Review

# New sorbents for extraction and microextraction techniques

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## ARTICLE INFO

## ABSTRACT

This review outlines recent progress in the research on some new classes of sorbents for extraction and microextraction techniques. Carbon nanotubes are allotropes of carbon with cylindrical structure. They are very stable systems having considerable chemical inertness due to the strong covalent bonds of the carbon atoms on the nanotube surface. Some applications of carbon nanotubes are presented in a perspective view. Molecular imprinting has proved to be an effective technique for the creation of recognition sites on a polymer scaffold. By a mechanism of molecular recognition, the molecularly imprinted polymers are used as selective tools for the development of various analytical techniques such as liquid chromatography, capillary electrochromatography, solid-phase extraction (SPE), binding assays and biosensors. Sol–gel chemistry provides a convenient pathway to create advanced material systems that can be effectively utilized to solve the solid phase microextraction fiber technology problems. This review is mainly focused on recent advanced developments in the design, synthesis and application of sol–gel in preparation of coatings for the SPME fibers.

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## Contents

## 1. Introduction

There is a growing demand from both the industry and academy to increase the performance, reliability and speed of analytical processes. As for some well-established analytical procedures related to problems like the determination of priority contaminants on environmental samples (atmospheric and indoor air, natural water, soils and sediments) or detection and quantitation of drugs and metabolites on clinical materials, the main goals are essentially the same since the past century: improvement of the speed and reduction of the cost of the methods, if possible providing better

sensitivity and selectivity as well. Even for these areas, some analytes previously disregarded or considered as non-relevant may come under the spotlight in view of new knowledge about their effects on human health and on the environment. Some of the recent concerns include the determination of endocrine disrupting compounds such as steroid hormones, alkylphenols and alkyl phthalates [1], polybrominated diphenyl ethers [2] and algal toxins [3] on natural and potable waters. In addition to new developments on traditional fields, in the past decade completely new issues have also challenged the analytical community. For example, the sequencing of the human (among others) genome created a whole new field – *proteomics* – heavily dependent on faster and more reliable procedures to identify and quantify the proteome, which can be defined as the set of proteins associated to each expressed gene on complex biological materials [4]. These studies also triggered the interest on the characterization of the profiles of metabolites synthesized by biological system (the metabolome):

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the *metabolomics*, which also call for improved and fast analytical techniques capable to process complex biological samples containing trace amounts of analytes [5,6] frequently unstable or labile. Other recent and completely different issue – the internal security efforts on US and European countries after the events of September 11, 2001 – has also been compelling analytical chemists to present new solutions based on different methods and instruments. Along with new procedures adequate for very fast *in situ* analysis, but for analytes already well studied such as chemical warfare agents, improved detection and eventual quantitation of species such as protein- and non-protein toxins with molar masses up to 100 kDa or biomarkers of human exposition to biological or chemical weapons [7,8] can also be considered as "hot" topics.

To meet these new demands, research on all branches of analytical science have been carried out; in particular, the techniques and strategies for sample preparation have been subject of extensive investigation. The goal of any sample preparation method is the transference of the target analytes from the sample matrix to a new media, compatible in nature and concentration with the analytical instrument to be employed [9]. The operations associated to sample preparation are usually the major source of inaccuracy and imprecision on analysis in general, as well as the more time-consuming steps. Consequently, improvement on chemical analysis at large is heavily dependent on development of innovative, fast and accurate sample preparation techniques [10]. For methods based on GC, HPLC or CE, the traditional sample preparation techniques often includes extraction and clean-up steps based on selective sorption of the analytes or interferents over adsorbents or absorbents, followed either by direct analysis of the resulting solution or desorption of the trapped species (thermal or using solvents) directly in the chromatographic column. Typical examples include Soxhlet extraction (for sediments and solid matrixes), liquid–liquid extraction, LLE (for water or aqueous samples) or NIOSH charcoal adsorbent tubes (for VOC on air). These methods are being replaced by new techniques based on different approaches. The pressure to reduce the use of the large amounts of solvents (mandatory on the conventional LLE or Soxhlet methods) prompted for the growing popularity of solid phase extraction – SPE [11] – presently, possibly the most popular sample preparation technique for chromatographic analysis. Along with SPE, microextraction techniques such as solid phase microextraction–SPME [12], liquid phase microextraction [13] and stir bar sorptive extraction–SBSE [14] have also experienced an increasing acceptance on routine analytical procedures. Contrary to SPE and to the classic procedures, the microextraction techniques rely on quantitative but non-exhaustive transference of analytes by equilibration of small portions of adsorbents or sorbents and larger amounts of samples, in direct or indirect contact (*i.e.*, through the headspace). The major advantages of the microextraction approach are the easy miniaturization and automation of devices, as well as the inherent speediness and relative straightforward adaptation of the methods for *on-site* analysis [10].

An important trend shared by the fundamental research on SPE and on microextraction is related to the development and characterization of new sorbents and adsorbents. Research on new advanced materials is a hot issue, involving several branches of science and technology. Depending on the format of the extraction technique as well as on the target analytes and samples, the main goals on the search of novel sorbents and adsorbents are variable: achievement of better selectivities (or even specificity towards definite target species), improvement of the sorptive or adsorptive capacity (and, therefore, of the sensitivities and detectabilities attainable), as well as to provide extractive media with enhanced thermal, chemical or mechanical stability, to improve the lifetime of devices employing them as sorbent/adsorbent media. In the fol-

lowing sections, we will present and discuss the state-of-the-art of the research on some new classes of sorbents for extraction and microextraction techniques.

## 2. Carbon nanotubes

Since the past decade, the preparation, the properties and applications of nano-structured novel materials such as nanoparticles, nanowires or nanotubes, has been a major scientific issue with remarkable impacts over the research and practice of Analytical Chemistry. Among these new nanomaterials, one of the foremost targets of interest is the carbon nanotubes (CNT). CNT – essentially, an allotropic form of graphitic carbon – were first described in 1991 by Iijima [15], after inspection of the deposit over the carbon negative electrodes employed for DC arc-discharge evaporation of carbon under argon atmosphere. CNT are needle-like structures consisting either on a single rolled graphite lamella forming a tube (single-wall carbon nanotubes, SWCNT), or several of these single tubes with growing diameters concentrically arranged around a common axis (multi-wall carbon nanotubes, MWCNT) [16]. The typical diameters range from ∼0.4 nm to 3 nm (SWCNT) and 1.4 nm to >100 nm (MWCNT), all with ends normally capped by fullerene-like structures [17,18].

