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Low-carbon silica sorbents for solid-phase extraction

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Abstract

The applicability of silica gels, modified with cyclic organosiloxanes, in solid-phase extraction (SPE) has been tested. Surface characteristics of the adsorbents prepared are determined by: elemental analysis, ^{29}Si cross-polarisation magic angle spinning nuclear magnetic resonance spectroscopy (^{29}Si CP MAS NMR) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The sorbents with low carbon contents are used for extraction of chlorinated pesticides, polychlorinated biphenyls and nitro-compounds from water. The properties of the sorbents are compared with commercial C_{18} ones. It is shown that the low-carbon silica SPE sorbents can ensure satisfactory recoveries and reveal some selectivity. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Chemically bonded phases; Solid-phase extraction; Silica gel; Polychlorinated biphenyls; Pesticides; Organosilicons, cyclic

1. Introduction

Solid-phase extraction is now widely used for isolation and determination of trace organic contaminants in water [1–4]. Chemically bonded silicas, usually with C_8 and C_{18} organic groups, are nowadays the materials most commonly used for SPE. Over the years, organochlorosilanes and alkoxy-silanes have been used as silylating agents for preparation of bonded phases [5]. The stability of the $\equiv\text{Si}-\text{O}-\text{Si}-$ bonds formed between the silylating agents and the hydroxyl groups on silica surface is the main advantage of the reagents. It is commonly believed that the more organic carbon bonded to the silica surface the better SPE sorbent. Due to stability of the

bonded phase and the cost of production, manufacturers use exclusively di- and trifunctional modifiers for production of SPE sorbents. That leads to polymeric bonded phases usually containing 15–19% of bonded carbon. This paper shows that very little bonded organic carbon can also assure high recoveries of several groups of analytes. An alternate approach to the formation of the $\equiv\text{Si}-\text{O}-\text{Si}-$ bonds is the use of cyclic siloxanes or cyclic silazanes. The cyclic siloxanes were applied for hydrophobisation of the silica surface [5–8]. They were also used for a deactivation of capillary column surfaces [9–11]. Cyclic organosilicons can react easily with the silica surface, but the structures that are created have not been exactly recognised. Modification of silica surface with cyclic siloxanes proceeds without by-products or liberation of water molecule. Also, cyclic silazanes are known to react easily with silica surface, releasing ammonia as a by-product, and it

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was evidenced that the silazane ring breaks up into smaller fragments [12]. It has been established that, despite low carbon content, the silica modified with cyclic siloxanes is strongly hydrophobic [6–8]. Loop type structures were proposed by Yu-Fu et al. [13]; however, they gave no sufficient proofs for the occurrence of this kind of structure. Rutten et al. [14] have shown, by ^{29}Si CP MAS NMR, that practically both, loop and straight (monodendate) structures, are possible. Contrary to Yu-Fu et al. [13] and Rutten et al. [14], Akapo et al. [5] suggest that the presence of acidic silanol groups on the silica surface favours high reactivity of cyclic siloxanes toward acidic cleavage, so such acidolytic attack leads to ring opening with one end of the chain attached to the silica surface and the other silanol terminated.

The aim of this paper is:

- to explain the molecular structures of cyclic siloxane modified surfaces;
- an application of low-carbon adsorbents for solid-phase extraction.

2. Experimental

2.1. Modification

2.1.1. Chemicals and apparatus

Solvents for the modification, pentane, heptane and hexadecane, were of analytical-reagent grade (Baker) and used as obtained. The cyclosiloxanes and silazane (Johnson Matthey Alfa Products) used in the experiments are listed in Table 1.

Polygosil 100 (Machery-Nagel, Düren, Germany) was used as the support for the preparation of chemically bonded phases. The physicochemical characteristics of this unmodified silica gel are listed in Table 2.

Metal impurities [15,16] were removed from silica

Table 2
Physical characteristics of bare Polygosil 100

Characteristics	Abbreviation	Value
Specific surface area (m^2/g)	S_{BET}	280
Particle size (μm)	d_p	40–63
Mean pore diameter (nm)	D	10
Pore volume (cm^3/g)	V_p	1.0

gel by an extraction in Soxhlet apparatus with 20% HCl for several days. Then the silica was rinsed with the distilled water, dried at 180°C in vacuum desiccator and stored over freshly dehydrated molecular 4A sieves. The porous structure of silica was determined on the basis of the complete nitrogen adsorption–desorption isotherms measured by Sorptomat 1800 (Carlo-Erba, Milan, Italy).

2.1.2. Procedure of modification

Five grams of dry, acid-washed silica, 70 ml of *n*-alkane and the 2 g of cyclosiloxane were placed for 2 days in a three-necked flask. Subsequently, the mixture was refluxed for 5 h under an inert argon atmosphere at the boiling point of *n*-alkane. After that, the solvent was decanted and the silica was thoroughly extracted. The product was again dried under vacuum and stored in a desiccator over molecular sieves. The end-capping of the silylated silica was performed in liquid phase using hexamethyldisilazane (HMDS). The carbon content was determined with a Perkin-Elmer Elemental Analyzer Model 240 and the surface concentration of the modifier was calculated from the carbon coverage. Solid-state NMR measurements were performed on a Bruker (Rheinstetten, Germany) MSL 300 spectrometer. Infrared spectra were obtained with diffuse reflectance infrared Fourier transform spectrometer (FTS-60, Bio-Rad Labs., Richmond, CA, USA).

