temperature programmed from 150°C to 210°C at 4°C/min. Peak identification methyl ester of: 0=solvent; 1=tridecanoic acid; 2=palmitic acid; 3=heptadecanoic acid; 4=stearic acid; 5=oleic acid; 6=nonadecanoic acid; 7=eicosanoic acid; 8=docosanoic acid.

both fullerene stationary phases. In addition, α/β -methylnaphthalene or xylene mixtures (see Table 3) were also well separated. The dispersion force and donor–acceptor interaction may play a key role in the separation mechanism.

3.3. The effect of fullerene content on separation

The fullerene content of C_{60} -PSO-1 (0.32% propylfullerene methyl, 99.68% dimethyl polysiloxane) and C_{60} -PSO-2 (0.68% propylfullerene methyl, 99.32% dimethyl polysiloxane) was 3%, 6% by weight respectively. From above discussion (see Section 3.1), it was known that the polarity and selectivity of C_{60} -PSO-2 were higher, but the efficiency of C_{60} -PSO-1 is higher. In other words, the polarity and selectivity increased with the fullerene content, but not the efficiency.

As could be seen from Tables 3 and 4, the retention factors on column C_{60} -PSO-2 were higher than that on column C_{60} -PSO-1. That meant the retention factors with the fullerene-polysiloxane phases also increased with fullerene content.

The influence of fullerene content on the sepa-

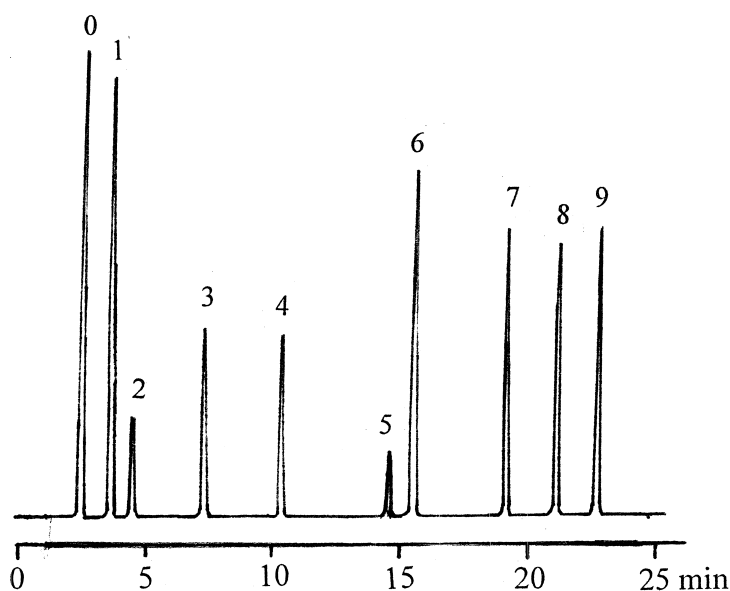


Fig. 6. Chromatogram of phthalic esters on the C₆₀-PSO-1 column. Conditions: Temperature programmed from 200°C to 290°C at 4°C/min. Peak identification: 0=solvent, 1=dimethyl phthalate, 2=diethyl phthalate, 3=di-*n*-butyl phthalate, 4=di-*n*-amyl phthalate, 5=di-*n*-hexyl phthalate, 6=di-iso-octyl phthalate, 7=di-*n*-octyl phthalate, 8=di-*n*-nonyl phthalate, 9=di-*n*-decyl phthalate.

Table 3
The retention behavior of studied compounds on PSO-C₆₀ stationary phase^a

Compound	Column 1			Column 2			Column temperature (°C)
	<i>k</i>	α_1	α_2	<i>k</i>	α_1	α_2	
Benzene	0.17	1.00		0.21	1.00		
Toluene	0.32	1.88	1.88	0.42	2.00	2.00	
Ethylbenzene	0.61	3.59	1.91	0.79	3.76	1.88	
<i>m</i> -Xylene	0.65	3.82	1.07	0.83	3.95	1.05	100
<i>p</i> -Xylene	0.66	3.88	1.02	0.84	4.00	1.01	
<i>o</i> -Xylene	0.75	4.41	1.14	0.97	4.62	1.15	
1,3,5-Trimethylbenzene	1.31	7.01	1.75	1.59	7.57	1.64	
2-Butanone	0.15	1.00		0.17	1.00		
2-Pentanone	0.33	2.20	2.20	0.36	2.12	2.12	
3-Pentanone	0.35	2.33	1.06	0.38	2.24	1.06	80
4-Heptanone	1.32	8.80	3.77	1.46	8.59	3.84	
2-Octanone	3.23	21.53	2.45	3.60	21.18	2.47	
5-Nonanone	8.10	54.00	2.51	9.07	53.35	2.52	
1-Pentanol	0.22	1.00		0.33	1.00		
1-Hexanol	0.42	1.91	1.91	0.66	2.00	2.00	
1-Heptanol	0.77	3.50	1.83	1.29	3.91	1.95	
1-Octanol	1.25	5.68	1.62	2.14	6.48	1.65	120
1-Nonanol	1.41	6.41	1.13	2.43	7.36	1.14	
1-Decanol	4.58	20.82	3.25	8.87	26.88	3.65	
1-Undecanol	8.28	37.64	1.81	16.65	50.45	1.88	
Aniline	0.61	1.00		0.65	1.00		
<i>m</i> -Methylaniline	0.93	1.52	1.52	1.09	1.68	1.68	140
2,4-Dimethylaniline	1.56	2.65	1.68	1.82	2.80	1.67	
<i>N</i> -ethyl- <i>m</i> -methylaniline	1.76	2.98	1.13	2.04	3.14	1.12	
<i>N,N</i> -diethyl- <i>m</i> -methylaniline	2.38	4.03	1.35	2.73	4.20	1.34	

^a *k* = Retention factor; $\alpha_1 = k_n/k_1$; $\alpha_2 = k_n/k_{n-1}$.

