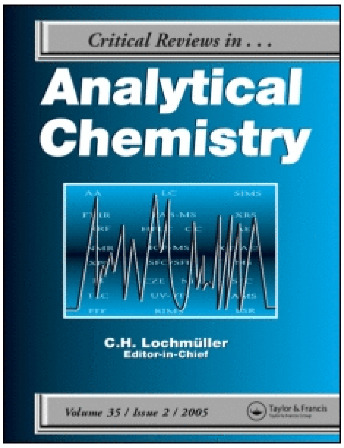

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Adam Kloskowski[a]; Michal Pilarczyk[a]; Wojciech Chrzanowski[a]; Jacek Namieśnik[b]
[a] Faculty of Chemistry, Department of Physical Chemistry, Gdańsk University of Technology, Gdańsk, Poland [b] Faculty of Chemistry, Department of Analytical Chemistry, Gdańsk University of Technology, Gdańsk, Poland

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Sol-Gel Technique—A Versatile Tool for Adsorbent Preparation

Adam Kloskowski,[1] Michał Pilarczyk,[1] Wojciech Chrzanowski,[1] and Jacek Namieśnik[2]
[1]*Faculty of Chemistry, Department of Physical Chemistry, Gdańsk University of Technology, Gdańsk, Poland*
[2]*Faculty of Chemistry, Department of Analytical Chemistry, Gdańsk University of Technology, Gdańsk, Poland*

Preparation of samples for analysis, first of all isolation and/or enrichment of analytes, is becoming a key stage of each analytical procedure including determination of trace components. Effectiveness of this stage, i.e., analyte enrichment, removal of interferents and change of the original sample matrix, depends both on the chosen extraction technique and utilized materials and reagents. Though liquid-liquid extraction is still widely used in analytical practice, it seems that solid phase extraction (SPE) techniques are gaining the dominating position. In these techniques, solid sorbents and pseudo-liquid materials are used as the analytes retaining media. Although a variety of sorbents and stationary phases usable in analytical procedures is known, due to an even larger assortment of analytes present in samples differing in matrix composition, the need for search for new types of sorbents exists. In this field, the sol-gel technique offers good opportunities of producing new sorption materials. Using this technique, one can obtain fit-for-purpose materials. Although sol-gel technique had been known for many years, its first applications in analytical chemistry were described in early 1990s. Since then, an increasing number of papers discussing the preparation of new sorbents using this technique and their applications is a proof positive of great opportunities offered by the technique.

Keywords sample preparation, sol-gel, extraction, adsorbents, polar analytes

INTRODUCTION

The progress of civilization enforces monitoring of chemical compounds contents in many types of samples and in many areas: beginning with waters containing industrial or biological pollutants, through pharmaceuticals, food, to analyses of biological materials. A vital stage in chemical analysis is sample pretreatment, allowing for the final identification and quantitative determination of analytes using a chosen analytical method, including detection technique. Generally, there are three goals of this pre-treatment stage: substitution of the original sample matrix by another one, more suitable for the final determination method, enrichment of the analytes in question in this secondary matrix, and removal of the components interfering in the final determination.

Many different techniques may be employed at the sample pre-treatment stage, beginning with the most common liquid-liquid extraction in many modes, like extraction in the Soxhlet apparatus, supercritical fluid extraction, microwave assisted extraction, and accelerated extraction. Some of these methods are time consuming, multi-step and their automation is a difficult task. Another basic drawback of these techniques is utilization of harmful organic solvents. The technique of extraction to a stream of gas (stripping) bypasses these disadvantages of liquid-liquid extraction, though it is restricted to volatile compound, weakly interacting with the matrix analytes.

Utilization of sorbents for isolation of analytes is the most frequent way of avoiding these limitations, yet suitable for almost any class of analytes. Here, two techniques play the leading role: solid phase extraction (SPE) and its variant — solid phase microextraction (SPME), including capillary microextraction (CME), also known as in-tube SPME. In both techniques, utilization of partition mechanism-based sorbents (like pseudo-liquid polymers) and classic adsorbents is possible. In the case of partition, analytes are dissolved in the retaining medium; this

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Address correspondence to Michał Pilarczyk, Department of Physical Chemistry, Chemical Faculty, Gdańsk University of Technology,11/12 G. Narutowicza St., Gdańsk 80-233, Poland. E-mail: chemfiz@pg.gda.pl process occurs with rather mean selectivity, based exclusively on sorbent polarity. The most important practical consequence of this fact is poor ability of the method to isolate polar organic compounds from aqueous matrices, when the difference in affinity of the analytes to both media is generally insignificant. Selectivity of extraction may be considerably improved by using adsorbents, due to the specific interactions between the analyte and the adsorbent. The principal obstacle here, however, is the relatively limited number of commercially available adsorbents. In SPE, the most frequently utilized materials are: silica based (C_2, C_8, C_{18}), poly(styrene-divinylbenzene (PS-DVB), methacrylate-DVB, and poly(N-vinylpyrrolidone-DVB). In the case of SPME, the situation is even more difficult. Due to the limited amount of the retaining phase, its affinity towards the analytes must be much larger than in SPE, when the amount of the adsorbent may be suitably adjusted, to ensure retention of sufficient amounts of the analytes. Besides, due to the specific way of manipulation of the sampler, the stationary phase must be durable. Among commercially available coatings, one can mention PDMS, polyacrylate, carboxen, carbowax, and DVB, met also in different combinations.

The situation described is itself a driving force of a further search for new materials of high extraction potential. In literature, three general trends may be noticed. First comes search for new applications of known sorbents, including their chemical modification (1–3). The second approach includes attempts of application for sample pre-treatment materials used in other fields like carbon nanotubes (4–6), supramolecular sorbents (7, 8), cigarette filters (9), TiO_2 nanotubes (10), biosorbents (11), and immunosorbents (12, 13). The third trend means using and modifying suitable techniques for preparation of sorbents specially tailored for specific applications. Two major techniques should be mentioned: preparation of molecularly imprinted polymers (MIP) (14–16) and the sol-gel technique (17). In both cases, the superior aim is obtaining an adsorbent characterized by maximum selectivity and revealing desired mechanical and chemical properties. It is worth observing, that the two techniques have a certain common area; namely, many molecularly imprinted polymers are obtained using the sol-gel technique. Additionally, using the latter technique provides some extra advantages like chemical bonding of the adsorbent to the substrate, ensuring suitable mechanical durability and stable working conditions. The presence of the inorganic part in the structure of adsorbents results in their significantly better chemical resistance.

A review of literature regarding utilization of the sol-gel technique in analytical applications is presented in this paper. Examples of preparative procedures are discussed, with special attention to the adsorption properties of the materials obtained. A short description of analytical applications of sorbents synthesized using the sol-gel technique is also included.

GENERAL OVERVIEW OF THE SOL-GEL TECHNIQUE

The sol-gel technique is a very convenient way of obtaining both inorganic and hybrid organic-inorganic polymers. Its basic advantage is carrying out the whole process at very gentle conditions. Analytical applications of the technique result principally from the possibility of binding the polymer formed with the substrate/support via a covalent bond, providing the latter has suitably exposed hydroxyl groups (18–20). Sol-gel obtained polymers, physically immobilized in the carrier, are also known (21), as well as monolithic sorbents (22). The technique is versatile enough to permit obtaining sorbents in almost any form: films, fibers, particles, etc.

Sol-gel chemistry includes hydrolysis of suitable precursors, usually metal alkoxides $M(OR)_x$, and their subsequent condensation with release of either water or an alcohol (Fig. 1). One can

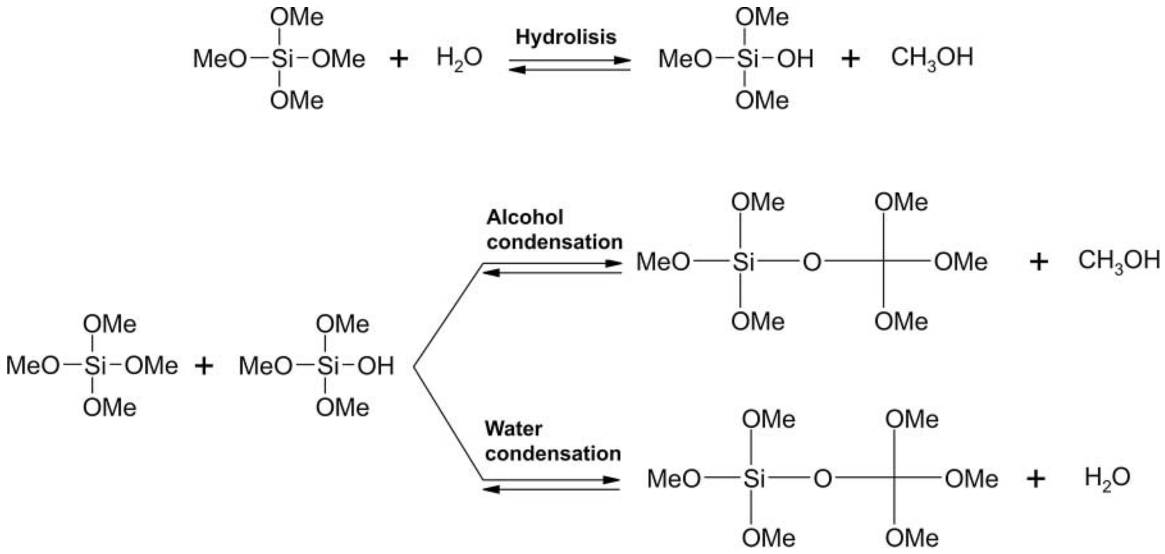


FIG. 1. Basic reactions in a sol-gel process.

see that the reaction is basically a substitution of alkoxyl groups with hydroxyl groups, followed by condensation of partially hydrolyzed alkoxides. The increase in polymer chain length leads to formation of nanoparticles constituting a sol. Aggregation of sol particles due to formation of bonds between their chains leads to formation of a macrostructure—physically revealed as formation of a gel.