Table 1
Cyclosiloxanes and silazane used in experiment

Name of compound	Abbreviation	Formula	Molecular weight
Hexamethylcyclotrisiloxane	HMCTS	$\text{C}_6\text{H}_{18}\text{O}_3\text{Si}_3$	222.46
Octamethylcyclotetrasiloxane	OMCTS	$\text{C}_8\text{H}_{24}\text{O}_4\text{Si}_4$	296.61
Octaphenylcyclotetrasiloxane	OPCTS	$\text{C}_{48}\text{H}_{40}\text{O}_4\text{Si}_4$	793.18
Hexamethyldisilazane	HMDS	$\text{C}_6\text{H}_{19}\text{NSi}_2$	161.39

2.2. Solid phase extraction

2.2.1. Chemicals and apparatus

Pesticides and PCB standards used in the experiments were obtained from Supelco SA (Switzerland). Nitro-compound standards were from Aldrich-Chemie (Steinheim, Germany). Solid-phase extraction was carried out with Baker SPE-12 system (Gross-Gerau, Germany). The C₁₈, SPE-500 and phenyl silica SPE cartridges were obtained from J.T. Baker. *n*-Hexane, diethyl ether and ethyl acetate (Merck, Darmstadt, Germany) were used as solvents for extraction. The organic pure water was obtained by Cobrabid-Aqua System (Warsaw, Poland). Chromatographic measurements were made with a gas chromatography system (Fisons Instruments, Models GC 6000 and GC 8000) equipped with a ⁶³Ni electron capture detector (ECD). The analytical column was a DB-5 (J&W) fused-silica capillary column (30 m×0.32 mm, 0.25 μm film) and the confirmation column was a Rtx-1301 (Restek) fused-silica capillary column (30 m×0.32 mm, 0.5 μm film). Helium and nitrogen were used as the carrier gas and the detector make-up gas, respectively. Table 3 presents the appropriate GC temperature programs used for an analysis of test compounds. The Chrom-Card system was used for collection and processing of the chromatographic data.

2.2.2. Procedures

Five hundred mg of the modified silica were packed dry into plastic columns with reservoir capacities of 6 ml. Each column contained polyethylene frits to support and cover the filler. The procedure of extraction was as follows: prior to initial use, the cartridges were conditioned by passing through 3 ml of methanol followed by 3 ml of organic pure water. The water sample was spiked with standard solution and then 100 ml water were

forced through the bed at a sample flow-rate of 3–5 ml/min. The following concentrations of organic pollutant in water were used: pesticides, 0.1 and 0.01 μg/l; PCBs, 0.5 μg/l; and nitro-compounds, 10 μg/l. After the adsorption step the SPE column was washed with organic pure water and air was blown through the column for 15 min to dry the bed. Three ml of hexane+ether (1+1) mixture were used for elution of pesticides and PCBs, while ethyl acetate was used for elution of nitro-compounds. The volume of the extract was reduced to 1 ml.

3. Results and discussion

3.1. Modification of silica gel

The effect of temperature and time of reaction on the results of modification was examined. The synthesis was carried out in boiling *n*-alkane for 3, 4, 5 or 7 h. As the results of 7-h experiments were similar to those of 4-h modification, we used as a standard a 5-h process. We have noted an improvement when the 'initial adsorption' step was included in the modification procedure; i.e., the silica and the cyclosiloxane were placed together in *n*-alkane for 2 days before the synthesis.

The temperature of synthesis process plays an important role [6,12]. For silica modified by HMCTS in pentane (at 36°C) the carbon coverage was slightly higher than that obtained in hexadecane. Previously, much higher temperatures were used [6,12,14]. For modification by OMCTS the best result was observed in heptane (at 98°C). We have found that, for silica modified by OPCTS, the higher the boiling point of the solvent, the higher the carbon coverage of the silica surface. The best result was acquired in boiling hexadecane, i.e., at 287°C.

The effect of the amount of a catalyst on the

Table 3
The temperature program GC used for compounds tested

Compounds tested	Temperature program
Chlorinated pesticides	80°C (2 min) $\xrightarrow{25^\circ\text{C}/\text{min}}$ 180°C $\xrightarrow{6^\circ\text{C}/\text{min}}$ 280°C $\xrightarrow{10^\circ\text{C}/\text{min}}$ 300°C
Polychlorinated biphenyls	50°C (1 min) $\xrightarrow{25^\circ\text{C}/\text{min}}$ 180°C $\xrightarrow{3^\circ\text{C}/\text{min}}$ 250°C $\xrightarrow{10^\circ\text{C}/\text{min}}$ 300°C
Nitro-compounds	80°C $\xrightarrow{5^\circ\text{C}/\text{min}}$ 180°C $\xrightarrow{20^\circ\text{C}/\text{min}}$ 290°C

Table 4
The reproducibility of sorbent preparation procedure^a

Serial number of experiment	Laboratory 1 ^b		Laboratory 2 ^c	
	%C	%H	%C	%H
I	4.39	0.72	4.21	0.60
II	4.76	0.80	4.81	0.78
III	4.67	0.77	4.60	0.69
IV	4.90	0.81	4.79	0.72
Average	4.68	0.78	4.60	0.70
SD	0.22	0.04	0.28	0.08

^a Modification of Polygosil 100 by octaphenylcyclotetrasiloxane.