CNT have several unique chemical and physical properties, which prompted for their application on piezoelectric gas sensors [19], voltammetric electrodes [20] and electrochemical biosensors [21], among several others. The adsorptive behavior of CNT would be expected to resemble other carbon-based alternates, such as conventional porous graphitic carbon (PGC), which consists of large graphitic lamellae held together by weak intermolecular Van der Waals forces. Both hydrophobic and electronic interactions contribute to retention of analytes by PGC: therefore, non-polar, polar and even ionic analytes may be strongly adsorbed (specially planar species with polar substituents and delocalized electronic charges via π-bonds and free electron pairs) [22]. However, one of the distinctive features of CNT – and in particular of the MWCNT – has a crucial influence on their application for adsorbents in SPE and SPME devices: their large surface-to-volume ratios [16]. As result, compared to other carbon-based adsorbents, the capacity of MWCNT is usually much larger. Long and Yang [23] showed that MWCNT can adsorb an amount of TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) up to $10^{34}$ larger than conventional activated carbon—a result both of the large specific surface and of the strong interaction of two benzene rings of TCDD and the graphene surfaces on the MWCNT. The first analytical application of MWCNT as adsorbent for SPE was presented by Jiang and co-workers [24], who employed cartridges packed with 500 mg of MWCNT (diameters from 30 nm to 60 nm and specific surface area of 131.74 $m^2 g^{-1}$ – Fig. 1) to extract the endocrine disruptors bisphenol A, 4-*n*-nonylphenol and 4-*tert*-octylphenol from water prior determination by HPLC with fluorimetric detection. Methanol was used to condition the cartridges and to elute the extracted analytes; no carry-over was observed. The adsorptive capacity was checked using deionized water spiked with 20 ng mL$^{-1}$ of each analyte as samples. It was determined that volumes up to 750 mL could be processed without significant breakthrough (recoveries >95%), where for $C_{18}$ cartridges only the recovery of bisphenol A was acceptable for such sample volumes; the performance of cartridges packed with XAD-2 resin was even worst. The recoveries for the analytes on real tap, river, sea water and wastewater ranged from 89.8% to 102.8%, and the detection limits on deionized water were 83 ng L$^{-1}$, 24 ng L$^{-1}$ and 18 ng L$^{-1}$ for bisphenol A, 4-*n*-nonylphenol and 4-*tert*-octylphenol, respectively. MWCNT has been systematically compared with other sorbents for SPE, with better performances especially for polar species on water and other water-rich matrixes. Zhou et al. compared MWCNT and

**Table 1**
Some applications of SPE using non-modified MWCNT as adsorbent media.

| Analytes | Matrix | Technique[a] | Ref. |
|---|---|---|---|
| Phthalate alkyl esters | Water | HPLC | [28] |
| Chlorobenzenes, POP | Water | GC | [29] |
| Pb, Hg, Sn (inorganic and organometallic) | Sediment | GC | [30] |
| Amygdalin | Apricot and downy cherry kernels | HPLC | [31] |
| Chlorophenols | Water | HPLC | [32] |
| Copper | Water | FAAS | [33] |
| Inorganic Cd | Water | TS-FF-AAS | [34] |
| Nicosulfuron, thifensulfuron-methyl, metsulfuron-methyl | Water | HPLC | [35] |
| Thiamethoxam, imidacloprid, acetamiprid | Water | HPLC | [36] |
| Dichlorodiphenyltrichloroethane and metabolites | Water | HPLC | [37] |
| 10 sulfonamides | Eggs, pork | HPLC | [38] |
| Diazepam, estazolam, alprazolam, triazolam | Pork | GC | [39] |
| Inorganic Ag | Water | FAAS | [40] |
| Atrazine, simazine | Water, wastewater | HPLC | [41] |
| Barbital, amobarbital, phenobarbital | Pork | GC | [42] |
| Prometryn and fungicides | Water | HPLC | [43] |
| Cyanazine, chlorotoluron, chlorbenzuron | Water | HPLC | [44] |
| Multiresidues of 12 pesticides | Water | GC | [45] |
| PAH | Water | HPLC | [46] |
| Tetracyclines | Water | CE | [47] |
| Triasulfuron, bensulfuron-methyl | Water | HPLC | [48] |
| Diazinon | Water | HPLC | [49] |
| Atrazine and metabolites | Water, soil | GC | [50] |
| Estrone, estradiol, estriol | Water | ELISA | [51] |

[a] Separation and/or detection technique: HPLC = high performance liquid chromatography; GC = gas chromatography; FAAS = flame atomic absorption spectrometry; CE = capillary electrophoresis and ELISA = enzyme linked immunosorbent assay.

conventional $C_{18}$ silica for extraction of some highly polar sulfonylurea herbicides (nicosulfuron, triasulfuron, metsulfuron-methyl, thifensulfuron-methyl and bensulfuron-methyl) [25] from water. In general, although the extraction efficiency of MWCNT and $C_{18}$ on test aqueous samples prepared using tap water were similar, the former was more efficient on seawater samples. MWCNT and SWCNT were also compared to $C_{18}$ silica and graphitized charcoal for extraction of cephalosporin antibiotics, sulfonamides and phenols from water [26]; except for phenols (where graphitized charcoal was superior), both CNT provided better extraction efficiencies than the conventional materials. Similar results were obtained by Pyrzynska et al. [27], after evaluating MWCNT and $C_{18}$ silica to extract phenoxyalkanoic acid herbicides (dicamba and 2,4,5-T) from water. Some representative applications of MWCNT as adsorbent on SPE methods for chromatographic and spectrometric analysis are listed in Table 1. Along with the traditional cartridge format, novel SPE approaches also employed MWCNT as adsorbent. In the μ-SPE technique described by Basheer et al. [52], a square (15 mm × 15 mm), heat-sealed polypropylene sheet membrane envelope was packed with 6 mg of MWCNT. This μ-SPE device may be dropped on stirred aqueous samples; analytes from the sample diffuse through the envelope wall and are adsorbed over the MWCNT filling. After extraction, the device is removed, rinsed, dried and dipped on organic solvents under ultrasound to desorb the extracted species.

CNT also have been employed as adsorbent for SPME fibers. Wang et al. [53] prepared a SPME fiber coated with a ~40 μm thick film of MWCNT, dipping a fused silica fiber on dispersion of the adsorbent on dimethylformamide. The fiber was applied on direct immersion extractions of polybrominated diphenyl ethers (PBDE) on water and milk extracts. The author reported that the fibers could be re-used up to 100 times, and a good inter-fiber reproducibility (RSD from 8% to 16%); however, the performance of the MWCNT fibers was checked only against self-made fibers with different coatings. Lü et al. [54] adopted a different approach to prepare SWCNT-coated SPME fibers: instead of simple mechanical deposition of the coating over fused silica, this adsorbent was dispersed on an organic binder (ethylcellulose plus dibuthylphthalate) and the suspension applied to metal wires, resulting an adsorbent

film of ~50 μm after conditioning of the fibers at 400 °C. The extraction efficiency of the SWCNT fibers was shown to be better than that of commercial 100 μm PDMS fibers, using aqueous solutions of organochlorine pesticides (α-, β-, γ- and δ-HCH, DDE, DDD, o-p′-DDT and p-p′-DDT). However, the most significant feature of these fibers is their thermal stability and life span: the fibers support up to 350 °C and can be re-used 150 times or more. Liu et al. [55] also used a binder (epoxy glue) to coat SPME fibers coated 100 μm films containing oxidized MWCNT. These fibers were tested to determine chlorophenols in water, using HPLC on the separation and detection of analytes [52].

Contrary to conventional carbon adsorbents, the surface of CNT can be easily modified, resulting on functionalized adsorbents with distinctive properties. Suárez et al. [56] employed carboxylate-modified SWCNT (prepared by oxidation of raw SWCNT) immobilized over 120–200 mesh porous glass beads to pack microcolumns used for pre-concentration of non-steroidal anti-inflammatory drugs (ketoprofen, tolmetin and indomethacin) on urine, coupled on-line with CE (Fig. 2). The modified SWCNT present the original typical adsorptive capabilities of CNT (due to the highly hydrophobic surface), but also retains polar or charged analytes by electrostatic interactions or hydrogen bonds with the carboxylic groups. Salam and Burke [57] compared non-modified MWCNT and MWCNT functionalized with polyethyleneglycol (PEG) and octadecylamine (ODA), for extracting pentachlorophenol (PCP), 2,4,5-trichlorophenol (TCP), 3,3′,4,4′-tetra-chlorobiphenyl (PCB77) and 2,2′,5,5′-tetrabromobiphenyl (PBB52) from aqueous samples. It was shown that the extraction efficiency was affected by factors such as sample pH and volume, as well as nature of desorption of solvent (acetone was the best solvent for all the analytes). ODA-MWCNT presented extraction recoveries near to 100% for all species, including phenols (due to electrostatic interactions).
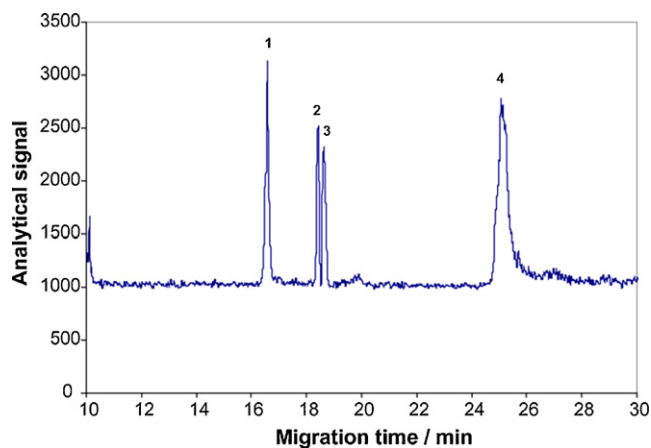
## 3. Molecularly imprinted polymers (MIP)

