

Preparation and properties of sorbents based on silica gel containing covalently linked fullerene C₆₀

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Sorbents containing 10–12 % fullerene C₆₀ were prepared by the reaction of C₆₀ with γ -aminopropylsilica gel. C₆₀-Silica gel possesses good chromatographic properties for the separation of aromatic, nitro, and heterocyclic compounds in the regimes of normal and reversed-phase HPLC.

Key words: immobilized fullerenes; silica gel; HPLC.

Fullerenes, spherical carbon clusters, are of considerable interest for researchers.¹ Examples of practical application of these compounds as sorbents are restricted to the work,² in which C₆₀ powder was used for sorption of metal complexes from aqueous solutions. Carrier-immobilized fullerenes can be of interest as catalysts and new sorbents for liquid and gas chromatography.

The chemical properties of C₆₀ have been studied in detail to date. In particular, it is known that C₆₀ rather readily reacts with amines.³ In a homogeneous medium, these reactions result in the addition of several amine molecules to the C₆₀ molecule and formation of a wide set of products. In our opinion, methods of solid-phase synthesis are more efficient for the preparation of mono-substituted derivatives of C₆₀. In this work, C₆₀ was immobilized directly on γ -aminopropylsilica gel.

Experimental

Synthesis of C₆₀-silica gel. γ -Aminopropylsilica gel Separon-NH₂ (1 g) with a particle size of 10 μ m prewashed with MeOH with addition of Et₃N and pure MeOH was added to a solution of fullerene C₆₀ (0.5 g) in 300 mL of *o*-xylene

("chemically pure" grade). The suspension was refluxed for 36 h in an argon atmosphere, and the sorbent was filtered off and washed with *o*-xylene (0.5 L). The combined filtrates were analyzed for the residual C₆₀ by HPLC on C18-silica gel, using xylene–MeOH (1 : 1) as a mobile phase. It was found that 150 mg of C₆₀ reacted with the carrier. Residual amino groups of the sorbent were acetylated by boiling in acetic anhydride for 1 h, then the sorbent was washed with water and MeOH, and the dark brown mass obtained (C₆₀-silica gel) was dried *in vacuo* for 1 h at 100 °C.

Packing of column for HPLC. C₆₀-Silica gel (200 mg) was suspended in a xylene–MeOH (1 : 1) mixture (10 mL). The suspension was placed in a packing system for HPLC columns. A stainless-steel column (60 mm \times 2.0 mm) was packed, pumping a xylene–MeOH mixture from bottom to top at a pressure of 30 MPa.

HPLC was performed on a Milikhrom chromatograph with UV detector (260 nm). A column with silica gel Separon (10 μ m) was used for comparison. The measured efficiency of the column with C₆₀-silica gel was 1050 t.p.

Results and Discussion

C₆₀ was immobilized on silica gel as shown in Scheme 1. The chromatographic properties of the C₆₀-silica gel obtained were studied in the regime of

Scheme 1

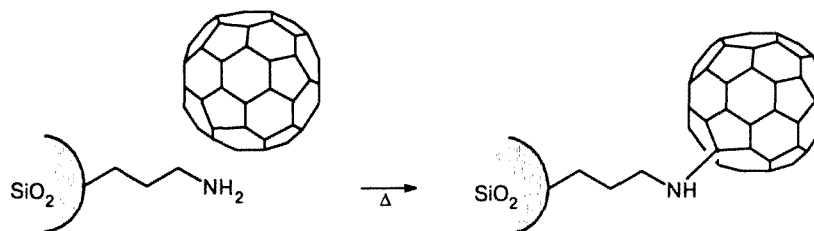


Table 1. Capacity factors (K') of aromatic compounds on silica gel Separon and C₆₀-silica gel. Chloroform—hexane (1 : 1, v/v) as mobile phase, eluent flow rate 0.6 mL min⁻¹

Compound	Silica gel Separon	C ₆₀ -silica gel
	<i>K'</i>	
Naphthalene	0.05	0.15
Phenanthrene	0.08	1.31
<i>p</i> -Nitrotoluene	0.05	0.27
2-Chloro-4-nitrotoluene	0.12	0.23
Anthraquinone	0.12	1.23
2,4,6-Trinitrotoluene	0.31	1.31
<i>o</i> -Nitrobiphenyl	0.15	0.32
<i>p</i> -Nitroaniline	5.0	5.00
<i>o</i> -Nitroaniline	1.15	3.15
2,6-Dinitroaniline	0.54	1.77
2,4,6-Trinitroaniline	1.54	7.00
2,2',4,4'-Tetranitrobiphenyl	2.31	6.54

Table 2. Capacity factors (K') of heterocyclic compounds on silica gel Separon and C₆₀-silica gel. Chloroform—propanol-2 (5 : 1, v/v) as mobile phase, eluent flow rate 0.6 mL min⁻¹