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^c Centre of Molecular and Macromolecular Research, Polish Academy of Sciences, Łódź, Poland.

results of synthesis was investigated. The following catalysts were used in the experiment: anhydrous acetic acid, hydrochloric acid and triethylamine. The amounts of the catalysts used were about 3% relative to the weight of the siloxane added. We estimated that the presence of the catalysts used has not considerably affected the reaction of synthesis. A slightly higher carbon content on silica Polygosil 100 was obtained:

- in the presence of concentrated hydrochloric acid for modification by HMCTS in pentane;
- in the presence of anhydrous acetic acid for modification by OMCTS in heptane.

The reproducibility of the surface modification procedure is of crucial importance for SPE sorbents. The modification of silica was repeated many times for all the modifiers studied. As an example of the reproducibility the results of Polygosil modification

Table 5
The results of modification of Polygosil 100 obtained at optimum conditions

Abbreviation	Conditions of modification	Carbon content (%)	Surface concentration, α ($\mu\text{mol}/\text{m}^2$)
PA	By hexamethylcyclotrisiloxane (HMCTS) in pentane, with HCl as a catalyst	5.05	2.97
PB	By octamethylcyclotetrasiloxane (OMCTS) in heptane, with acetic acid as a catalyst	2.60	1.05
PC	By octaphenylcyclotetrasiloxane (OPCTS) in hexadecane	4.67	0.31

Table 6
Literature values for HMCTS and OMCTS modified silicas

Literature	Surface coverage, α ($\mu\text{mol}/\text{m}^2$)	
	HMCTS	OMCTS
[5]	2.39	1.61
[6]	1.7	0.8
[17]	2.49	1.6
This paper	2.97	1.05
Average	2.39	1.27

are presented in Table 4. The results obtained at the optimum conditions are presented in Table 5.

Despite the structural similarity of the compounds used in synthesis of HMCTS and OMCTS, the surface concentration values after modification were much different. The surface concentration of HMCTS is much higher than that of OMCTS. Consequently, the lower surface concentration for OMCTS was obtained by other authors despite of the different conditions of experiments. The results are shown in Table 6 [5,6,17]. On average, the surface concentration of HMCTS is twice as much as that of OMCTS. To explain these differences we have end-capped the modified silicas with HMDS and the results are listed in Table 7.

The surface concentration of trimethylsilyl groups (TMS; $\alpha=4.36 \mu\text{mol}/\text{m}^2$) on bare Polygosil 100 corresponds to the maximum surface concentration of trimethylsilyl groups on the silica surface [15,18]. This value confirms proper efficiency of the modification process. However, the results of end-capping of PA, PB and PC are surprising taking into account a relatively low surface concentration of the modified sorbents. For end-capped HMCTS silica the total

Table 7
Characteristics of sorbent end-capped with HMDS

		Carbon content, C (%)	Total surface concentration, α ($\mu\text{mol}/\text{m}^2$)	TMS surface concentration, α ($\mu\text{mol}/\text{m}^2$)
P0	Bare silica gel silylated with HMDS	4.04	4.36	–
PA1	Sorbent PA end-capped	5.86	3.98	1.01
PB1	Sorbent PB end-capped	3.15	2.56	1.51
PC1	Sorbent PC end-capped	5.62	1.40	1.09

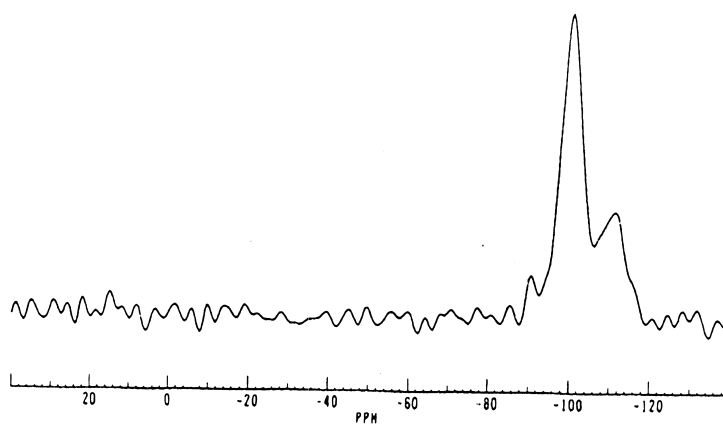
surface concentration is nearly $4 \mu\text{mol}/\text{m}^2$, but for OMCTS and OPCTS silicas the results are much lower. The results suggest that the silica surfaces modified with HMCTS, OMCTS and OPCTS are almost equally deactivated, i.e., there are almost the same numbers of silanols available for end-capping.