One of the tools to create highly selective extraction procedures is the incorporation of biomolecules and biological-like processes in the methodologies. However, despite of the specificity of these procedures, natural biomolecules usually are expensive and chem-
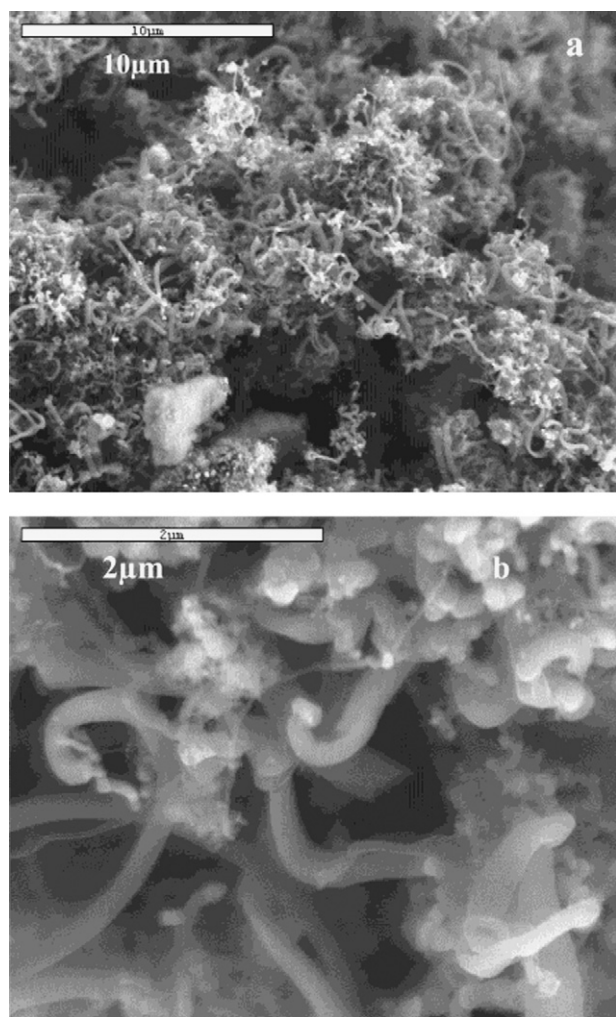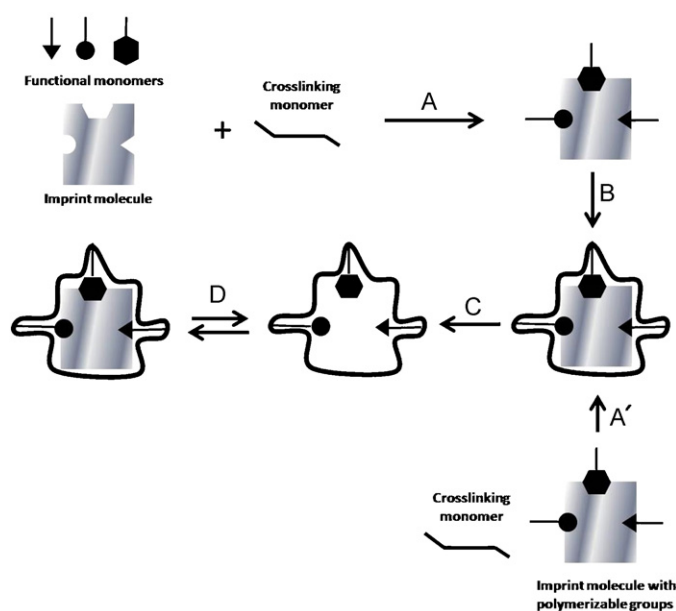
**Fig. 1.** Scanning electron microscopy images of the MWCNT employed by Jiang and co-workers.
From Ref. [24].



**Fig. 3.** Main approaches to MIP synthesis (modified from Ref. [65]). Non-covalent approach: (A) mixture of functional monomers, cross-linking agents, polymerisation initiator and templates dissolved on porogenic solvent to form template/functional monomer complex; (B) polymerisation; (C) removal of template (by solvent extraction) and (D) analyte binding (via non-covalent interactions) on the specific imprinted site. Covalent approach: (A′) template containing polymerisable groups mixed with cross-linking agent and initiator in proper solvent; (C) removal of template after polymerisation (with breaking of covalent bonds between template and polymer) and (D) analyte binding (via covalent bonds) on the specific imprinted site.

ically unstable. Synthetic materials such as molecularly imprinted polymers (MIP) are valid alternatives to these biological matrices. The concept of molecular imprinting was originally proposed by Pauling [58] as a possible mechanism for the production of



**Fig. 2.** Electropherogram from an urine sample spiked with 15 μg L$^{-1}$ of esteroids extracted by carboxylate-modified SWCNT (from Ref. [56]). Peak identification: (1) ketoprofen, (2) tolmetin, (3) indomethacine and (4) pentachlorophenol (internal standard).

antibodies by living systems. According to his model, the synthesis of antibodies was based on the use of the aggressor chemical molecules as templates. Weak intermolecular forces such as hydrogen bonding or van der Waals forces drove proper monomer units to organize themselves around the antigen; polymerization of the organized monomers and removal of the template would render macromolecules with cavities where the template or other species with similar structure could be highly selectively bound, due to the morphology of the site. Due to the high specific nature of the interaction between the molecularly imprinted materials and selectable molecules, they have been employed in several analytical techniques, including as stationary phase on liquid chromatography [59], on capillary electrophoresis [60] and capillary electrochromatography [61,62] and on immunoassay determinations [63]. MIP have been also extensively studied and applied as sorbents for SPE (MISPE). They are especially helpful when selective extraction of analytes is deemed and where commercial sorbents lack selectivity. MISPE, therefore, potentially allows simultaneous and efficient pre-concentration of target analytes and clean-up of the extracts, removing undesirable sample matrix components. The first description of MISPE was presented by Sellergren in 1996 [64]: an ethyleneglycoldimethacrylate/methacrylic acid copolymer molecularly imprinted with pentamidine was prepared and applied to isolate this antibiotic drug from urine. The enrichment factor was 54× (for 30 nM of the drug on urine), and the selectivity was enough high to allow direct detection of the analyte in the extract, without chromatographic analysis.