As mentioned before, selectivity of the adsorbent may be influenced by introducing suitable functional agents into the inorganic structure. This may be achieved in two ways. First, it is carried out by introducing a reagent capable of reaction with the hydroxyl groups of the precursor, formed in the hydrolysis, which leads to chemical binding of groups active in the extraction process with the sorption material. The most frequently used compounds are organoalkoxysilanes of general formula R'_{4-x}-Si(OR)$_x$ (23), where R′ denotes a suitable functional group. Another way is physical immobilization of the active agent within the lattice of the gel formed. In this way such compounds as crown ethers, enzymes, color indicators, cyclodextrins, antibodies, chelating compounds, etc., may be used.

In a typical case, the basic components of the reaction mixture are: precursor, solvent, and catalyst. Sometimes certain extra reagents are used. Although the most frequently used precursor is tetramethoxysilane (TEOS), other silanes like tetraethoxysilane (TEOS) or methyltrimetoxysilane (MTMOS) are also mentioned (see Table 1). Important factors influencing the kinetics of the process, thus determining whether the polymer obtained is more or less cross-linked, are the type of catalyst and its concentration and temperature (24–26). Utilization of acid catalysts, like, for example, trifluoroacetic acid, accelerates hydrolysis leading to the formation of (RO)$_x$Si-OH molecules. On the other hand, protonation of the next silanol groups of the molecule formed is slower, thus reducing the extent of hydrolysis and leading to domination of molecules with a single reactive hydroxyl group only. This subsequently results in the formation of long chains and low cross-linking of the polymer.

Utilization of basic catalysts causes rapid hydrolysis of all silanol groups of the precursor, therefore facilitating reactions between molecules and leading to a high degree of cross-linking. It also means a very rapid gelling process and an increase in solution viscosity. Also, the amount of monomers in the reaction mixture is relatively high. These molecules are subsequently removed when the gel is dried, finally yielding polymer of very "loose," porous structure.

Another important reactant involved in sol-gel chemistry is a deactivating agent. Its task is derivatization of the remaining silanol groups. This is done to reduce chances of interactions of analytes with strongly polar hydroxyl groups. Such interactions would mean a necessity of high temperatures if thermal desorption was employed for liberation of the analytes.

Summarizing, one can enumerate the following advantages of the sol-gel technique in synthesis of adsorbents:

- Obtaining adsorbents in practically any form and configuration;
- Free choice of compounds modifying adsorption properties, therefore permitting preparation of tailor-made adsorbents;
- Chemical binding of adsorbents with the support, increasing their mechanical durability and chemical stability;
- Control of synthesis conditions permitting preparation of materials of different porosity;
- Presence of inorganic skeleton increases chemical resistances of the polymer;
- Synthesis at room temperature facilitates usage of different modifiers of adsorption properties;
- Chemical binding of functional reagents with the silica lattice prevents their losses in the extraction processes.

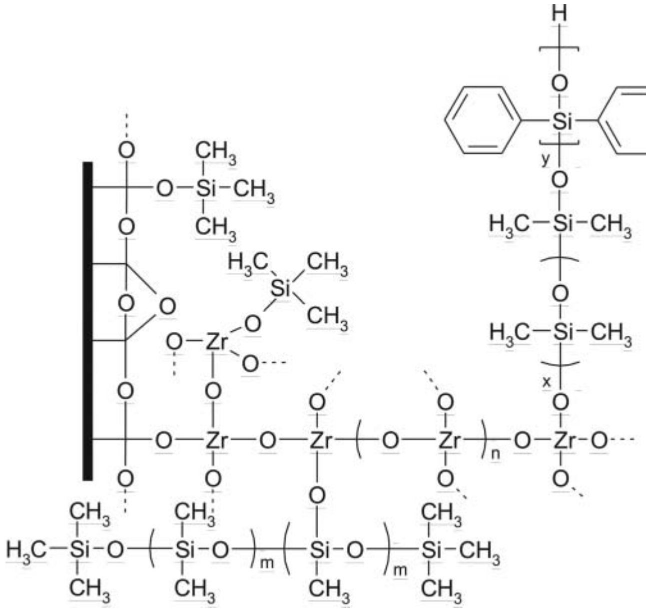
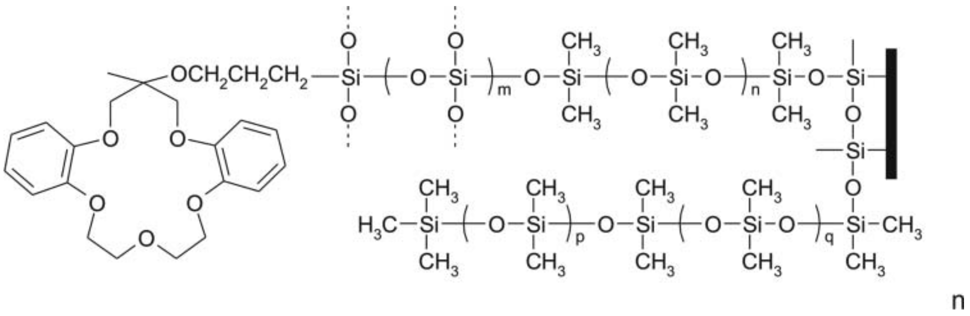
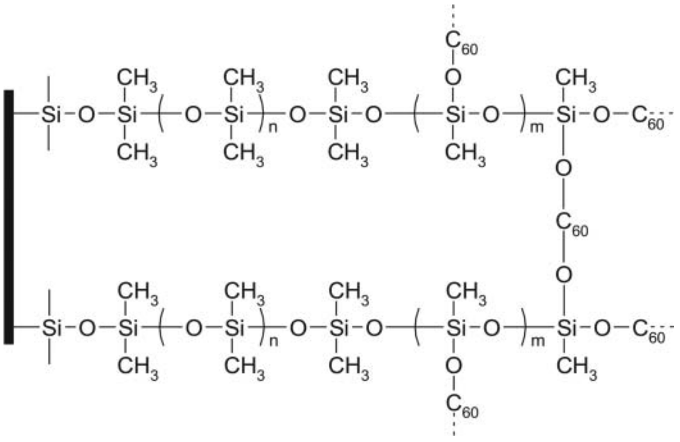
PREPARATION OF ADSORBENTS

The driving force of development of the sol-gel technique — enabling syntheses of new sorption materials, alternative to the commercially available ones — is the low diversity of the latter ones. For example, stationary phases used in the SPME technique offer only a single mechanism influencing selectivity of adsorption, i.e., difference in polarity of sorbents. Additionally, the precise selection of an adsorbent for a specific analytical application is also limited by its chemical and thermal stability. On the other hand, utilization of the sol-gel technique can significantly enhance working temperature range of known polymers, for example, polyethyleneglycol, which — after chemical binding to the silica lattice — may be used at desorption temperatures up to 400°C (27, 28). A similar effect was observed for crown ethers used as modifiers, whose thermal resistance after binding to the silica skeleton rose to 350°C (29), and also PDMS (28).

Not all problems with chemical resistance can be, however, eliminated using sol-gel technique. Quite frequently, examples may be found in CME technique, employing stationary phases typical for gas chromatography, which require special ways of preparation. Silica-based materials also cause restrictions regarding pH, due to the labile character of Si-O-Si bonds, which undergo hydrolysis at pH above 8 (30). Therefore, new preparative methods appear, aiming at enhancement of applicability of sol-gel polymers (31, 32). One of the suggested approaches is the introduction of metal oxides into the polymer structure (33). Another example may be using germanium, as a structural analog of silicon (34). Tetramethoxygermanium was used as a precursor, being hydrolyzed at the presence of trifluoroacetic acid (TFA) as a catalyst. The final structure of the coating obtained is shown in Fig. 2.