Fig. 1A shows the ^{29}Si CP MAS NMR spectrum of bare Polygosil 100. The signal at -90 ppm corresponds to surface silicon atoms containing two siloxane linkages and two hydroxyl groups, i.e., geminal silanols. The signal at -100 ppm corresponds to surface silicon atoms containing three siloxane linkages and a hydroxyl group, i.e., isolated silanol; and the signal observed at -110 ppm corresponds to the siloxane backbone of the silica. The signals between -18 and -22 ppm in Fig. 1B represent the various silicon atoms with methyl groups from cyclic siloxane, i.e., silicon atoms containing two methyl groups and two siloxane bonds. Such silicon atoms are present in siloxane chains and, according to Albert and Bayer [19], ^{29}Si NMR spectra cannot differentiate between the loop and monofunctionally attached chains in which the terminal silicon atom bears a silanol. Thus, as follows from ^{29}Si NMR CP MAS spectra, both structures are possible. However, the spectra do not confirm the presence of fragments of cyclosiloxane break-up, i.e., there is no evidence of $-\text{O}-\text{Si}(\text{CH}_3)_2-\text{O}-$ groups which should produce a signal at -10 ppm [19]. Therefore, assuming that the siloxane ring breaks up at one siloxane bond (at temperatures used throughout the paper) only, we can expect D3 or D4 fragments [19] on the silica surface, depending on the siloxane used. According to Rutten et al. [14], octamethylcyclosiloxane forms loops on the silica surface but (as they used much higher temperatures

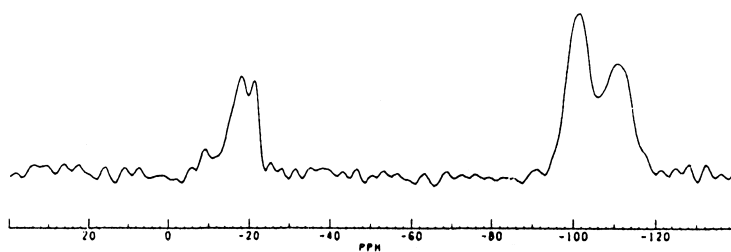
for modification) they suggest the break-up of the siloxane into smaller fragments.

Now let's take into account the results of silylation of the silica surface: the coverage of the silica with HMCTS molecules is on average twice that for OMCTS; the process of end-capping, with HMDS for both modified surfaces, does not differ much. This can lead to the conclusion that OMCTS molecules are attached as loops (i.e., as a bidentate ligands) to the silica surface, while HMCTS molecules are attached as monofunctional moieties, as shown in Fig. 2. This explains fairly well, an exceptionally good surface deactivation at low coverages of octamethylcyclotetrasiloxanes. If the OMCTS molecule forms the loop it blocks two silanols. Molecular models reveal that the loop structure is sufficiently long to shield the additional, third silanol, as shown in Fig. 3. This allows one molecule of OMCTS to block three silanols and that also explains quite well, a low-molecular coverage obtained for OMCTS modified surface.

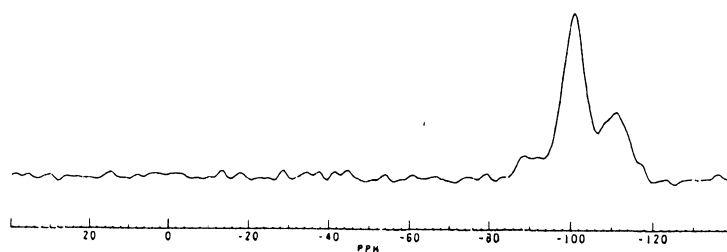
Another cyclotetrasiloxane OPCTS binds to the surface at a very low concentration. The result of end-capping (PC1) suggests that the OPCTS is also attached bifunctionally to the silica surface (i.e., it forms loops on this surface, Fig. 4). Thus, the calculation of the blocked silanols is as follows: assuming full rotation of the $-\text{Si}(\text{Ph})_2-$ groups around Si–O bond, these groups would shield $2 \times 1.65 \mu\text{mol}/\text{m}^2$ (two ends of the loop bound to the silica) plus $0.31 \mu\text{mol}/\text{m}^2$ (one silanol shield in the loop), this equals $3.61 \mu\text{mol}/\text{m}^2$. End-capping additionally blocks $1.09 \mu\text{mol}/\text{m}^2$ of $-\text{OH}$ groups, therefore, the total sum is $4.70 \mu\text{mol}/\text{m}^2$. This number is apparently high. Molecular models show, however, that with regard to the C–Si–C bond angle



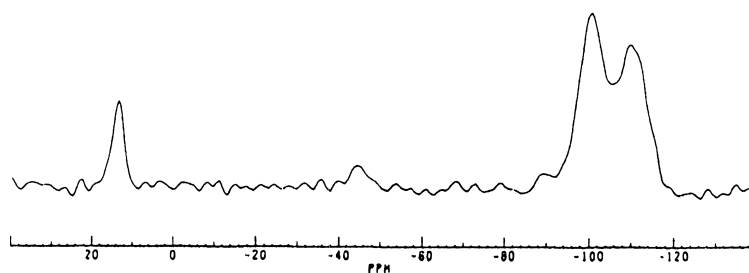
(A)



(B)



(C)



(D)

Fig. 1. ^{29}Si CP MAS NMR spectrum of Polygosil 100: (A) without modification; (B) modified with HMCTS; (C) modified with OPCTS; and (D) modified with OPCTS + end-capping HMDS.