There are three basic approaches for MIP synthesis: non-covalent, covalent and semi-covalent imprinting [65] (Fig. 3). In the non-covalent imprinting—the most extensively used, due to its relative simplicity, a template (the target analyte or an structurally related species) is mixed with an appropriate functional monomer, a suitable porogenic solvent, cross-linking agents and catalysts or polymerization initiators. Specific binding sites are formed by

self-assembling of template and the functional monomer, who should be capable to form a fairly stable complex with the template via dipole interaction, hydrogen bonding, ion pair, etc. After the synthesis, the template is removed from the polymer simply by exhaustive washing it with solvents—habitually on a Soxhlet-type apparatus. The resulting material dried, sieved and used to pack SPE cartridges or columns. On the covalent approach, the template and the functional monomer are covalently bound prior to polymerization; afterwards, the template is removed from the polymer matrix after synthesis by cleaving the covalent bonds before the washing step. Sorbents prepared using covalent imprinting tend to have well defined and more homogeneous binding sites than those resulting from non-covalent approach: the interaction between template and functional monomers are much more stable during the polymerization. Compared to non-covalent MIP (where analyte binding to imprinted sites take place by weaker interactions), this leads to higher selectivities, with less non-specific retention, and better extraction efficiencies. Finally, on non-covalent MIP preparation the synthesis of the adsorbent is carried out through a covalent procedure but the extraction mechanism is more related to a non-covalently prepared MIP [66]. Semi-covalent imprinting combines the advantages of both covalent and non-covalent approaches: as the template is covalently bound to a polymerizable group whose functionality is recovered after cleavage of the template.

Most of the MIP described on the literature for use as specific SPE adsorbents and for other applications are acrylate-based materials prepared by bulk polymerization [68], using methacrylic acid (MAA) and similar compounds as functional monomers, ethylene glycol dimethacrylate (EDMA) as cross-linker and azo-compounds such as azo(bis)-isobutyronitrile as radicalar polymerization initiator. Alternated methodologies such as two-step swelling polymerization [69], suspension polymerization [70] and precipitation polymerization [71] were also reported for MISPE media, although bulk polymerization has been almost universal due to its simplicity. A proper choice of the solvent employed (aprotic and non-polar solvents are more appropriate, since they do not interfere on the functional monomer/template equilibrium) and of the monomers is critical to produce a selective MIP [72]. A recent trend on the optimization of MIP synthesis is the use of molecular modeling software to aid the selection of the best functional monomer to an specific template, by calculation of binding energies and the spatial configuration template/monomer complexes [73–76]. Another recent development on the optimization of MIP composition is the adoption of combinatorial synthetic procedures, devised by Sellergren group [77]; especially when combined with chemometric tools, this approach allows faster screening of a large range of different formulations [78–80]. Various functional monomers have been studied against different template molecules; however, this generality makes difficult to select the appropriate monomers for a given template. Selection of the various functional monomers usually involves time-consuming trial and error, or intuition. Molecular imprinting using combinatorial chemistry models allows for rapid screening of combinatorial libraries of MIPs to permit identification of a candidate monomer with the desired levels of capacity and selectivity for a given target molecule [81], since it allows automated, simultaneous preparation and evaluation of tens of different materials prepared using diverse monomers and reactional proportions.

Some of recent applications of MISPE using acrylate-based sorbents are listed in Table 2. A possible drawback on some of these polyacrylate MIP is the presence of non-specific binding, which causes loss of selectivity; careful selection of the sample and desorption solvents can minimize or even eliminate non-specific extraction [110]. Organically modified silicas prepared through sol–gel procedures can be possible alternative molecular imprinted media with reduced non-specific activity, as shown

by Marx and Liron [67], after comparing propranolol-imprinted thin films of sol–gel silica and polyacrylate as specific sensors. Some sol–gel silicas prepared for MISPE include materials specific for 2-aminopyridine [111] and methylxanthines [112,113]. A serious shortcoming of sol–gel molecularly imprinted (MI) silicas results from the limited range of possible functional monomers, which restricts the classes of templates that could be successfully imprinted [114].

## 4. Sol–gel coatings for SPME fibers and related techniques

SPME is a widely accepted and applied sample preparation technique due to its simplicity, offering a relatively fast extraction and pre-concentration approach particularly attractive as replacement of solvent-based techniques. The appropriate selection of the fiber coating is one of the most critical steps on SPME method development. The nature of the coating should be selected based on the chemical properties of the target analytes and affects the overall extraction performance, including method sensitivity, selectivity and reproducibility. However, currently only a limited number of different fiber coatings are commercially available, notably pure polymeric phases such as polydimethylsiloxane (PDMS and polyacrylate) and dispersions of solid adsorbents as Carboxen and divinylbenzene in polymeric agglutinants. Apart from the reduced assortment of coatings with different properties, these materials may present some problems depending on its nature and film thickness; these problems include instability and swelling towards direct exposure to organic solvents, reduced operating temperature and mechanical fragility of the fused silica support. Therefore, the search for new coatings for SPME fibers that overcome those inconvenients is an active research topic. One of the goals is the investigation of sorbent films with strong adhesion with the base substrate – fused silica (FS) raw fibers or others – which may result in fibers with improved chemical and thermal stability and longer lifetimes. The most popular approach employed is, by far, the use coatings prepared through sol–gel synthetic routs. SPME sorptive coatings prepare by sol–gel procedures typically are chemically bonded to the FS base fibers, being also porous and highly cross-linked; the sorbents are prepared and deposed *in situ* over the surface of raw FS fiber. The first description of sol–gel technology for preparation of SPME fibers was presented by Malik and co-workers in 1997 [115]: the organic modifier was hydroxyl-PDMS, and the resulting chemically bound film was an organically modified silica (ormosil). The procedure there described included a preliminary step for activation of the raw fiber surfaces before the deposition and immobilization of the extracting phase—which, on its turn, occurs on a single-pot operation, and is followed by the deactivation of remaining –OH groups and conditioning. The pre-treatment of the FS surface is necessary to generate free superficial silanol groups, which will act as anchoring points where the sorbent phase will be chemically linked. The coating media usually consisted of a mixture of an alkoxysilane reticulant precursor such as metyltrimethoxysilane (MTMS), a hydroxylated organic modifier—hydroxy-PDMS and small amounts of water and catalyst (trifluoroacetic acid, TFA). Under appropriate conditions, the alkoxysilanes hydrolyze producing silanols (Fig. 4a), which immediately condensate creating silica aggregates (Fig. 4b). The hydroxylated organic modifier present in the media can simultaneously condense with the aggregates, being incorporated to the silica network (Fig. 4c). These organically modified silica nanoparticles form a colloidal suspension on the liquid reagents and reaction products (a sol phase); the continuing growing of the aggregates eventually lead to a silica monolith, where water and the liquid reaction products are trapped (a gel). However, if an activated fiber is exposed to the sol phase before complete gelation, the aggre-

**Table 2**
Selected SPE methods using acrylic-based MIP. Unless stated, the separation and/or detection technique adopted after extraction was HPLC.