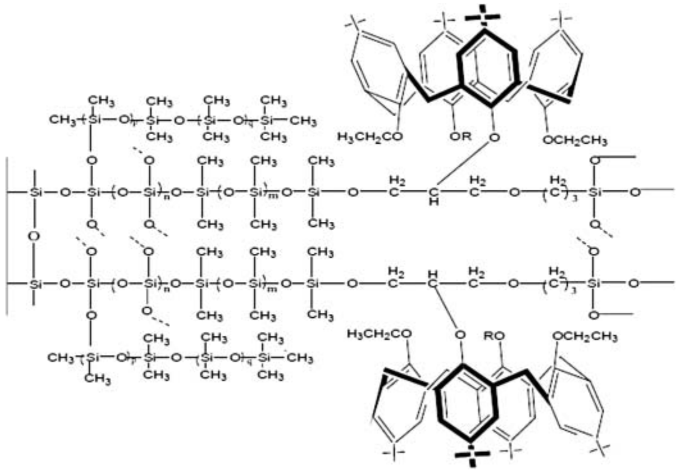
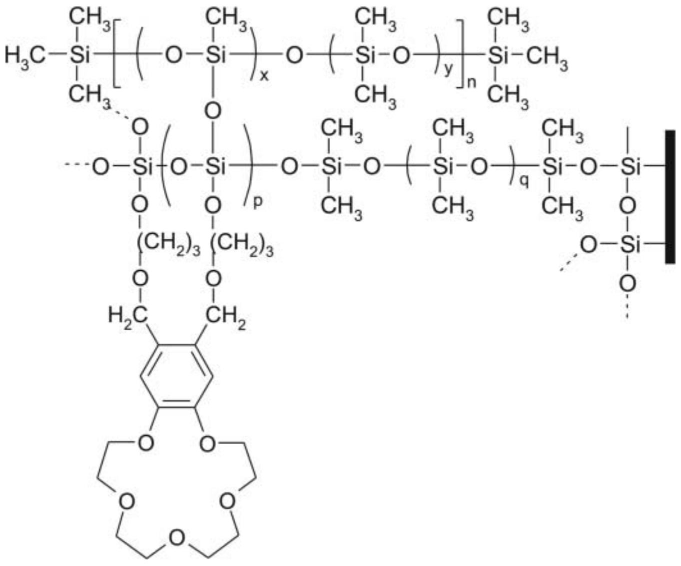
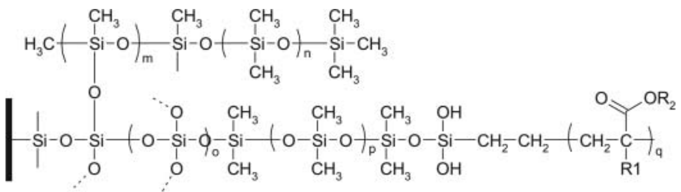
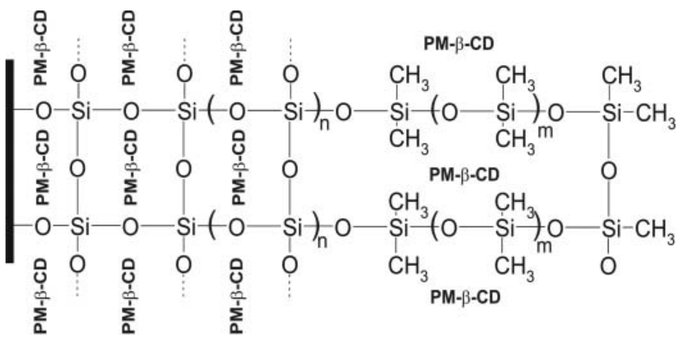
The polymer obtained did not reveal any loss in extraction properties even after cycles of rinsing with both 0.05 M HCl and 0.1 M NaOH. A similar effect was observed when titanium(IV)butoxide was used as the precursor (35). The obtained coating worked in a stable manner even after rinsing with 3 M HCl or 3 M NaOH. Additionally, due to its ability of acid-base

TABLE 1
Functional components of the sol-gel solution and chemical structures of the synthesized coatings

Reagents	Adsorbent structure	Ref.
Zirconium(IV) butoxide; silanol-terminated poly(dimethyldiphenylsiloxane)		(49)
Allyloxy bisbenzo 16-crown-5 trimethoxysilane		(50)
Fullerol (fullerene derivative)		(51)

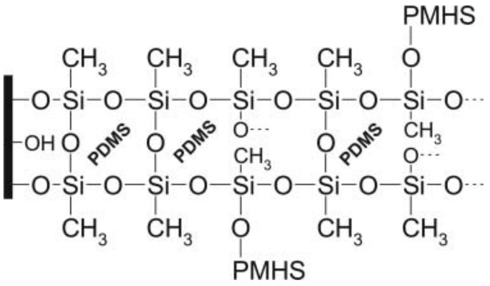
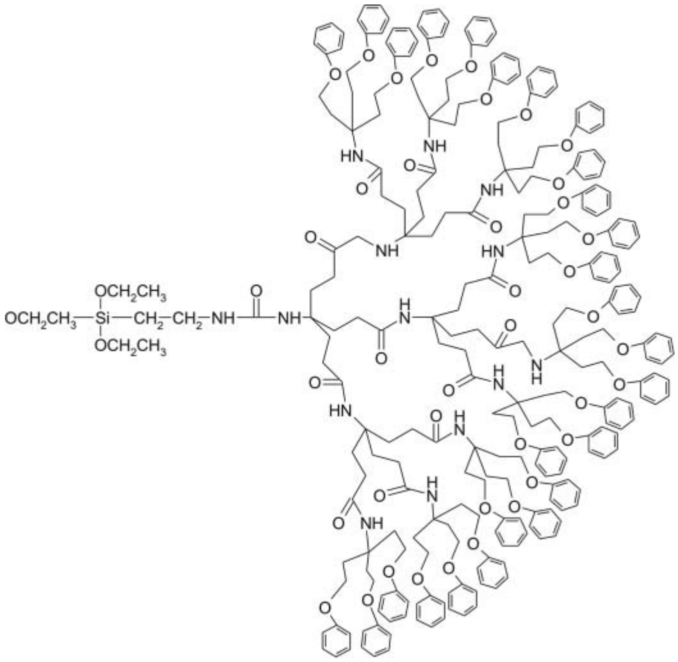
(Continued on next page)

TABLE 1
Functional components of the sol-gel solution and chemical structures of the synthesized coatings *(Continued)*

Reagents	Adsorbent structure	Ref.
5,11,17,23-tetra-*tert*-butyl-25,27-diethoxy-26,28-dihydroxycalix[4]arene; 3-(2-cyclooxypropoxyl)-propyltrimethoxysilane		(52)
Dihydroxy-terminated benzo-15-crown-5; hydroxy-terminated silicone oil		(53)
Hydroxy-terminated silicone oil (OH-TSO); methyl acrylate (MA); methyl methacrylate (MMA); butyl methacrylate (BMA)		(54)
Permethylated-β-cyclodextrin; hydroxyl-termination silicone oil		(55)

(Continued on next page)

TABLE 1
Functional components of the sol-gel solution and chemical structures of the synthesized coatings *(Continued)*

Reagents	Adsorbent structure	Ref.
PDMS (physically incorporated into the sol–gel network)		(56)
Phenyl-terminated dendrimer with a triethoxysilyl containing root (57)		(58)

interactions of both Brönsted-and Lewis-type, its effectiveness in extraction of aromatic amines, phenols and PAHs was significantly higher than that of a silica-based sol-gel coating.

An important, aforementioned aspect of using the sol-gel technique is the opportunity of the introduction of compounds, capable of interactions with a very wide spectrum of analytes, into the polymer structure. One of the most frequently adopted methods is the synthesis of templated polymers. Several instances of this method may be found in literature, for example a polymer imprinted with compounds containing aromatic compounds with two or three 3-aminopropyltriethoxysilane side groups (36), hybrid organic–inorganic sol–gel polymeric systems leading to a propranolol-imprinted sorbent (37), sorbent obtained using 2,4-dichlorophenoxyacetic acid as a template, 3-[N,N-bis(9-anthrylmethyl)amino] propyltriethoxysilane, as a functional monomer (38), sol–gel system for polymer imprinting with lisinopril dihydrate (39) and many others.

An interesting comparison was demonstrated in a paper (40), where two sorbents were synthesized, the first was obtained using a pore-forming agent (lactic acid), while the second was obtained using ammonium solution as a base catalyst in a sol-gel process. Different methods of template removal (extraction with methanol and calcination at 600°C) were also compared. Competition adsorption experiments with caffeine (CAF) and its structural analog theophylline (TH) have been performed using HPLC. Addition of the pore-forming agent ensured better adsorption of caffeine (ca. 20 μmol/g) than in the case of sorbents obtained with the base catalyst. The latter sorbent, however, revealed better selectivity (ca. four times; selectivity (α) is expressed here as a ratio of the amount of adsorbed CAF to that of the adsorbed TH). In yet another publication, dysprosium(III)-imprinted thenoyltrifluoroacetone (TTA) deposited on silica was used as a template (41). Ion imprinted polymer was formed by binding 3-aminopropyl trimethoxysilane