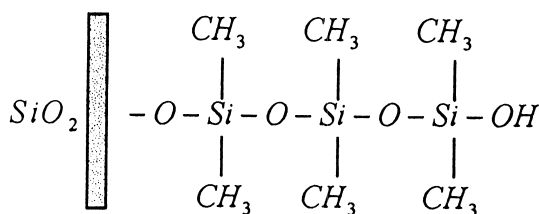


Fig. 2. Schematic representation of the point-wise linkage of HMCTS with the silica.

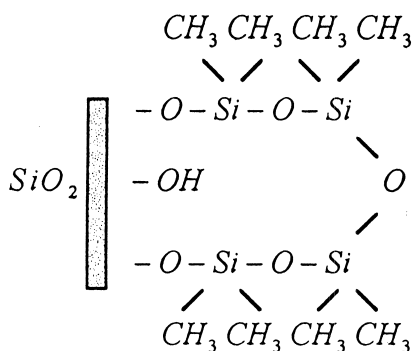


Fig. 3. Schematic representation of the loop structure of OMCTS bonded with the silica.

of 110° in the phenyl groups, these groups would shield $2 \times 1.15 \mu\text{mol}/\text{m}^2$ (assuming a full rotation), thus the total would be $3.70 \mu\text{mol}/\text{m}^2$ (together with the effects of the end-capping). The latter number is similar to that obtained for the PA1 sorbent. On the other hand, assuming a fully hindered rotation of the phenyl groups, the result seems to be too low, i.e., $3.2 \mu\text{mol}/\text{m}^2$ ($2 \times 0.9 \mu\text{mol}/\text{m}^2$ plus $0.31 \mu\text{mol}/\text{m}^2$

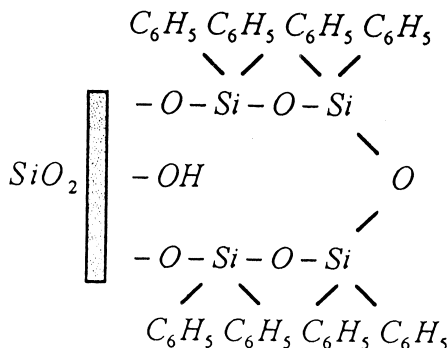


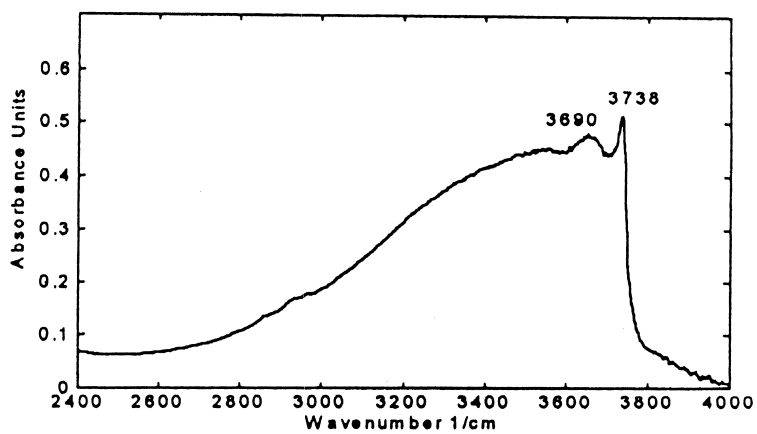
Fig. 4. Schematic representation of the loop structure of OPCTS bonded with the silica.

plus $1.09 \mu\text{mol}/\text{m}^2$); furthermore, if the bond angle is taken into the consideration, the result will be even lower, i.e., $2.84 \mu\text{mol}/\text{m}^2$. Therefore, according to the results, the most likely hypothesis must assume a free rotation of the phenyl groups, and a 110° bond angle of phenyl group. This gives $3.70 \mu\text{mol}/\text{m}^2$ of blocked silanols; however, we suspect that the loop of the OPCTS can shield more than one silanol per molecule, i.e., the number of silanols shielded by the loop should be higher than $0.31 \mu\text{mol}/\text{m}^2$.

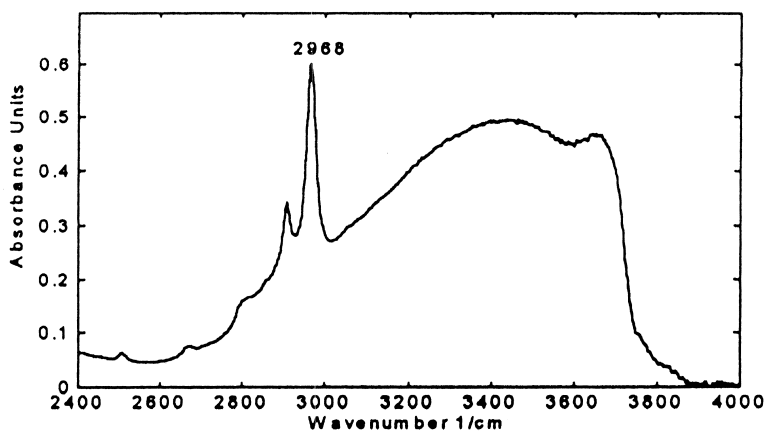
DRIFT and solid-state NMR spectroscopic studies confirmed the bonding of siloxanes onto the silica surface. Fig. 5A shows the DRIFT spectra of bare Polygosil 100 (silica gel without modification). The bands observed at 3738 and 3690 cm^{-1} are free (including geminal silanols) and weakly hydrogen-bonded silanol groups, respectively. Fig. 5B,C shows the DRIFT spectra of HMCTS and OPCTS bonded phases. The modification process remarkably diminished the OH area. In particular, the band at 3738 cm^{-1} disappeared almost completely. The appearance of the strong C–H stretching band near 2970 cm^{-1} indicates in Fig. 5B the presence of the methyl groups which have been bonded to the silica surface. The stretching band near 3030 cm^{-1} , evidenced in Fig. 5C, is characteristic of the C–H aromatic bond from phenyl groups. The presence of a strong band near 1430 cm^{-1} (not shown in the figure), characteristic of Si–Ph stretching (silicon–phenyl), confirms a successful bonding of octaphenylcyclotetrasiloxane.