Compound	Silica gel Separon	C ₆₀ -silica gel
	<i>K'</i>	
Benzotriazole	0.15	1.31
Benzimidazole	0.54	5.15
2-Trifluoromethylbenzimidazole	0.62	6.10
2-Amino-4,6-dimethylpyrimidine	1.85	1.5
Methylnitrofuroxane*	0.15	0.92
2-Methyl-4,5-dinitro- 1,2,3-triazole 1-oxide	3.60	8.23

* Chloroform—hexane (1 : 1) as the eluent.

normal-phase HPLC by comparison with the standard silica gel (Tables 1 and 2) and in the regime of reversed-phase chromatography (Tables 3 and 4). The data presented in Tables 1 and 2 show that the presence of C₆₀ on the silica gel surface considerably increases the retention of aromatic, nitro, and heterocyclic compounds. This effect is especially pronounced for polycyclic aromatic hydrocarbons and nitro compounds. It is likely that the C₆₀ molecule with a large effective surface area and a powerful π -electronic system is capable of strong intermolecular π — π^* -interaction with these sorbates. Probably, the enhancement in the retention of di- and trinitroaromatic compounds is due to the formation of donor—acceptor π -complexes with C₆₀.

Application of C₆₀-silica gel as the chromatographic carrier was studied in the regime of reversed-phase chromatography (see Tables 3 and 4). Such π -acceptors as di- and trinitroanilines, trinitrotoluene, tetranitrobiphenyl, and methylnitrofuroxan are rather strongly retained on a column with C₆₀-silica gel when

Table 3. Capacity factors (K') of aromatic and heterocyclic compounds on C₆₀-silica gel in the regime of reversed-phase HPLC

Compound	K'
Hydrocarbons	
Benzene	0.31
Toluene	0.42
<i>p</i> -Xylene	0.77
<i>o</i> -Xylene	1.92
Naphthalene	2.10
Triphenylmethane	4.92
Phenanthrene	8.00
<i>p</i> -Dichlorobenzene	1.67
Anthraquinone	19.8
Aromatic nitro compounds	
<i>p</i> -Nitrotoluene	1.70
<i>p</i> -Nitroanisole	2.08
<i>o</i> -Nitroaniline	2.00
<i>p</i> -Nitroaniline	1.62
2,6-Dinitroaniline	4.15
2,4,6-Trinitroaniline	5.46
2,4,6-Trinitrotoluene	2.40
2,2',4,4'-Tetranitrobiphenyl	7.00
Phenols	
Phenol	0.46
2-Amino-4-nitrophenol	2.46
2,4-Dinitrophenol	5.15
Aromatic acids	
Acetylsalicylic	0.62
<i>p</i> -Aminobenzoic	0.69
<i>p</i> -Nitrobenzoic	2.23
Salicylic	3.23
<i>N</i> -Phenylanthranilic	6.15
Methanilic	1.92
<i>p</i> -Toluenesulfonic	2.85
Heterocyclic compounds	
Methylnitrofuroxan	0.69
Benzotriazole	1.08
2-Methyl-3,4-dinitro-1,2,3-triazole 1-oxide	1.15
Benzimidazole	1.38
Hexogen	2.08
Octogen	4.38

Note. MeOH—H₂O (5 : 1, v/v) mixture as eluent; for carboxylic acids, 1 % acetic acid was added; for sulfonic acids, 0.5 % succinic acid was added. Mobile phase flow rate 0.6 mL min⁻¹.

Table 4. Capacity factors (K') of polycyclic aromatic compounds on C₆₀-silica gel in the regime of reversed-phase HPLC (MeOH as mobile phase)

Compound	K'
Naphthalene	0.54
1-Methylnaphthalene	0.85
Phenanthrene	1.77
Perylene	8.05

MeOH—H₂O mixtures with a low content of water are used as mobile phases. Hexogen and octogen are considerably more strongly retained on this column than on standard C18-silica gel and can be well separated. The retention of polycyclic aromatic hydrocarbons such as naphthalene, phenanthrene, and perylene by C₆₀-silica gel is so strong that they can be eluted with pure MeOH. The retention of fullerenes on immobilized C₆₀ is also considerably stronger than on the C18-phase, but C₆₀, C₇₀, and C₈₄ are not separated, likely, due to the fact that the forces of the intermolecular interaction of these fullerenes with the immobilized C₆₀ are approximately equal.

Compounds that are difficult to separate, such as phenols and aromatic acids, are well retained on C₆₀-silica gel when a strong eluent (MeOH—H₂O, 5 : 1) is used resulting in rather narrow symmetric chromatographic peaks. The selectivity of a sorbent toward aromatic acids is a valuable advantage, because they are usually separated by ion-pair chromatography. The re-

tention during this separation is sensitive to slight changes in the composition of the mobile phase, ionic strength, concentration of organic modifier, and temperature of the column. In addition, the ion-pair reagent adsorbs irreversibly. C₆₀-silica gel does not have these disadvantages and can be used for the separation of many compounds because it provides reproducible results, good retention of sorbates, and long column life. After continuous work for 10 months, the properties of the C₆₀-silica gel sample described in this work remained unchanged.

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