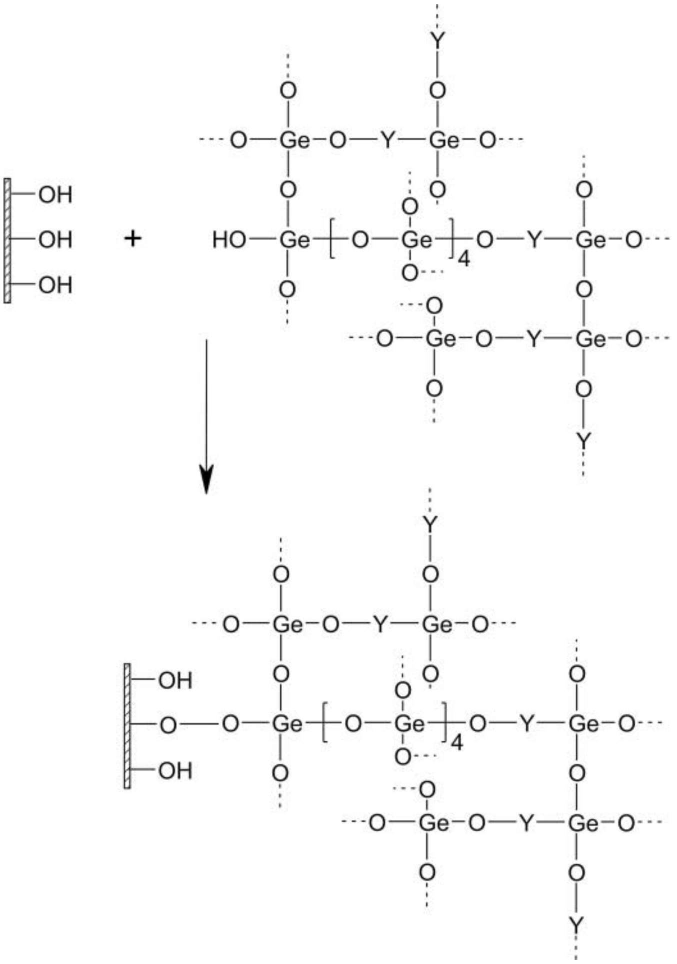


FIG. 2. Structure of germanium based polymer and its binding to the fused silica substrate.

molecules to the hydroxyl groups and the complex metal ions—TTA had been formed before co-hydrolysis and co-condensation with silane groups occurred. This sorbent was later used for selective adsorption of Dy(III) ions in the presence of La(III), Nd(III) and Gd(III) ions. Another example of combining the sol-gel technique with the surface imprinting technique is a sorbent synthesized for use in immobilized metal affinity chromatography (IMAC), a novel, rapidly developing technique used for separation and purification of proteins in biochemistry, biology and the pharmaceutical industry (42, 43). Separation of proteins in this technique is based on a kind of "identification" process occurring between the protein and a pseudo-biospecific ligand (immobilized metal ion). In this case the inorganic precursor used was γ-glycidoxypropyltrimethoxysiloxane (GPTMS), while the functional biopolymer was chitosan (CS) in the presence of polyethylene glycol (PEG) (44). Autohydrolysis of GPTMS, autohydrolysis and co-condensation of silane groups (Si-OH) together with *in situ* covalent cross-linking CS resulted in the formation of coating on the surface of silica gel. The sorbent obtained was subsequently characterized by X-ray energy dispersion spectroscopy (EDX), scanning electron microscopy (SEM) and mercury intrusion porosimetry. This adsorbent revealed high sorption capacity towards copper ions and subsequently also towards bovine serum albumin (BSA) used as a model protein. Immobilization of functional groups on the surface of the polymer frequently leads to reduction of the available surface area and also diminishing of the volume of the pores up to 60–84% (45). This may also result in non-uniform distribution of ligands on the surface. Sorbents with immobilized groups prepared using the sol-gel technique are characterized by much more ordered distribution of the functional groups, high concentration of ligands and long life cycles (46). The basic condition of obtaining a coating of good adsorption properties is independent hydrolysis and homo-condensation of both the functional precursor and the cross-linking agent, followed by their co-condensation (45, 47). Synthesis of a pyrazole-functionalized adsorbent for extraction and separation of palladium(II), platinum(IV) and gold(III) ions may serve as an example. The synthesis is shown schematically in Fig. 3.

The functional polymer N-(trimethoxysilylpropyl)-pyrazole (PzPs) was synthesized by N-alkylation of 1H-pyrazole 3-chloropropyltrimethoxysilane in the presence of diisopropylethylamine (48).

These examples certainly do not exhaust the topic of the potential of the sol-gel technique that regards wide chemical diversity of the materials obtained. Table 1 may serve as a supplement; containing different types of functional compounds along with structures of some of the adsorbents obtained.

APPLICATIONS

The sol-gel technique is principally used for the preparation of materials for coatings of the extraction fiber of the SPME device (59), although its applications for SPE (60), capillary microextraction (CME) (61), as well as stir bar sorptive extraction (SBSE) (62–64) can also be found. Considering the properties of the adsorbents obtained in this way, they are dedicated for extraction of polar compounds (65, 66) like pesticides (67, 68), phenols (69, 70), polychlorinated biphenyls (71) and metal ions (72). Nonetheless, one can also find examples of utilization of such coatings for determination of polycyclic aromatic hydrocarbons (52, 71) and less polar compounds like, for example, BTEX (27, 73, 74).

EXTRACTION OF METAL IONS

Standard techniques of extraction of metal ions, like LLE or CPE, require high consumption of solvents. Besides, relatively large samples are usually required, which may become difficult in analyses of biological material, esp. in forensic analysis. Utilization of adsorbents obtained by the sol-gel technique for extraction of metal ions is also favored for their pH resistance. Chelating compounds, e.g., polysaccharides (75), may be included in the polymer structure as metal

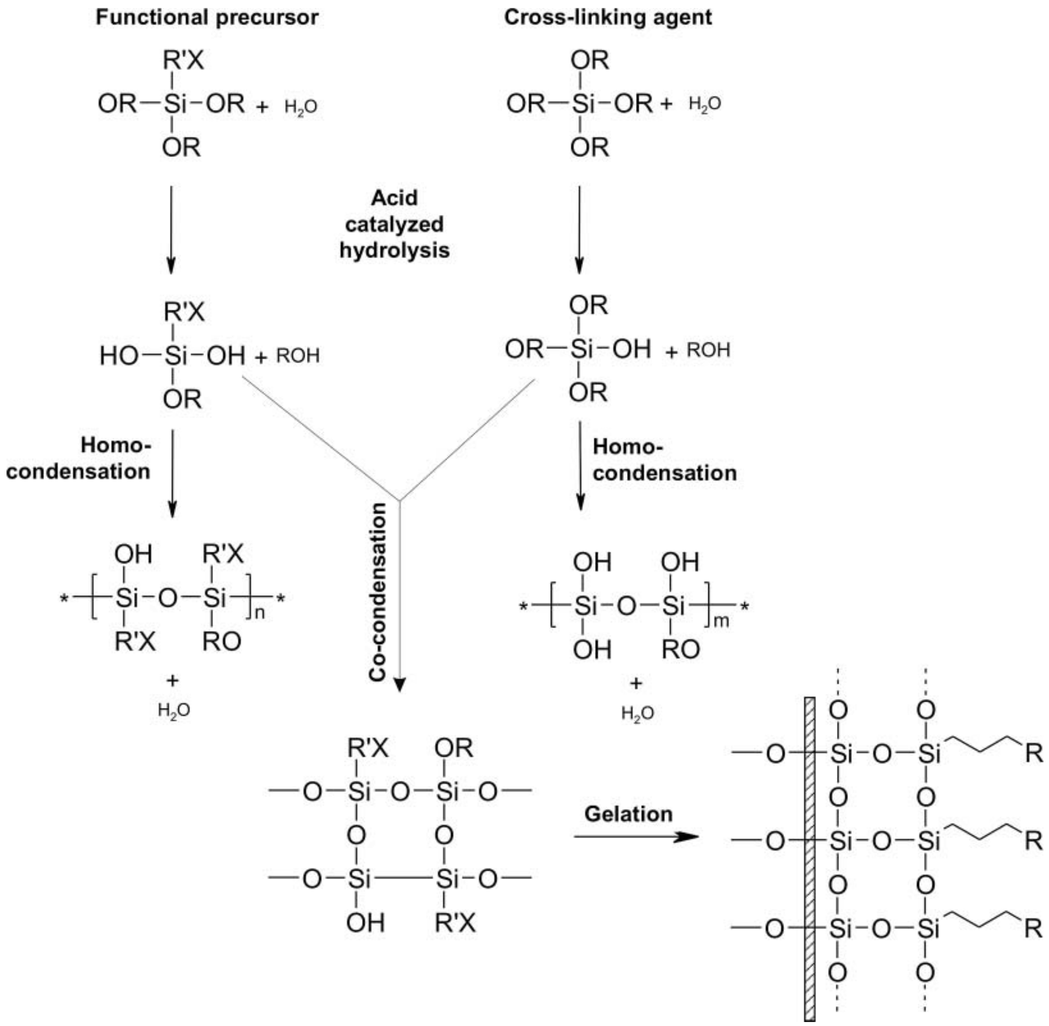


FIG. 3. Scheme of synthesis of surface imprinted polymer using the sol-gel technique.

ions retaining agents. Authors used chitosan, which is a natural and a biodegradable compound. Additionally, it blends smoothly with polymers, which facilitates the synthesis. γ-glycidoxypropyltrimethoxysiloxane (GPTMS) was used as a precursor capable of covalent bonding with chitosan in the polymer lattice. Cadmium(II) ions were also introduced to the reaction mixture, where they played the role of template—in the structure of the polymer, metal ions were surrounded by chitosan molecules. Actually, the amino groups were responsible for the adsorption process; hence, the pH working range permitting effective extraction of ions is above pH = 6.5. In more acidic media nitrogen atoms become protonated, lowering extraction effectiveness. Another example of utilization of an amine groups containing a compound capable of chelating metal ions is utilization of *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPTS) (76). Cetyltrimethylammonium bromide (CTAB) was used as a template. The technique of sample pre-treatment tested in the paper was CME. Structure of the coating obtained was characterized by IR techniques, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Extraction conditions for this coating (pH, eluent volume, sample flow rate, sample volume) were optimized. Finally, the optimized procedure was employed for determination of such ions like copper, zinc, nickel, mercury and cadmium in samples of human hair, human serum and human urine. The coating was much more robust as compared with the conventional SPME fibers. The detection limit on the order of pg-mL was achieved. Another frequently used way of extraction of metal ions is using thiacrown ethers as the active component of the coating. Very interesting results were obtained when crown compounds were either chemically bonded to the sorption phase (sol-gel) or introduced on a surface of a standard SPE column packing (Florisil) (77). Authors used three thiacrown ethers: 1,4,7,10-tetrathiacyclododecane, 1,4,7,10,13-pentathiacyclopentadecane, and 1,4,7,10.13,16-hexathiacyclooctadecane. Comparison of sorption properties using a mixture of eleven metal ions (Mg^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, V^{4+}, Hg^{2+}) did not reveal