| Analytes | Template | Matrix | Ref. |
|---|---|---|---|
| Levonorgestrel | Levonorgestrel | Human serum | [82] |
| Sulfonylurea-herbicides | Bensulfuron-methyl | Soybean | [83] |
| Triterpene acids | 18-β-Glycyrrhetinic acid | Plan extracts | [84] |
| Creatine | Creatine | Human serum[a] | [85] |
| Carbamazepine | Carbamazepine | Urine, wastewater | [86] |
| α-Tocopherol | α-Tocopherol | Bay leaves | [87] |
| Nicotine | Nicotine | Hair | [88] |
| Alkylmethylphosphonic acids | Pinacolylmethylphosphonic acid | Soil extracts | [89] |
| Benzodiazepinic drugs and metabolites | Diazepam | Hair | [90] |
| Chloramphenicol | Chloramphenicol | Honey | [91] |
| Flavonoid antioxidants | Rutin and quercetin | Wine, tea, orange juice | [92] |
| Epicatechin | Epicatechin | Tea | [93] |
| Tetracycline | Tetracycline | Fish tissues | [94] |
| Ciprofloxacin | Ciprofloxacin | Urine[b] | [95] |
| Triazine herbicides | Cianazine | Water[c] | [96] |
| Sinomenine | Sinomenine | Blood | [97] |
| Cotinine | Cotinine | Urine | [98] |
| p-Hydroxybenzoic acid derivatives | Protocatechuic acid | Plant extract | [99] |
| Tetracycline antibiotics | Oxytetracycline and tetracycline | Pig kidney tissue extract | [100] |
| Non-steroidal anti-inflammatory drugs | Ibuprofen | River water, wastewater | [101] |
| Monocrotophos and analogs | Monocrotophos | Water and soil | [102] |
| Triazine herbicides and metabolites | Propazine | River water | [103] |
| Naproxen | Naproxen | Urine | [104] |
| (+)-Catechin | (+)-Catechin | Green tea extract | [105] |
| Propanolol | Propanolol | Blood plasma | [106] |
| Bisphenol A | Bisphenol A | Water | [107] |
| Naphthalene sulfonates | 1-Naphthalenesulfonic acid | Water | [108] |
| Ochratoxin A | Ochratoxin A | Red wine | [109] |

*Notes.* FAAS = flame atomic absorption spectrometry; CE = capillary electrophoresis; ELISA = enzyme linked immunosorbent assay.

[a] Separation and/or detection technique: voltammetry.
[b] Separation and/or detection technique: gas chromatography.
[c] Separation and/or detection technique: fluorimetry.

gates may condense with the surface –OH groups on this substrate (Fig. 4d), forming a ormosil film. On this first paper, the coating thickness obtained was about 10 μm, and the sorptive film had a highly porous structure, as observed by scanning electronic micrography. A remarkable feature of this fiber was its outstanding thermal stability, when compared to conventional pure polymeric PDMS films: the fibers could be heated up to 320 °C without degradation of their performance or significant bleeding, suggesting that the coating was indeed chemically bonded to the silica core. It was pointed out that since sol–gel ormosil films usually possess microporous structures, they offer a high surface area and allow high extraction efficiencies even with thin extracting layers, which result also on fast sample/headspace/fiber equilibration times.

Sol–gel technology was subsequently applied with success to prepare SPME fibers with different coatings, mostly using FS fibers as support; Table 3 presents a selection of different fibers applications from the literature. For several of these studies the same basic approach described above was employed, either using different organic modifiers to give different selectivity characteristics, as well as other alkoxysilanes than MTMS such as tetraethoxysilane (TEOS) or minor alterations on the general procedure, such as use of alternative sol–gel catalysts (weak organic acids or bases as aqueous ammonium hydroxide). For example, Bianchi and co-workers [142,143] described a sol–gel SPME fiber prepared using 3-aminopropyltriethoxysilane (APTES) and diethoxydiphenylsilane as reticulants; the coating was shown to have an outstanding thermal and chemical stability (useful up to 400 °C) and was applied on determination of PAH on water and milk samples. Biajoli and Augusto [144] described a fiber coated with sol–gel silica prepared from MTMS/3-aminopropyltrimethoxysilane (APTMS) precursor mixture and modified by hydroxy-PDMS, and applied it on the characterization of the volatile fraction of Pilsner beer. The selectivity of the fiber was remarkably different from simple sol–gel PDMS fiber prepared using pure MTMS as precursor: as result from the incor-

poration of the primary amino groups on the silica network, it had a high affinity for acidic analytes, such as acetic and caproic acids. Interesting alternatives as organic modificators are crown ethers, as proposed by Zeng and co-workers [121], who prepared a sol–gel fiber using hydroxy-dibenzo-14-crown-4-ether (OH-DB14C4) and hydroxy-PDMS as modifiers. These coatings are expected to have higher affinity for aromatic and other polarizable compounds due to the electronegativity of the heteroatoms on the *corona* ring. This fiber was successfully applied to determination of halophenols in water, comparing favorably to commercial SPME fibers. The same group also described the application of these sol–gel OH-DB14C4-coated fibers to the determination of basic compounds (anilines), along with fibers modified with similar *corona*-ethers (dihydroxy-urushiol crown ether and 3,5-dibutyl-unsymmetric-dibenzo-14-crown-4-dihydroxy crown ether) [145]. Calixarenes, cyclodextrins and fullerenes can also result on selective coatings, and hydroxycalix4arenes (Fig. 5) [146–148], peralkylated-β-cyclodextrins [149,128] and hydroxyfullerenes [118] as well have been successfully applied on sol–gel fibers. Yu et al. [150] also prepared sol–gel SPME modified with a *corona* ether, but using a different approach: a custom-synthesized alkoxysilane (allyloxy-*bis*-benzo-16-crown-5-trimethoxysilane) already containing the crown ether radical was employed as reticulant precursor. The same strategy was already employed by Gbatu et al. [151], who used n-octyltriethoxysilane as one of the reticulating precursors; this fiber was successfully applied to the HPLC determination of organometallic compounds (triphenylarsine, diphenylmercury and trimethylphenyltin). This application address a remarkable general feature of sol–gel fibers: due to the higher chemical stability of the coating, compared to conventional fibers they are particularly resistant to direct exposure to solvents, and therefore are highly suitable for procedures involving solvent desorption.

In addition to their significance to determine the selectivity of the coating, some organic modifiers can also improve other desir-

**Table 3**
Sol–gel-based SPME fibers: selected papers and applications.

| Support and coating | $d_f/\mu m^a$ | Analytes | Ref. |
|---|---|---|---|
| FS-PEG | 40 | BTEX, chloro- and nitrophenols, phthalates, pesticides | [116] |
| FS-Calix[4]arene | 60 | Phenols | [117] |
| FS-Bis-benzo-Crown ether | 40 | Pesticides | [118] |
| FS-PDMS/PVA | 5 | PCB | [119] |
| FS-open crown ether | 55 | Phenols, BTEX, phthalates | [120] |
| FS-hydroxi-crown ether | 73 | Phenols | [121] |
| FS-polyphenylmethylsiloxane (PPMS) | 70 | Organochlorine pesticides | [122] |
| FS-trimetoxisilil-propyl-methacrilate (TMSPMA) | 70 | Volatiles from beer | [123] |
| FS-anilinemethyltrietoxysilane/PDMS (AMTEOS/PDMS) | 85 | MAH, PAH | [124] |
| FS-butylmethacrilate/divynilbenzene (BMA/DVB) | 70 | Volatiles from wine | [125] |
| FS-hydroxyfullerene | 30 | PCB, PAH, aromatic amines | [118] |
| FS-trimethoxysilylpropylamine/PDMS (TMSPA/PDMS) | 4 | Pesticides | [126] |
| FS-polymethylphenylsiloxane (PMPS) | 70 | Biphenylpolybromine ethers | [127] |
| FS-permethylated-β-cyclodextrine hydroxy-terminated silicone (PM- β-CD/OH-TSO) | 65 | BTEX | [128] |
| FS-tetra-n-butylortotitanate/graphite | 30 | BTEX | [129] |
| NiTi–ZrO$_2$–PDMS | 25 | BTEX, THM, alcohols | [130] |
| NiTi–ZrO$_2$–PDMS | 25 | Organochlorine pesticides | [131] |
| NiTi–ZrO$_2$–PEG | 17 | Halophenols, phthalates, adipates | [132] |
| NiTi–ZrO$_2$–PEG | 17 | Haloanisoles | [133] |
| Calix[6]arene | 60 | Phthalates | [134] |
| SWCNT/TSO | – | Polybrominateddiphenylethers | [135] |
| Cu-tetrabutylortotitanate/polymethylmethacrylate (TBOT/PMMA) | 25 | Aliphatic alcohols | [136] |
| NiTi–PDMS + C$_{18}$ silica | 30–60 | Benzaldehyde, acetophenone and dimethylphenol | [137] |
| Al-tetrabutylorthototitanate/poly(ethyleneglycol) | 25 | BTEX | [138] |
| FS-phenyltrimethoxysilane/tetraethoxysilane molecularly imprinted with decabromodiphenyl ether (PTMS/TEOS/DBE-209) | 9.5 | Polybrominateddiphenylethers | [139] |
| FS-hydroxyl-terminated silicone oil-poly (methylhydrosiloxane) (OH/TSO-PMHS) | 30 | Tamoxifen, cis- and trans-clomiphene citrate | [140] |
| FS-3-(trimethoxysilyl) propyl amine/hydroxyl-terminated polydimethylsiloxane (TMSPA/OH-PDMS) | 4 | Phenol, chlorophenols | [141] |