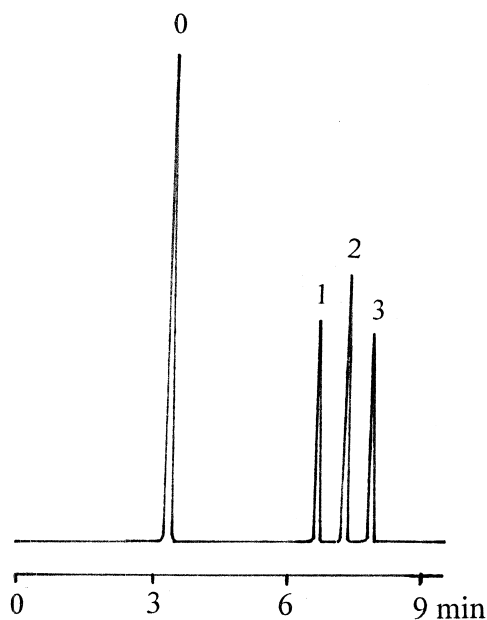


Fig. 7. Chromatogram of *o*-, *m*-, *p*-dinitrobenzene mixture on the C_{60} -PSO-2 column. Conditions: Column temperature 170°C. Peak identification: 0=solvent, 1=*p*-dinitrobenzene, 2=*m*-dinitrobenzene, 3=*o*-dinitrobenzene.

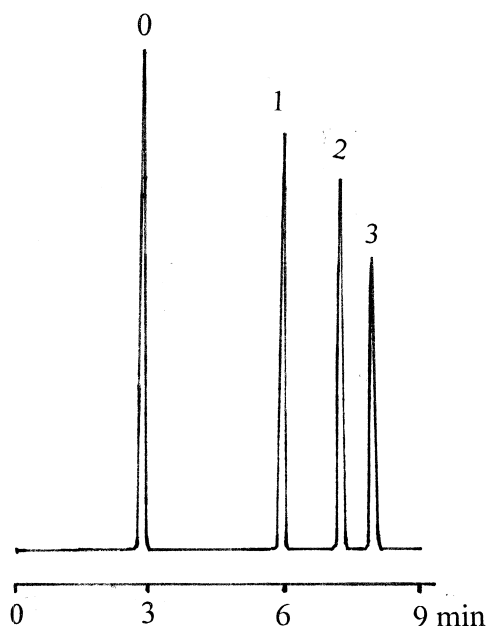


Fig. 8. Chromatogram of 2-, 3-, 4-ethylnitrobenzene mixtures on the C_{60} -PSO-2 column. Conditions: Column temperature 170°C. Peak identification: 0=solvent, 1=2-ethylnitrobenzene, 2=3-ethylnitrobenzene, 3=4-ethylnitrobenzene.

Table 4

Retention data for position isomer on C_{60} -PSO column^a

Compound	Column 1			Column 2			Column temperature (°C)
	k	α_1	α_2	k	α_1	α_2	
1-Nonanol	1.93	1.00		1.96	1.00		
4-Nonanol	2.36	1.22	1.22	2.40	1.23	1.23	110
3-Nonanol	2.49	1.29	1.06	2.51	1.28	1.05	
2-Nonanol	2.58	1.34	1.04	2.61	1.33	1.04	
2,3-Butanediol	0.44	1.00		0.49	1.00		
1,3-Butanediol	0.84	1.91	1.91	1.04	2.01	2.01	110
1,4-Butanediol	1.53	3.48	1.82	1.81	3.88	1.74	
<i>p</i> -Nitrotoluene	2.83	1.00		3.09	1.00		
<i>m</i> -Nitrotoluene	2.92	1.04	1.04	3.23	1.05	1.05	130
<i>o</i> -Nitrotoluene	3.11	1.11	1.07	3.42	1.11	1.06	
<i>m</i> -Nitrochlorobenzene	2.85	1.00		3.08	1.00		
<i>p</i> -Nitrochlorobenzene	2.93	1.03	1.03	3.20	1.04	1.04	130
<i>o</i> -Nitrochlorobenzene	3.09	1.09	1.05	3.73	1.11	1.17	
<i>o</i> -Chlorophenol	0.25	1.00		0.34	1.00		
<i>m</i> -Chlorophenol	0.71	2.80	2.80	0.94	2.78	2.78	170
<i>p</i> -Chlorophenol	0.80	3.15	1.13	1.05	3.12	1.12	
<i>o</i> -Benzenediol	0.53	1.00		0.77	1.00		
<i>p</i> -Benzenediol	0.66	1.24	1.24	0.92	1.19	1.19	170
<i>m</i> -Benzenediol	0.88	1.66	1.33	1.32	1.71	1.43	

^a k = Retention factor; $\alpha_1 = k_n/k_1$; $\alpha_2 = k_n/k_{n-1}$.

ration factors depended on the nature of solutes. However, most of the α_2 value (k_n/k_{n-1}) was much above 1.04 indicating the compounds being separated effectively.

The columns have been used extensively over a period of 5 months and no significant changes in retention and selectivity have been observed.

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