TABLE 2
Reagents used in sol-gel syntheses and applications of the adsorbents obtained

Functional monomer	Precursor	Catalyst	Analyte/matrix	Analytical technique	Reference
3-aminopropyltrimethoxysilane/caffeine	TEOS	Ammonium hydroxide	Methylxanthines/water,urine	SPE	(93)
5,11,17,23-Tetra-*tert*-butyl-25,27-diethoxy-26,28-dihydroxycalix[4]arene (C[4]), 3-(2- cyclooxypropoxyl)propyltrimethoxysilane (KH-560), hydroxy-terminated silicone oil (OH-TSO)	TEOS	TFA (5% water)	BTEX, PAH, aromatic amines/water	SPME	(52)
Hydroxy-terminated silicone oil (OH-TSO)	Tetraethoxysilane (TEOS), 3-(trimethoxysilyl)propyl methcrylate (TMSPMA)	TFA (5% water), benzophenone	Aroma compounds/beer	SPME	(94)
5,11,17,23-Tetra-*tert*-butyl-25,27-diethoxy-26,28-diglycidyloxycalix[4]arene (diglycidyloxy-C[4]), 3-aminopropyltriethoxysilane (KH-550), OH-TSO	TEOS	N.A.	Enantiomers of propranolol/urine	SPME	(95)
OH-PDMS	Methyltrimethoxysilane (MTMOS)	TFA (5% water)	Gasoline residues/fire debris	HS-SPME	(96)
—	Methyltrimethoxysilane (MTMOS), phenyltrimethoxysilane (PTMOS)	HCl, HF, NaOH	Benzene, toluene, ethylbenzene, 2-octanone, benzaldehyde, acetophenone, dimethylphenol, tridecane/water	SPME	(97)
Hydroxy-terminated dibenzo-14-crown-4 (OH-DB14C4), urushiol crown ether (DHSU14C4), 3,5-dibutyl-unsymmetrydibenzo-14-crown-4-dihydroxy crown ether (DBUD14C4), OH-TSO	TEOS	TFA (5% water)	Aromatic amines/wastewater	HS-SPME	(98)
(OH-PDMS), poly(vinyl alcohol) (PVA)	Methyltrimethoxysilane (MTMOS)	TFA (5% water)	*o*-xylene,naphthalene, ethyl caprate,*p*-chlorotoluene, polychlorinated biphenyls/water	HS-SPME	(71)
Hydroxy-terminated dibenzo-14-crown-4 (OH-DB14C4), KH-560, OH-TSO	TEOS	TFA (5% water)	Phenols/wastewater	SPME	(99)
Carbowax 20M	MTMOS	TFA (5% water)	BTEX/water	SPME	(27)

Dihydroxy-terminated benzo-15-crown ether (DOH-B15C5), hydroxy-terminated silicone oil (OH-TSO)	TEOS	TFA (5% water)	BTEX, chlorobenzenes, carcinogenic arylamines/ water	HS-SPME	(29)
OH-TSO, 4/-allyl dibenzo-18-crown-6 (allyl DB18C6), allyloxy ethoxymethyl-18-crown-6 (allyl PSO18C6), 3/-allyl benzo-15-crown-5 (allyl B15C5)	Tetraethoxysilane (TEOS), vinyltriethoxysilane (VTEOS)	TFA (5% water)	Organophosphorus pesticedes/water, apple juice, tomato	HS-SPME	(100)
OH-PDMS	Titanium(IV) isopropoxide	TFA (27% water)	Alkylbenzenes, ketones, PAH/water	In-tube SPME	(101)
Butyl methacrylate, OH-TSO, γ-Methacryloxypropyltrimethoxysilane	TEOS	TFA (5% water), benzophenone	Ephedrine derivatives/water, urine	HS-SPME	(102)
Hydroxy-terminated silicone oil (OH-TSO), butylmethacrylae (BMA), methylmethacrylate (MMA)	TEOS, vinyltriethoxysilane (VTEOS)	TFA (5% water), benzophenone	2-chloroethyl ethyl sulphide/soil	HS-SPME	(54)
n-Octyltriethoxysilane (C8-TEOS)	Methyltrimethoxysilane (MTMOS)	0.1M HCl	Organometals/water	SPME	(103)
OH-PDMS	TEOS	TFA (5% water)	Aromatic hydrocarbons/water	SPME	(104)
2,6-di-*O*-Methyl)-β-cyclodextrin (DM-β-CD), hydroxy-terminated silicone oil (OH-TSO), KH-560	TEOS	TFA (5% water)	Ephedrin, methamphetamine/urine	HS-SPME	(105)
3,5′,3″-Trisbenzyloxy-2-dodecyloxy-[1,1′,4′,1″]terphenyl, 2_,5’-bisbenzyloxy-[1,1′;4′,1″]terphenyl	TEOS	Ammonium hydroxide	Organochlorine pesticide, triazine herbicide, estrogens, alkylphenols, bisphenol-A/water	SPME	(106)
OH-TSO	Allyloxy bisbenzo-16-rown-5-trimethoxysilane, TEOS	TFA (5% water)	Organophosphorus pesticide/honey, orange juice, vegetable	SPME	(50)
Hydroxy-terminated silicone oil (OH-TSO), Fullerom	MTMOS	TFA	PCB, PAH aromatic amines/water	HS-SPME	(51)
OH-PDMS	MTMOS	TFA (5% water)	PAH, alkanes, aniline derivatives, alcohols, phenolic compounds/water	SPME	(28)
Silanol-terminated poly(dimethyldiphenylsiloxane) copolymer (PDMDPS)	Zirconium(IV) butoxide	Glacial acetic acid	PAH, ketones, aldehydem/water	In-tube SPME	(49)

any significant differences between the two ways of using the ethers. On the other hand, thermogravimetric analysis, performed in a nitrogen atmosphere in the 30–700°C temperature range, revealed decomposition of unbounded thiacrown ethers. They decomposed in a single step at 280, 330 and 340°C for 12S4-SG, 15S5-SG and 18S6-SG, respectively. Thermogravimetry of ethers bonded to the support demonstrated that the larger the ether molecule, the higher gain in thermal stability of the ether. For ethers immobilized in a sol-gel matrix, decomposition temperatures were within the 480–520°C temperature range. Immobilized ethers revealed thermal stability similar to that of non-templated sorbents.

BIOLOGICAL SAMPLES

Isolation and purification of DNA molecules from biological samples is of top importance in medical, biochemical or forensic studies. Cloning, sequencing and hybridyzation of DNA all require removal of such impurities like RNA, proteins, salts or endotoxins. Using traditional methods of DNA purifications (organic extraction phenol/chloroform or Chelex extraction), automation or miniaturization of the procedure was impossible. Besides, a relatively large DNA sample was needed, large amounts of reagents consumed and the procedure itself was complex and time-consuming (78). The application of SPE in DNA purification is described in literature (79, 80). There are problems, however, regarding a support having both high sorption capacity and suitable size of the capillary channel. Some authors suggested obtaining by sol-gel technique monolithic columns with hydroxyapatite support (Hap, $Ca_{10}(PO_4)_6(OH)_2$) for further usage in DNA extraction at gentle conditions (81). Hap is a ceramic material present in nature as a minerale and is also an inorganic component of bones and teeth. It is biocompatible and is capable of Winding biomolecules (82, 83). Sorbent was obtained as a monolothic filling of a capillary column. The precursor (TMOS) was accompanied in the reaction mixture by chitosan, addend as a solution in acetic acid (2.5%, w/v). In the course of reaction, particles of Hap were forming a skeleton structure with macropores. At optimized conditions, effective extraction of PBE2 plasmide from cells of the *Baacillus subtilis* bacteria was possible. Additionally, due to low concentration of salts in the sample, it is possible to use the extracted DNA directly in PCR analysis.

Determination of fatty acids in lung tissue is another example of utilization of the sol-gel technique for analysis of biological samples (84). Sorbent, obtained from hydroxyterminated silicone oil (OH-TSO) and butyl methacrylate, permitted extraction of derivatized moderate- and long-chained fatty acids with efficiency above 75%.

Another example of molecular imprinting in the sol-gel technique is as an adsorbent with caffeine used as a template. Caffeine was introduced into the polymer without forming any chemical bonds. Caffeine is an indicator of water pollution, but it is also a heart-stimulating compound influencing relaxation of the heart muscle and, therefore, its concentration is one of the parameters monitored at the anti-doping tests (85). In the synthesis of polymer, 3-aminopropyltrimethoxysilane (APTMS) was used as a functional monomer and tetraethyl orthosilicate (TEOS) as the cross-linking agent. Fine particles of adsorbent were used as an SPE column filling. Extraction of caffeine and its structural analogs, like theophylline and theobromine, from samples of water and human urine was performed, yielding detection limits of 53, 44 and 85 μg/L, respectively.