[a] Coating thickness.

able characteristics of the SPME fibers. For example, the selectivity of the sol–gel fiber described by Lopes and Augusto [119], based on poly(vinyl alcohol) (PVA) and PDMS-OH, is quite similar to that conventional and of sol–gel pure PDMS fibers, being shown as suitable for conventional GC applications such as the determination organochlorine and organophosphor pesticides in herbal infusions of *Passiflora* L., using GC-ECD for separation and detection [152]. However, the PDMS/PVA coating has also enhanced thermal stability: thermogravimetric analysis (TGA) data has shown that it is stable for temperatures up to 350 °C, possibly due to the additional cross-linking between silica reticulates promoted by the presence of PVA in the sol–gel reaction mix. This enhancement on the thermal stability of the PDMS/PVA sol–gel sorbent film was also evident on its application on FIMS (fiber introduction mass spectrometry), where a SPME fiber is directly introduced in the ionization zone of a mass spectrometer. The heating caused by the irradiation from the MS ionization filaments and the high vacuum induces the desorption, ionization and fragmentation of previously extracted species. During the determination of pesticides on herbal infusions by FIMS [153] it was observed that the PDMS/PVA fiber was usable for up to 400 FIMS extraction/desorption cycles, where conventional PDMS/DVB fibers are severely degraded after 150 operations due to the stress imposed during the harsh desorption conditions. Polyethyleneglycol (PEG) is also an organic modifier, which result sorbent layers with distinctive structural and morphological features. Silva and Augusto [154] described a sol–gel fiber using PEG (Carbowax 20 M, average molar mass of 14 kg mol$^{-1}$) as silica modifier (Fig. 6). The coating had a distinctive, sponge-like structure appearing to be an agglomerate of microspheres with up to 2 μm diameter. This morphology was not deemed as result of chemical incorporation of PEG to silica network, and possibly was an effect

the increase on the viscosity of the sol phase prior incorporation to the FS support.

Besides sorbents based on modified sol–gel silica, more recently materials prepared from alkoxides of other transition metals have also been suggested as sorbent phases for SPME and similar extraction microtechniques. Malik and co-workers [155] evaluated capillary microextraction devices coated with sol–gel PDMS-modified titania: TiO$_2$ is known to possess both better chemical stability and mechanical strength when compared to silica, and is an alternative to circumvent the limited window of pH stability of those silica-based coatings. The PDMS-titania coated microextraction device was successfully applied to determinations of PAH, ketones, and alkylbenzenes by HPLC, being shown as resistant to exposure to highly basic aqueous solutions (pH = 13) for up to 12 h. Sol–gel titania SPME fibers have also been described, with incorporation organic modifiers such as PDMS [156], polymetacrylate [140] and poly(tetrahydrofuran) [130].

Other promising trend is the coating of alternate supports with sol–gel sorbent films to obtain SPME fibers with improved properties, in replacement of conventional raw FS silica fibers. Carasek and co-workers [131–133] studied sol–gel coated fibers prepared using as support thin rods of 65% SiO$_2$ vitreous ceramic containing Li, Ba and Zr. Due to the zirconium oxide fraction, this ceramic is much more acidic than pure FS and has more surface silanol groups available to anchor the modified silica aggregates. Using hydroxy-PDMS as modificator, a coating thickness of 44 μm was obtained, which had a higher extracting capability than the a 6 μm thick film which resulted when coating a FS fiber using the same procedure. Metallic wires also have been used as base for sol–gel SPME fibers, in order to improve the ruggedness and mechanical resistance of the fiber. The same group later proposed the use of
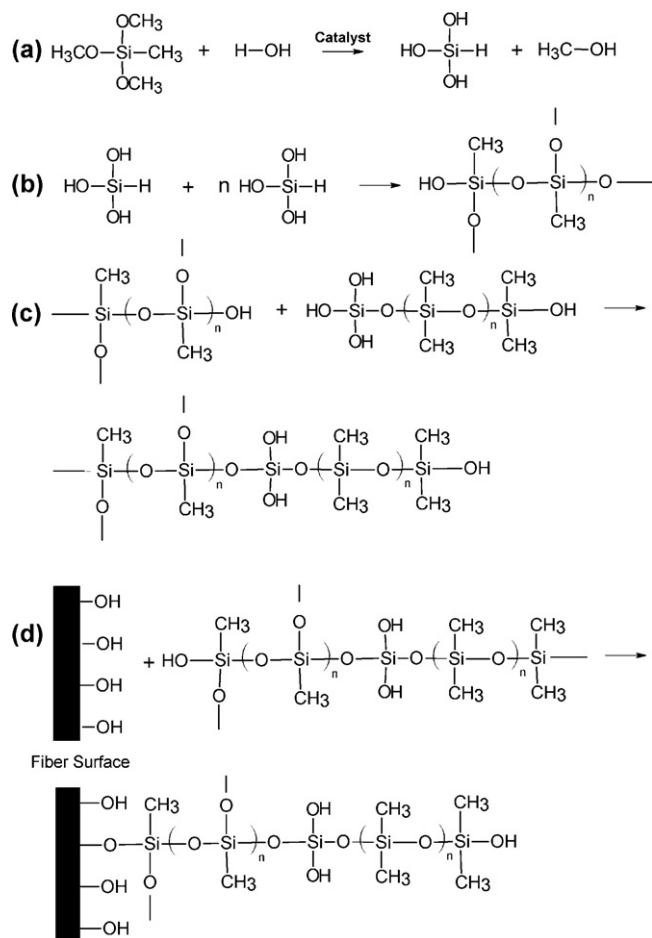
**Fig. 6.** Electron scanning micrography (600× magnification) of a sol–gel Carbowax 20M ormosil fiber.
From Silva and Augusto [154].

[134]; fibers coated with PEG-modified sol–gel over Ni–Ti–ZrO$_2$ were also prepared and used on the headspace determination of halophenols and phthalate esters in water [135] and of haloanisoles in cork stopper samples [136]. Both fibers showed excellent thermal stability up to the maximum temperature evaluated of 320 °C, which was credited to the strong interaction between the zirconia substrate surface and the silica coating.

Azenha and co-workers [157] employed pure titanium wires as support for a sol–gel sorbent coating: before deposition of the sol–gel film, the titanium wires were immersed for 1 h on 1 mol L$^{-1}$ NaOH to activate the surface, generating titanol groups where the ormosil were anchored through Ti–O–Si bonds. To overcome problems related to the high ductibility of pure Ti wires, later the same group studied different alloys of this metal as support: a 250 μm 90% Ti:6% Al:4% V wire (coated with a pure chromatographic SiO$_2$ particles dispersed over PDMS-modified sol–gel silica) [158] and a 152 μm 56% Ni:44% Ti wire (coated with a dispersion of C$_{18}$ silica particles dispersed over a sol–gel silica film) [141]. For the later fiber, further mechanical and chemical stability was achieved after incorporation of vinyltriethoxysilane (VTEOS) to the sol phase and subsequent exposure of the fiber to UV radiation, to induce crosslinking between the vinyl fragments on the silica reticulate.