In Fig. 1C, which shows the ^{29}Si CP MAS NMR spectra of the sorbent modified with OPCTS, no signals corresponding to the bonded siloxane can be seen, which can be interpreted as being due to a very low surface concentration of OPCTS (Table 5). However, in Fig. 1D, the spectrum of the same sorbent is shown after the end-capping process (sorbent PC1), and a strong signal at $+12 \text{ ppm}$ representing the trimethylsilyl groups appears.

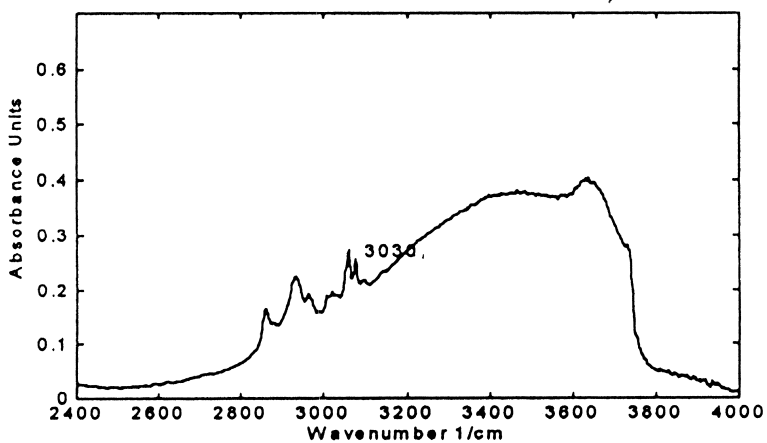
The results of elemental analysis, ^{29}Si CP MAS NMR, DRIFT and molecular modelling suggest that HMCTS binds to the silica surface monofunctionally, while it is highly probable that OMCTS and OPCTS form loops on the silica surface. Such structures are responsible for an excellent deactivation of surface silanols, despite their relatively low surface concentration.



(A)



(B)



(C)

Fig. 5. DRIFT spectrum of Polygosil 100: (A) without modification; (B) modified with HMCTS; and (C) modified with OPCTS.

3.2. Results of SPE

The recoveries of the low-carbon adsorbents in SPE were compared with those of the commercially available C₁₈ and phenyl SPE phases. For the sake of comparison we used chlorinated pesticides, PCB and nitro-compounds. Recovery is the most easily comparable parameter of synthesised and commercial packing. A comparison of chlorinated pesticide recoveries is shown in Table 8. The same experiments were performed at the following concentration of pesticides: 100 and 10 ng/l. The results in both cases are quite similar. Our limit of detection allows the determination of single ng/l amounts of the chlorinated pesticides.

The results are as follows:

- the recoveries of end-capped packings are slightly worse than those obtained on modified ones;
- the recoveries of pesticides on low-carbon and commercial packings are comparable;

Table 8
Pesticides recovery for various types of SPE sorbents

Sorbents	%C	Recovery ± standard deviation ^a (%) for concentration 100 (≠) and 10 ng/l (\$)			
		γ-HCH	Heptachlor	DDT	Methoxychlor
<i>Low-carbon adsorbents:</i> ^b					
HMCTS (PA)	5.05	(≠) 92 ± 14 (\$) 90 ± 15	56 ± 9 58 ± 10	60 ± 10 60 ± 12	75 ± 14 74 ± 14
HMCTS + end-capping (PA1)	5.86	(≠) 88 ± 8 (\$) 84 ± 14	51 ± 7 50 ± 11	55 ± 9 52 ± 11	69 ± 9 65 ± 12
OMCTS (PB)	2.60	(≠) 84 ± 15 (\$) 85 ± 15	54 ± 11 52 ± 11	55 ± 12 52 ± 14	70 ± 13 69 ± 14
OMCTS + end-capping (PB1)	3.15	(≠) 79 ± 7 (\$) 79 ± 10	49 ± 8 45 ± 10	48 ± 9 45 ± 11	66 ± 8 65 ± 11
OPCTS (PC)	4.67	(≠) 96 ± 14 (\$) 95 ± 14	69 ± 16 69 ± 16	69 ± 14 65 ± 15	78 ± 12 75 ± 12
OPCTS + end-capping (PC1)	5.62	(≠) 82 ± 10 (\$) 79 ± 13	62 ± 9 60 ± 11	61 ± 8 60 ± 10	72 ± 9 70 ± 11
<i>Baker's phases:</i> ^c					
Ph	11.30	(≠) 84 ± 9 (\$) 82 ± 10	56 ± 10 56 ± 11	54 ± 12 50 ± 14	70 ± 11 68 ± 12
C ₁₈	18.50	(≠) 87 ± 7 (\$) 85 ± 10	58 ± 6 52 ± 11	66 ± 9 60 ± 11	73 ± 6 72 ± 8
SPE-500	16.01	(≠) 104 ± 3 (\$) 104 ± 6	65 ± 10 64 ± 12	69 ± 5 68 ± 9	75 ± 9 72 ± 12

^a Standard deviation for $n=6$.