OTHER SAMPLES

Adsorbents obtained using immunosorbents also have potentially wide applicability in the sol-gel technique. Immunosorbents have already been used in analytical procedures on supports such as silica gel or agarose gel (86, 87). Examples of their utilization in the sol-gel technique are scarce and include extraction of PAH (88), triazine herbicides (89), malathion (90) or bisphenols (91). An interesting example is the application of this kind of adsorbent for determination of sulfonylurea herbicides in food samples (92). Authors suggested utilization of sol-gel immunosorbents either in a form of crushed monolith or as a coating of highly porous silica particles with polyclonal anti-SU (sulfonyloureas) antibodies. In both cases, a selected fraction of immunoglobulin (IgG) from polyclonal rabbit anti-SU anti-serum (pAb-R03) was used. Sixteen different sulfonyloureas, extracted from water and food samples, were tested. Depending on the matrix type, extraction efficiencies of about 70% were observed for water and about 75% for food samples. Detection limits were determined and their levels amount to several dozen ng-L for water and 10 μg-kg for food.

A number of other applications of adsorbents prepared using the sol-gel technique are collected in Table 2.

CONCLUSIONS

The basic advantage of the sol-gel technique is its unusual flexibility in influencing the physicochemical and mechanical properties of the adsorbents synthesized. Conditions of synthesis permit usage of a wide spectrum of compounds capable of modification of the adsorption properties of the polymer. Moreover, in many cases it is possible to use chemically or thermally unstable compounds, which gain stability and resistance after being placed in the silica lattice. Flexible procedures of synthesis permits application of the sol-gel technique for making adsorbents for practically any of the three solid extraction techniques, SPE, SPME, and relatively new SBSE.

Such a flexibility and diversity may also produce some negative consequences. The procedure of synthesis is a rather complex one, with many parameters subject to optimization. The procedures described in literature can hardly be reproduced in other laboratories. Also, at this point in the history of the sol-gel technique development, one should not expect its early commercialization, which almost certainly would facilitate wider application of the adsorbents synthesized.

REFERENCES

1. M. Giardina, L. Ding, and S.V. Olesik, Devlopment of fluorinated low temperature glassy carbon films in solid-phase microextraction. *J. Chromatogr.* 1060 (2004):15–224.
2. C.O. Ania, B. Cabal, C. Pevida, A. Arenillas, J.B. Parra, F. Rubiera, and J.J. Pis, Removal of naphthalene from aqueous solution on chemically modified activated carbons, *Water Res.* 41 (2007):333–340.
3. M. Josefsson and A. Sabanovic, Sample preparation on polymeric solid phase extraction sorbents for liquid chromatographic-tandem mass spectrometric analysis of human whole blood—A study on a number of beta-agonists and beta-antagonists. *J. Chromatogr. A* 1120 (2006):1–12.
4. J.-X. Wang, D.-Q. Jiang, Z.-Y. Gu, and X.-P. Yan, Multiwalled carbon nanotubes coated fibers for solid-phase microextraction of polybrominated diphenyl ethers in water and milk samples before gas chromatography with electron-capture detection. *J. Chromatogr. A* 1137 (2006):8–14.
5. W. Den, H.-Ch. Liu, S.-F. Chan, K.T. Kin, and Ch. Huang, Adsorption of phthalate esters with multiwalled carbon nanotubes and its applications. *J. Environ. Eng. Manage.* 16 (2006):275-282.
6. X. Kan, Y. Zhao, Z. Geng, Z. Wang, and J.-J. Zhu, Composites of multiwalled carbon nanotubes and molecularly imprinted polymers for dopamine recognition. *J. Phys. Chem. C* 112 (2008):4849–4854.
7. A. Moral, M.D. Sicilia, S. Rubio, and D. Perez-Bendito, Determination of bisphenols in sewage based on supramolecular solid-phase extraction/liquid chromatography /fluorimetry. *J. Chromatogr. A* 1100 (2005):8–14.
8. F. Merino, S. Rubio, and D. Perez-Bendito, Evaluation and optimization of an on-line admicelle-based extraction-liquid chromatography approach for the analysis of ionic organic compounds. *Anal. Chem.* 76 (2004):3878–3886.
9. H.-D. Liang, D.-M. Han, and X.-P. Yan, Cigarette filter as sorbent for on-line coupling of solid-phase extraction to high-performance liquid chromatography for determination of polycyclic aromatic hydrocarbons in water. *J. Chromatogr. A* 1103 (2006):9–14.
10. Q. Zhou, Y. Ding, J. Xiao, G. Liu, and X. Guo, Investigation of the feasibility of TiO2 nanotubes for the enrichment of DDT and its metabolites at trace levels in environmental water samples. *J. Chromatogr. A* 1147 (2007):10–16.
11. M. Iqbal, A. Saeed, and S.I. Zafar, Hybrid biosorbent: An innovative matrix to enhance the biosorption of Cd(II) from aqueous solution. *J. Hazard. Mater.* 148 (2007):47–55.
12. P.P. Carrasco, R. Escola, M.P. Marco, and J.M. Bayona, Development and application of immunoaffinity chromatography for the determination of the triazinic biocides in seawater. *J. Chromatogr. A* 909 (2001):61–72.
13. J. Cai and J. Henion, Quantitative multi-residue determination of β-agonists in bovine urine using on-line immunoaffinity extraction-coupled column packed capillary liquid chromatography-tandem mass spectrometry. *J. Chromatogr. B* 691 (1997):357–370.
14. N. Pérez-Moral and A.G. Mayes, Comparative study of imprinted polymer particles prepared by different polymerisation methods. *Anal. Chim. Acta* 504 (2004):15–21.
15. P.A.G. Cormack and A.Z. Elorza, Molecularly imprinted polymers: synthesis and characterization. *J. Chromatogr. B* 804 (2004):173–182.
16. A. Martín-Esteban, Molecularly imprinted polymers: new molecular recognition materials for selective solid-phase extraction of organic compounds. *Fresenius J. Anal. Chem.* 370 (2001):795–802.
17. M.M. Collinson, Recent trends in analytical applications of organically modified silicate materials. *TrAC* 21 (2002):31–39.
18. S. Hofacker, M. Mechtel, M. Mager, and H. Kraus, Sol-gel: A new tool for coatings chemistry. *Prog. Org. Coat.* 45 (2002):159–164.
19. N.A. Alcantar, E.S. Aydil, and J.N. Israelachvili, Polyethylene glycol-coated biocompatibile surfaces, Biomed. *Mater. Res.* 51 (2000):343–351.
20. A. Kumar, Gaurav, A.K. Malik, D.K. Tewary, and B. Singh, A review on development of solid phase microextraction fibers by sol–gel methods and their applications. *Anal. Chim. Acta* 610 (2008):1–14.
21. R. Allabashi, M. Arkas, G. Hörmann, and D. Tsiourvas, Removal of some organic pollutants in water employing ceramic membranes impregnated with cross-linked silylated dendritic and cyclodextrin polymers. *Water Res.* 41 (2007):476–486.
22. S. Yu, J. Geng, P. Zhou, J. Wang, X. Chen, and J. Hu, New hydroxyapatite monolithic column for DNA extraction and its application in the purification of Bacillus subtilis crude lysate. *J. Chromatogr. A* 1183 (2008):29–37.
23. A.V. Rao, G.M. Pajonk, S.D. Bhagat, and P. Barboux, Comparative studies on the surface chemical modification of silica aerogels based on various organosilane compounds of the type R_nSiX_{4--n}. *J. Non-Cryst. Solids* 350 (2004):216–223.
24. J. Sanchez, S.E. Rankin, and A.V. McCormick, 29Si NMR Kinetic Study of Tetraethoxysilane and ethyl-substituted ethoxysilane polymerization in acidic conditions. *Ind. Eng. Chem. Res.* 35 (1996):117–129.
25. A.V. Rao and R.R. Kalesh, Comparative studies of the physical and hydrophobic properties of TEOS based silica aerogels using different co-precursors. *Sci. Technol. Adv. Mater.* 4 (2003):509–515.
26. C.J. Brinker, R. Sehgal, S. L. Hietala, R. Deshpande, D.M. Smith, D. Loy, and C.S. Ashley, Sol-gel strategies for controlled porosity inorganic materials. *J. Membr. Sci.* 94 (1994):85–102.
27. R.G.D.C. Silva and F. Augusto, Highly porous solid-phase microextraction fiber coating based on poly(ethylene glycol)-modified ormosils synthesized by sol–gel technology. *J. Chromatogr. A* 1072 (2005):7–12.
28. S.L. Chong, D. Wang, J.D. Hayes, B.W. Wilhite, and A. Malik, Sol−gel coating technology for the preparation of solid-phase microextraction fibers of enhanced thermal stability. *Anal. Chem.* 69 (1997):3889–3898.
29. D. Wang, J. Xing, J. Peng, and C. Wu, Novel benzo-15-crown-5 sol–gel coating for solid-phase microextraction. *J. Chromatogr. A* 1005 (2003):1–12.
30. A. Wehrli, J.C. Hildenbrand, H.P. Keller, R. Stampfli, and R.W. Frei, Influence of organic bases on the stability and separation properties of reversed-phase chemically bonded silica gels. *J. Chromatogr.* 149 (1978):199–210.
31. J. J. Kirkland, J. L. Glajch, and R. D. Farlee, Synthesis and characterization of highly stable bonded phases for high-performance liquid chromatography column packings. *Anal. Chem.* 61 (1989):2–11.