Beyond the technical sol gel coatings for SPME can be obtained by electrodeposition. Carasek and co-workers [159] prepared a new



**Fig. 4.** Main reactions involved on sol–gel process for SPME fiber coating.
Modified from Malik and co-workers [115].

Ni–Ti alloy wires pre-coated with an electrolytically deposited zirconium oxide layer as a substrate for sol–gel fibers. The Ni–Ti alloy have some remarkable mechanical features, which include shape memory, superelasticity and corrosion resistance, and the zirconia coating provides extra surface hydroxy groups available to participate on the sol–gel reaction. Ni–Ti–ZrO$_2$ fibers coated with sol–gel silica modified with PDMS were applied to determinations of BTEX in water [130] and of organochlorine pesticides in herbal infusions
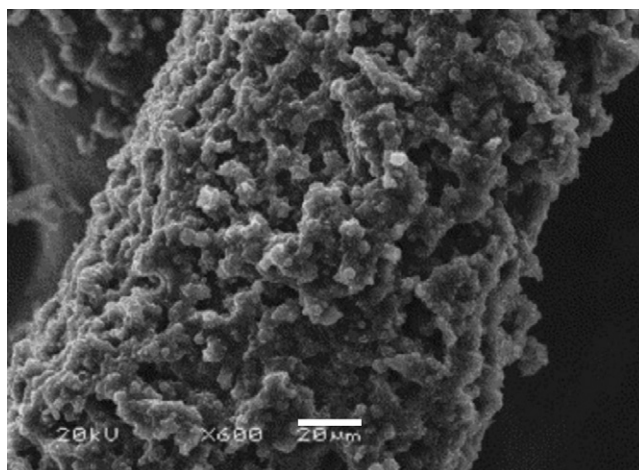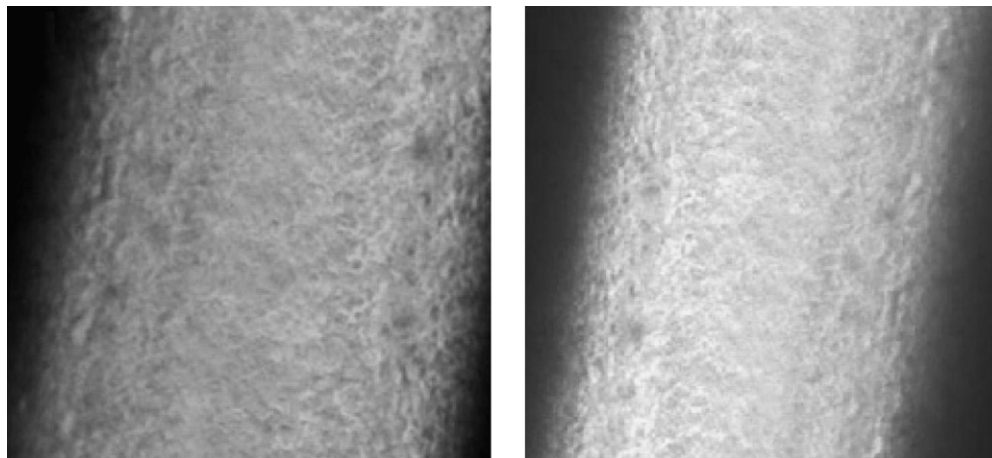




**Fig. 5.** Micrographies of sol–gel 5,11,17,23-tetra-tertbutyl-25,27-dihydroxy-26,28-diglycidyloxycalix[4]arene/hydroxy-terminated silicone oil fiber.
Extracted from Li et al. [147].

SPME fiber through electrodeposition of $ZrO_2$ onto NiTi wires. The new fibers were evaluated and applied in applied in the extraction of alcohols, BTEX and THM from gaseous samples. The extraction efficiency was compared with commercial silica-based materials with different coatings. The results showed that the extraction efficiency is comparable to 7 μm PDMS even though its coating thickness is considerably lower.

## 5. Conclusions and perspectives

The investigation of new sorbent materials for use in extraction and microextraction techniques is both a growing and promising field. The compilation presented here is far from comprehensive in terms of different trends, as well as the diversity of approaches and methodologies used. However, the materials and devices selected are representative of the main targets of research on novel sorbents and adsorbents: materials with improved (ad)sorptive capacity, capable to provide higher extraction efficiencies and, therefore, better analytical detectabilities and sensitivities, as well as high selectivity (or even specificity towards target species), chemical stability and morphology compatible to fast mass transfer during extractions. Of course, it is virtually impossible to combine all those features on a single sorbent: different classes of sorptive materials are designed to address primarily one of these goals (e.g., selectivity/specificity for MIP; fast mass transfer and chemical stability for SPME fiber coatings, and so forth).

When browsing the literature referent to some of the "novel" (ad)sorbents, one point has to be carefully considered. The properties of several of the sorbents and adsorbents described in the recent literature are literally the same of materials already well known, or even available commercially. For example, some of the sol–gel SPME fibers recently reported, prepared from different organic modifiers and alkoxysilanes, have almost the same features of the original sol–gel coating described by Malik more than 10 years from now [115]. Therefore, claims of improved selectivity, stability or extraction efficiency of new sorbents and adsorbents should be carefully considered.

Finally, it should be mentioned that the number of new materials and devices described in the literature which results on products available commercially to be applied by general users is limited. Several innovative sorbents and adsorbents do not go beyond the stage of academic research, despite their potential utility on relevant analytical problems. The reasons for this range from the lack of experience (and even interest) of some research groups on enter partnerships with analytical instrumentation industries, to the excessive rigor on the application of analytical validation and certification protocols, which sometimes delays or even hinder at all the acceptance of new analytical techniques and approaches.

## References

[1] M. Petrovic, E. Eljarrat, M.J.J. de Alda, D. Barceló, Anal. Bioanal. Chem. 378 (2004) 549.
[2] L.S. Birnbaum, D.F. Staskal, Environ. Health Perspect. 112 (2004) 9.
[3] R. Molica, H. Onodera, C. Garcia, M. Rivas, D. Andrinolo, S. Nascimento, H. Meguro, Y. Oshima, S. Azevedo, N. Lagos, Phycologia 41 (2002) 606.
[4] L. Hu, M. Ye, X. Jiang, S. Feng, H. Zou, Anal. Chim. Acta 598 (2007) 193.
[5] O. Fiehn, Plant. Mol. Biol. 48 (2002) 155.
[6] S.G. Villas-Boas, J. Højer-Pedersen, M. Akesson, J. Smedsgaard, J. Nielsen, Yeast 22 (2005) 1155.
[7] B. Papouskova, P. Bednar, P. Bartak, P. Frycak, J. Sevcik, Z. Stranski, K. Lemr, J. Sep. Sci. 29 (2006) 1531.
[8] S.D. Richardson, Anal. Chem. 76 (2004) 3337.
[9] E. Baltussen, C.A. Cramers, P.J.F. Sandra, Anal. Bioanal. Chem. 373 (2002) 3.
[10] J. Pawliszyn, S. Pedersen-Bjergaard, J. Chromatogr. Sci. 44 (2006) 291.
[11] M.C. Hennion, C. Cau-Dit-Coumes, V. Pichon, J. Chromatogr. A 823 (1998) 147.
[12] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[13] S. Pedersen-Bjergaard, K.E. Rasmussen, Electrophoresis 21 (2000) 579.
[14] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcol. Sep. 11 (1999) 737.
[15] S. Iijima, Nature 354 (1991) 56.