^b For a description of the adsorbents, see Tables 5 and 7.

^c Baker's sorbents: Ph, Bakerbond SPE* phenyl (C₆H₅); C₁₈, Bakerbond SPE* octadecyl; SPE-500, for the rapid SPE of organochlorine pesticides from aqueous samples.

Table 9
Column capacities for γ-HCH

Column, 500 mg	Carbon content (%)	Adsorption capacity (mg/500 mg)
<i>Low-carbon adsorbents:</i>		
HMCTS (PA)	5.05	1.8
OMCTS (PB)	2.60	1.7
OPCTS (PC)	4.67	1.7
<i>Baker's phases:</i>		
C ₁₈	18.5	7.6
Ph	11.3	7.3

- low-carbon (PC) phenyl phase reveals a better recovery than that of commercial phenyl phase;
 - the efficiency of Baker's SPE-500 phase, particularly suitable for chlorinated pesticides, is comparable to that of the low-carbon PC sorbent.
- We have also determined adsorption capacities of low-carbon phases for γ-HCH and compared them

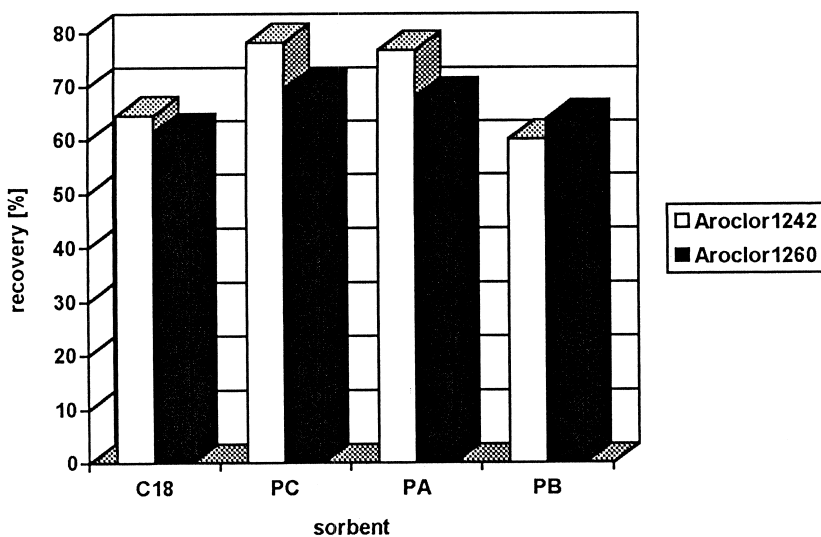


Fig. 6. PCB recoveries for various types of SPE sorbents (for a description of the sorbents, see Table 5).

with the capacity of commercial SPE adsorbents. The results are shown in Table 9.

As expected, the capacities of low-carbon phases are lower than those of commercial phases. However, the capacity of 1.7–1.8 mg is far above the analytical needs in practical environmental analysis. Usually, a cartridge containing 500 mg of the SPE phase is used for an extraction of 1 l (or less) of

water sample which contains no more than $\text{ng}/\mu\text{g}$ of the analyte.

For further examination of low-carbon SPE phases we have selected PCBs. The recoveries of PCBs (Aroclor 1242 and Aroclor 1260) are again compared to those on commercial Baker phases. Fig. 6 clearly shows that the efficiencies of PC and PA phases are better than those on commercial C_{18} phase.

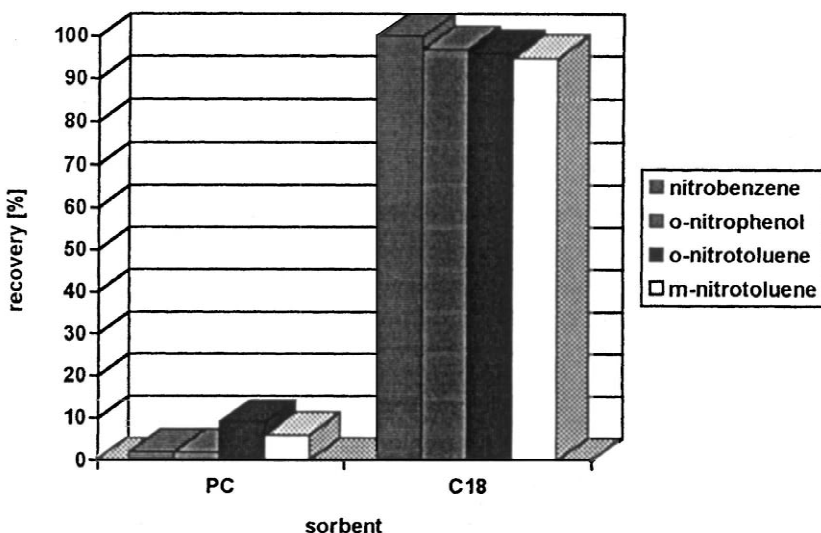


Fig. 7. Nitro-compound recoveries for various types of SPE sorbents (for a description of the sorbents, see Table 5).