32. L.C. Sander; S.A. Wise; and C.H. Lochmuller, Recent advances in bonded phases for liquid chromatography Crit. *Rev. Anal. Chem.* 18 (1987):299–415.
33. J. Nawrocki, C. Dunlap, A. McCormick, P.W. Carr, Part I. Chromatography using ultra-stable metal oxide-based stationary phases for HPLC. *J. Chromatogr. A* 1028 (2004):1–30.
34. L. Fang, S. Kulkarni, K. Alhooshani, and A. Malik, Germania-based, sol−gel hybrid organic−inorganic coatings for capillary microextraction and gas chromatography. *Anal. Chem.* 2007 (2007):9441–9451.
35. X. Li, J. Gao, and Z. Zeng, pH-resistant titania hybrid organic–inorganic sol–gel coating for solid-phase microextraction of polar compounds. *Anal. Chim. Acta* 590 (2007):26–33.
36. A. Katz and M.E. Davis, Molecular imprinting of bulk, microporous silica. *Nature* 403 (2000):286–289.
37. S. Marx and Z. Liron, Molecular imprinting in thin films of organic−inorganic hybrid sol−gel and acrylic polymers. *Chem. Mater.* 13 (2001):3624–3630.
38. M.K.-P. Leung, C.-F. Chow, and M.H.-W. Lam, A sol–gel derived molecular imprinted luminescent PET sensing material for 2,4-dichlorophenoxyacetic acid. *J. Mater. Chem.* 11 (2001):2985–2991.
39. A. Olwill, H. Hughes, M. O'Riordain, and P. McLoughlin, The use of molecularly imprinted sol–gels in pharmaceutical separations. *Biosens. Bioelectron.* 20 (2004):1045–1050.
40. H.-S. Wei, Y.-L. Tsai, J.-Y. Wu, and H. Chen, Preparation of inorganic molecularly imprinted polymers with higher adsorption and selectivity by sol–gel method. *J. Chromatogr. B* 836 (2006):57–62.
41. N. Zhang, B. Hu, and C. Huang, A new ion-imprinted silica gel sorbent for on-line selective solid-phase extraction of dysprosium(III) with detection by inductively coupled plasma-atomic emission spektrometry. *Anal. Chim. Acta* 597 (2007):12–18.
42. D.Z. Liu, Y.L. Lu, H.C. Cheng, and W.C. Hou, Immobilized Zinc Affinity Chromatography of Pectin Hydroxamic Acids for Purification of Trypsin Inhibitors from Soybean and Sweet Potato. *J. Agric. Food Chem.* 53 (2005):10219–10223.
43. A. Dubrovska and S. Souchelnytskyi, Efficient enrichment of intact phosphorylated proteins by modified immobilized metal-affinity chromatography. *Proteomics* 5 (2005):4678–4683.
44. F. Li, X.-M. Li, and S.-S. Zhang, One-pot preparation of silica-supported hybrid immobilized metal affinity adsorbent with macroporous surface based on surface imprinting coating technique combined with polysaccharide incorporated sol–gel process. *J. Chromatogr. A* 1129 (2006):223–230.
45. J.S. Lee and L.L Tavlarides, Application of organo-ceramic adsorbents functionalized with imidazole for noble metal separations. *Solvent Extraction and Ion Exchange* 20 (2002):407–427.
46. K.H. Nam, S. Gomes-Salazar, and L.L. Tavlarides, Mercury(II) Adsorption from wastewaters using a thiol functional adsorbent. *Ind. Eng. Chem. Res.* 42 (2003):1955–1964.
47. J.S. Lee, S. Gomez-Salazar, and L.L. Tavlarides, Synthesis of thiol functionalized organo–ceramic adsorbent by sol–gel technology. *React. Funct. Polym.* 49 (2001):159–172.
48. L. L. Tavlarides, J. S. Lee, K. H. Nam, and N. Agarwal, Sol-gel synthesized adsorbents for metal separation. *Tsinghua Science & Technology* 11 (2206):233–240.
49. K. Alhooshani, T.-Y. Kim, A. Kabir, and A. Malik, Sol–gel approach to in situ creation of high pH-resistant surface-bonded organic–inorganic hybrid zirconia coating for capillary microextraction (in-tube SPME). *J. Chromatogr. A* 1062 (2005):1–14.
50. J. Yu, C. Wu, and J. Xing, Development of new solid-phase microextraction fibers by sol–gel technology for the determination of organophosphorus pesticide multiresidues in food. *J. Chromatogr. A* 1036 (2004):101–111.
51. J. Yu, L. Dong, C. Wu, L. Wu, and J. Xing, Hydroxyfullerene as a novel coating for solid-phase microextraction fiber with sol–gel technology. *J. Chromatogr.* A, 978 (2002):37–48.
52. X. Li, Z. Zeng, S. Gao, and H. Li, Preparation and characteristics of sol–gel-coated calix[4]arene fiber for solid-phase microextraction. *J. Chromatogr. A* 1023 (2004):15–25.
53. D. Wang, J. Xing, J. Peng, and C. Wu, Novel benzo-15-crown-5 sol–gel coating for solid-phase microextraction. *J. Chromatogr. A* 1005 (2003):1–12.
54. M. Liu, Z. Zeng, and H. Fang, Preparation and application of the sol–gel-derived acrylate/silicone co-polymer coatings for headspace solid-phase microextraction of 2-chloroethyl ethyl sulfide in soil. *J. Chromatogr. A* 1076 (2005):16–26.
55. J. Zhou, F. Yang, D. Cha, Z. Zeng, and Y. Xu, Headspace solid-phase microextraction with novel sol–gel permethylated-β-cyclodextrin/hydroxyl-termination silicone oil fiber for determination of polybrominated diphenyl ethers by gas chromatography–mass spectrometry in soil. *Talanta* 73 (2007):870–877.
56. W. Liu, Y. Hu, J. Zhao, Y. Xu, and Y. Guan, Physically incorporated extraction phase of solid-phase microextraction by sol–gel technology. *J. Chromatogr. A* 1102 (2006):37–43.
57. G.R. Newkome, K.S. Yoo, A. Kabir, and A. Malik, Synthesis of benzyl-terminated dendrons for use in high-resolution capillary gas chromatography. *Tetrahedron Lett.* 42 (2001):7537–7541.
58. A. Kabir, C. Hamlet, K.S. Yoo, G.R. Newkome, and A. Malik, Capillary microextraction on sol–gel dendrimer coatings. *J. Chromatogr. A* 1034 (2004):1–11.
59. C. Dietz, J. Sanz, and C. Cámara, Recent developments in solid-phase microextraction coatings and related techniques. *J. Chromatogr. A* 1103 (2006):183–192.
60. N. Fontanals, R.M. Marce, and F. Borrull, New hydrophilic materials for solid-phase extraction. *TrAC* 24 (2005):394–406.
61. Y. Fan, Y.-Q. Feng, S.-L. Da, and Z.-H. Wang, In-tube solid phase microextraction using a β-cyclodextrin coated capillary coupled to high performance liquid chromatography for determination of non-steroidal anti-inflammatory drugs in urine samples. *Talanta* 65 (2005):111–117.
62. W. Liu, H. Wang, and Y. Guan, Preparation of stir bars for sorptive extraction using sol–gel technology. *J. Chromatogr. A* 1045 (2004):15–22.
63. M. Kawaguchi, R. Ito, K. Saito, and H. Nakazawa, Novel stir bar sorptive extraction methods for environmental and biomedical analysis. *J. Pharm. Biomed. Anal.* 40 (2006):500–508.
64. X. Huang, N. Qiu, D. Yuan, and B. Huang, A novel stir bar sorptive extraction coating based on monolithic material for apolar, polar organic compounds and heavy metal ions. *Talanta* 78 (2009):101–106.
65. N. Fontanals, R.M. Marce, and F. Borrull, New materials in sorptive extraction techniques for polar compounds. *J. Chromatogr. A* 1152 (2007):14–31.

66. J.B. Quintana and I. Rodriguez, Strategies for the microextraction of polar organic contaminants in water samples. *Anal. Bioanal. Chem.* 384 (2006):1447–1461.
67. J. Yu, C. Wu, and J. Xing, Development of new solid-phase microextraction fibers by sol–gel technology for the determination of organophosphorus pesticide multiresidues in food. *J. Chromatogr. A* 1036 (2004):101-111.
68. L. Cai, S. Gong, M. Chen, and C. Wu, Vinyl crown ether as a novel radical crosslinked sol–gel SPME fiber for determination of organophosphorus pesticides in food samples. *Anal. Chim. Acta* 559 (2006):89–96.
69. S.S. Segro, and A. Malik, Sol–gel methyl coating in capillary microextraction hyphenated on-line with high-performance liquid chromatography: Counterintuitive extraction behavior for polar analytes. *J. Chromatogr. A* 1200 (2008):62–71.
70. H. Bagheri, E. Babanezhad, and F. Khalilian, A novel sol–gel-based amino-functionalized fiber for headspace solid-phase microextraction of phenol and chlorophenols from environmental samples. *Anal. Chim. Acta* 616 (2008):49–55.
71. A. Le. Lopes and F. Augusto, Preparation and characterization of polydimethylsiloxane/poly(vinylalcohol) coated solid phase microextraction fibers using sol–gel technology. *J. Chromatogr. A* 1056 (2004):13–19.
72. Ch. Dietz, J. Sanz, E. Sanz, R. Munoz-Olivas, and C. Camara, Current perspectives in analyte extraction strategies for tin and arsenic speciation. *J. Chromatogr. A.* 1153 (2007):114–129.
73. Z. Wang, C. Xiao, C. Wu, and H. Han, High-performance polyethylene glycol-coated solid-phase microextraction fibers using sol–gel technology. *J. Chromatogr. A* 893 (2000):157–168.
74. M. Giardina and S.V. Olesik, Application of low-temperature glassy carbon films in solid-phase microextraction. *Anal. Chem.* 73 (2001):5841–5851.
75. F. Li, H. Jiang, and S. Zhang, An ion-imprinted silica-supported organic–inorganic hybrid sorbent prepared by a surface imprinting technique combined with a polysaccharide incorporated sol–gel process for selective separation of cadmium(II) from aqueous solution. *Talanta* 71 (2007):1487–1493.
76. F. Zheng, and B. Hu, Preparation of a high pH-resistant AAPTS-silica coating and its application to capillary microextraction (CME) of Cu, Zn, Ni, Hg and Cd from biological samples followed by on-line ICP-MS detection. *Anal. Chim. Acta* 605 (2007):1–10.
77. B. Saad, C.C. Chong, A.S.M. Ali, M.F. Bari, I.A. Rahman, N. Mohamad, and M.I. Saleh, Selective removal of heavy metal ions using sol–gel immobilized and SPE-coated thiacrown ethers. *Anal. Chim. Acta* 555 (2006):146–156.
78. C.W. Kan, C.P. Fredlake, E.A.S. Doherty, and A.E. Barron, DNA sequencing and genotyping in miniaturized electrophoresis systems. *Electrophoresis* 25 (2004):3564–3588.
79. N.R. Deshmukh and A.M. Lali, Adsorptive purification of pDNA on superporous rigid cross-linked cellulose matrix. *J. Chromatogr. B* 818 (2005):5–10.
80. F. Sousa, S. Freitas, A.R. Azzoni, D.M. Prazeres, and J. Queiroz, Supercoiled plasmid DNA purification, Biotechnol. *Appl. Biochem.* 45 (2006):131–140.
81. S. Yu, J. Geng, P. Zhou, J. Wang, X. Chen, and J. Hu, New hydroxyapatite monolithic column for DNA extraction and its application in the purification of Bacillus subtilis crude lysate. *J. Chromatogr. A* 1183 (2008):29–37.
82. T. Watanabe, K. Makitsuru, H. Nakazawa, S. Hara, T. Suehiro, A. Yamamoto, T. Hiraide, and T. Ogawa, Separation of double-strand DNA fragments by high-performance liquid chromatography using a ceramic hydroxyapatite column. *Anal. Chim. Acta* 386 (1999):69–75.
83. S. Bisht, G. Bhakta, S. Mitra, and A. Maitra, pDNA loaded calcium phosphate nanoparticles: Highly efficient non-viral vector for gene delivery. *Int. J. Pharm.* 288 (2005):157–168.
84. D. Cha, M. Liu, Z. Zeng, D. Cheng, and G. Zhan, Analysis of fatty acids in lung tissues using gas chromatography–mass spectrometry preceded by derivatization-solid-phase microextraction with a novel fiber. *Anal. Chim. Acta* 572 (2006):47–54.
85. R. Ventura, C. Jimenez, N. Closas, J. Segura, and R.D. Torre, Stability studies of selected doping agents in urine: Caffeine. *J. Chromatogr. B* 795 (2003):167–177.
86. R. Ghildyal and M. Kariofillis, Determination of triasulfuron in soil: Affinity chromatography as a soil extract cleanup procedure. *J. Biochem. Biophys. Methods* 30 (1995):207–215.
87. C. Sheedy and J.C. Hall, Immunoaffinity purification of chlorimuron — ethyl from soil extracts prior to quantitation by enzymelinked immunosorbent assay. *J. Agric. Food Chem.* 49 (2001):1151–1157.
88. M. Cichna, P. Markl, D. Knopp, and R. Niessner, On-line coupling of sol-gel-generated immunoaffinity columns with highperformance liquid chromatography. *J. Chromatogr. A* (2001):51–58.
89. C. Stalikas, D. Knopp, and R. Niessner, Sol-gel glass immunosorbent- based determination of s-triazines in water and soil samples using gas chromatography with nitrogen phosphorous detection system. *Environ. Sci. Technol.* 36 (2002):3372–3377.
90. L.E. Vera-Avila, J.C. Vazquez-Lira, M. Garcia de Llaserna, and R. Covarrubias, Sol-gel immunosorbents doped with polyclonal antibodies for the selective extraction of malathion and triazines from aqueous samples. *EnViron. Sci. Technol.* 39 (2005):5421–5426.
91. R. Braunrath, D. Podlipna, S. Padlesak, and M. Cichna-Markl, Determination of bisphenol A in canned foods by immunoaffinity chromatography, HPLC, and fluorescence detection. *J. Agric. Food Chem.* 53 (2005):8911–8917.
92. P. Degelmann, S. Egger, H. Jürling, J. Müller, R. Niessner, and D. Knopp, Determination of Sulfonylurea Herbicides in Water and Food Samples Using Sol−Gel Glass-Based Immunoaffinity Extraction and Liquid Chromatography−Ultraviolet/Diode Array Detection or Liquid Chromatography-Tandem Mass Spectrometry. *J. Agric. Food Chem.* 54 (2006):2003–2011.
93. R.G. da Costa Silva, and F. Augusto, Sol–gel molecular imprinted ormosil for solid-phase extraction of methylxanthines. *J. Chromatogr. A* 1114 (2006):216–223.
94. M. Liu, Z. Zeng, and B. Xiong, Preparation of novel solid-phase microextraction fibers by sol–gel technology for headspace solid-phase microextraction-gas chromatographic analysis of aroma compounds in beer. *J. Chromatogr. A* 1065 (2005):287–299.
95. X. Zhou, X. Li, and Z. Zeng, Solid-phase microextraction coupled with capillary electrophoresis for the determination of propranolol enantiomers in urine using a sol–gel derived calix[4]arene fiber. *J. Chromatogr. A* 1104 (2006):359–365.
96. M.A. Azenha, P.J. Nogueira, and A.F. Silva, Unbreakable solid-phase microextraction fibers obtained by sol−gel deposition on titanium wire. *Anal. Chem.* 78 (2006):2071–2074.

97. M. Azenha, C. Malheiro, and A.F. Silva, Ultrathin phenyl-functionalized solid phase microextraction fiber coating developed by sol–gel deposition. *J. Chromatogr. A* 1069 (2005):163–172.
98. Z. Zeng, W. Qiu, M. Yang, X. Wei, Z. Huang, and F. Li, Solid-phase microextraction of monocyclic aromatic amines using novel fibers coated with crown ether. *J. Chromatogr. A* 934 (2001):51–57.
99. Z. Zeng, W. Qiu, and Z. Huang, solid-phase microextraction using fused-silica fibers coated with sol−gel-derived hydroxy-crown ether. *Anal. Chem.* 73 (2001):2429–2436.
100. L. Yun, High extraction efficiency solid-phase microextraction fibers coated with open crown ether stationary phase using sol–gel technique. *Anal. Chim. Acta* 486 (2003):63–72.
101. T.Y. Kim, K. Alhooshani, A. Kabir, D.P. Fries, and A. Malik, High pH-resistant, surface-bonded sol–gel titania hybrid organic–inorganic coating for effective on-line hyphenation of capillary microextraction (in-tube solid-phase microextraction) with high-performance liquid chromatography. *J. Chromatogr. A* 1047 (2004):165–174.
102. H. Fang, M. Liu, and Z. Zeng, Solid-phase microextraction coupled with capillary electrophoresis to determine ephedrine derivatives in water and urine using a sol–gel derived butyl methacrylate/silicone fiber. *Talanta* 68 (2006):979–986.
103. T.P. Gbatu, K.L. Sutton, and J.A. Caruso, evelopment of new SPME fibers by sol–gel technology for SPME-HPLC determination of organometals. *Anal. Chim. Acta* 402 (1999):67–79.
104. Y.L. Hu, Y.L. Fu, and G.K. Li, Preparation of anilinemethyltriethoxysilane/ polydimethylsiloxane sol–gel coatings for solid-phase microextraction of aromatic compounds. *Anal. Chim. Acta* 567 (2006):211–217.
105. J. Zhou and Z. Zeng, Novel fiber coated with β-cyclodextrin derivatives used for headspace solid-phase microextraction of ephedrine and methamphetamine in human urine. *Anal. Chim. Acta* 556 (2006):400–406.
106. C. Basheer, S. Jegadesan, S. Valiyaveettil, and H.K. Lee, Sol–gel-coated oligomers as novel stationary phases for solid-phase microextraction. *J. Chromatogr. A* 1087 (2005):252–258.