All the measured recoveries on cyclosiloxane modified phases are in the range 60–80%, which indicates that low-carbon adsorbents may be useful for solid-phase extraction.

3.3. Selectivity

We have examined the sorbents in SPE method also for nitro-compounds. Nitrobenzene, *o*-nitro-

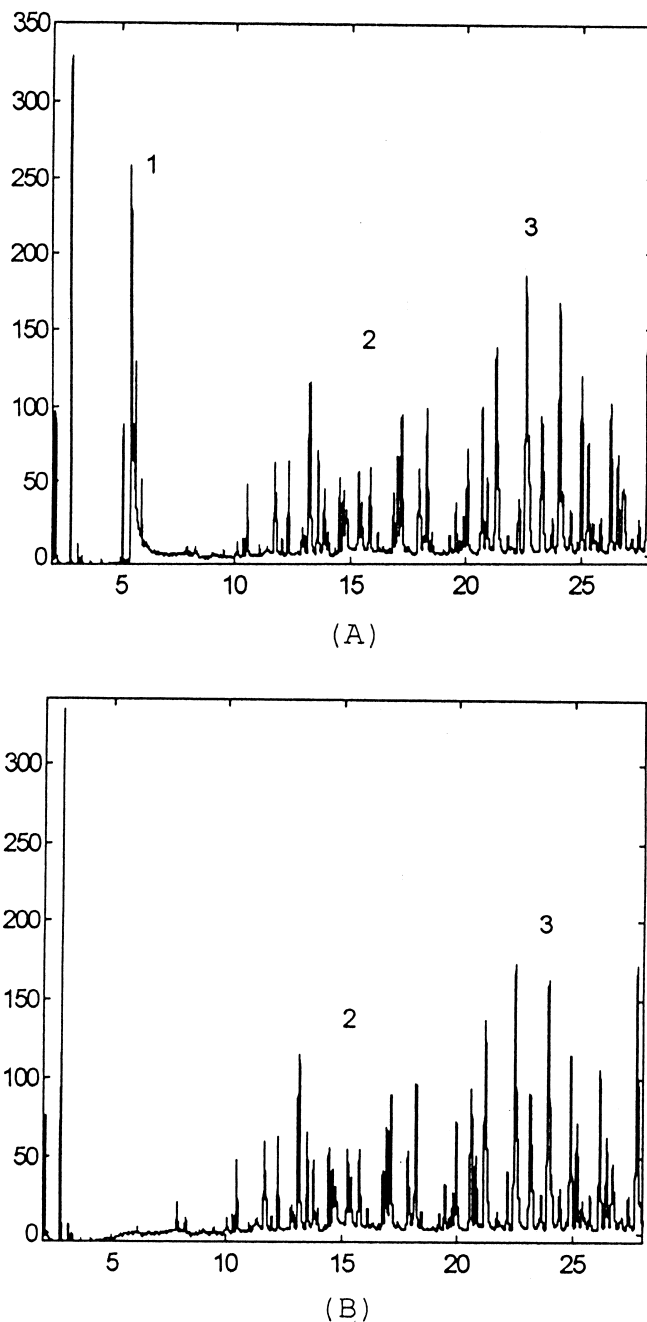


Fig. 8. Separation of the analyte eluted from: (A) C_{18} sorbent and (B) PC sorbent (PC, Polygosil 100 modified with OPCTS).

phenol, *o*-nitrotoluene and *m*-nitrotoluene were used as a test mixture. The recoveries for this group of compounds on cyclosiloxane-modified sorbents were very low, less than 9%, whereas the recoveries obtained on Baker sorbents were about 100%. The results shown in Fig. 7 are indicative of some unexpected selectivity of the cyclosiloxane-modified silica. This selectivity can lead to a selective enrichment of certain groups of compounds in the presence of complex matrix.

To illustrate such a possibility we prepared a mixture of water polluted with PCBs and nitro-compounds. The sample was extracted on PC phase as well as on Baker's octadecyl sorbent. For the studied mixture of nitro-compounds with PCBs, the procedure developed for PCBs was applied, assuming that the nitro-compounds were the only interference. In Fig. 8 there are two chromatograms, which show the separation of analytes eluted from C₁₈ sorbent (Fig. 8A) and from PC sorbent (Fig. 8B). It is evident that nitro-compounds as well as PCBs are concentrated on the octadecyl sorbent, while on the PC sorbent only polychlorinated biphenyls are found. The reason for such a selectivity has not yet been ascertained.

4. Conclusion

Low-carbon SPE adsorbents obtained by modification of the silica surface with cyclosiloxanes appeared to be suitable for chlorinated hydrocarbon enrichment from polluted waters. The recoveries observed on such adsorbents are similar to those found on commercial C₁₈ phases.

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