[16] L. Dai, P. He, S. Li, Nanotechnology 14 (2003) 1081.
[17] R.G. Ding, G.Q. Lu, Z.F. Yan, M.A. Wilson, J. Nanosci. Nanotechnol. 1 (2001) 7.
[18] Z.K. Tang, L.Y. Zhang, N. Wang, X.X. Zhang, G.H. Wen, G.D. Li, J.N. Wang, C.T. Chan, P. Sheng, Science 292 (2001) 2462.
[19] J.F. Smalley, K. Chalfant, S.W. Feldberg, T.M. Nahir, E.F. Bowden, J. Phys. Chem. B 103 (1999) 1676.
[20] G.G. Wildgoose, H.C. Leventis, I.J. Davies, A. Crossley, N.S. Lawrence, L. Jiang, T.G.J. Jones, R.G. Compton, J. Mater. Chem. 15 (2005) 2375.
[21] J. Li, R. Stevens, L. Delzeit, H.T. Ng, A. Cassell, J. Han, M. Meyyappan, Appl. Phys. Lett. 81 (2002) 910.
[22] M.C. Hennion, J. Chromatogr. A 885 (2000) 73.
[23] R.Q. Long, R.T. Yang, J. Am. Chem. Soc. 123 (2001) 2058.
[24] Y. Cai, G. Jiang, J. Liu, Q. Zhou, Anal. Chem. 75 (2003) 2517.
[25] Q. Zhou, J. Xiao, W. Wang, Anal. Sci. 23 (2007) 189.
[26] H. Niu, Y. Cai, Shi, F. Wei, J. Liu, S. Mou, G. Jiang, Anal. Chim. Acta 594 (2007) 81.
[27] K. Pyrzynska, A. Stafiej, M. Biesaga, Microchim. Acta 159 (2007) 293.
[28] Y.Q. Cai, G.B. Jiang, J.F. Liu, Q.X. Zhou, Anal. Chim. Acta 494 (2003) 149.
[29] G. Liu, J. Wang, Y. Zhu, X. Zhang, Anal. Lett. 37 (2004) 3085.
[30] J. Munoz, M. Gallego, M. Valcarcel, Anal. Chem. 77 (2005) 5389.
[31] W.F. Lu, M.Y. Ding, R. Zheng, J. Chromatogr. Sci. 43 (2005) 383.
[32] Y.Q. Cai, Y.E. Cai, S.F. Mou, Y.Q. Lu, J. Chromatogr. A 1081 (2005) 245.
[33] P. Liang, Q. Ding, F. Song, J. Sep. Sci. 28 (2005) 2339.
[34] C.R.T. Tarley, A.F. Barbosa, M.G. Segatelli, E.C. Figueiredo, P.O. Luccas, J. Anal. Atom. Spectrom. 21 (2007) 1305.
[35] Q. Zhou, W. Wang, J. Xiao, Anal. Chim. Acta 559 (2006) 200.
[36] Q. Zhou, Y. Ding, J. Xiao, Anal. Bioanal. Chem. 385 (2006) 1520.
[37] Q. Zhou, J. Xiao, W. Wang, J. Chromatogr. A 1125 (2006) 152.
[38] G.Z. Fang, J.X. He, S. Wang, J. Chromatogr. A 1127 (2006) 12.
[39] L. Wang, H. Zhao, Y. Qiu, Z. Zhou, J. Chromatogr. A 1136 (2006) 99.
[40] Q. Ding, P. Liang, F. Song, A. Xiang, Sep. Sci. Technol. 41 (2006) 2723.
[41] Q. Zhou, J. Xiao, W. Wang, G. Liu, Q. Shi, J. Wang, Talanta 68 (2006) 1309.
[42] H. Zhao, L. Wang, Y. Qiu, Z. Zhou, W. Zhong, X. Li, Anal. Chim. Acta 586 (2007) 399.
[43] Q. Zhou, J. Xiao, Y. Ding, Anal. Chim. Acta 62 (2007) 223.
[44] Q. Zhou, Y. Ding, J. Xiao, Chromatographia 65 (2007) 25.
[45] S. Wang, P. Zhao, G. Min, G. Fang, J. Chromatogr. A 1165 (2007) 166.
[46] W.D. Wang, Y.M. Huang, W.Q. Shu, J. Cao, J. Chromatogr. A 1173 (2007) 27.
[47] B. Suarez, B. Santos, B.M. Simonet, S. Cardenas, M. Valcarcel, J. Chromatogr. A 1175 (2007) 127.
[48] Q. Zhou, J. Xiao, W. Wang, Microchim. Acta 157 (2007) 93.
[49] H. Katsumata, T. Matsumoto, S. Kaneco, T. Suzuki, K. Ohta, Microchem. J. 88 (2008) 82.
[50] G. Min, S. Wang, H. Zhu, G. Fang, Y. Zhang, Sci. Tot. Environ. 396 (2008) 79.
[51] S. Wang, Y. Wang, W. Huang, G. Fang, Z. Duan, H. Qiao, Y. Zhang, Anal. Lett. 40 (2007) 2338.
[52] B. Basheer, A.A. Alnedhary, B.S.M. Rao, S. Valliyaveettil, H.K. Lee, Anal. Chem. 78 (2006) 2853.
[53] J.X. Wang, D.Q. Jiang, Z.Y. Gu, X.P. Yan, J. Chromatogr. A 1137 (2006) 8.
[54] J. Lü, J. Liu, Y. Wei, K. Jiang, S. Fan, J. Liu, G. Jiang, J. Sep. Sci. 30 (2007) 2138.
[55] X. Liu, Y. Ji, Y. Zhang, H. Zhang, M. Liu, J. Chromatogr. A 1165 (2007) 10.
[56] B. Suarez, B.M. Simonet, S. Cardenas, M. Valcarcel, J. Chromatogr. A 1159 (2007) 203.
[57] M.A. Salam, R. Burke, Anal. Bioanal. Chem. 390 (2008) 2159.
[58] L. Pauling, J. Am. Chem. Soc. (1940) 2643.
[59] B. Sellergren, J. Chromatogr. A 906 (2001) 227.
[60] M. Ogiso, N. Minoura, T. Shinbo, T. Shimiz, Biosens. Bioelectron. 22 (2007) 1974.
[61] L. Schweitz, P. Spegel, S. Nilsson, Electrophoresis 22 (2001) 4053.
[62] M. Quaglia, B. Sellergren, E. De Lorenzi, J. Chromatogr. A 1044 (2004) 53.
[63] J.L. Urraca, M.C. Moreno-Bondi, G. Orellana, B. Sellergren, A.J. Hall, Anal. Chem. 79 (2007) 4915.
[64] B. Sellergren, Anal. Chem. 66 (1996) 1578.
[65] F. Qiao, H. Sun, H. Yan, K.H. Row, Chromatographia 64 (2006) 625.
[66] P. Spégel, L. Schweitz, S. Nilsson, Anal. Bioanal. Chem. 372 (2002) 37.
[67] S. Marx, Z. Liron, Chem. Mater. 13 (2001) 3624.
[68] F.G. Tamayo, E. Turiel, A. Martín-Esteban, J. Chromatogr. A 1152 (2007) 32.
[69] M. Nakamura, M. Ono, T. Nakajima, Y. Ito, T. Aketo, J. Haginaka, J. Pharm. Biomed. Anal. 37 (2005) 231.
[70] S.G. Hu, S.W. Wang, X.W. He, Analyst 128 (2003) 1485.
[71] F.G. Tamayo, J.L. Casillas, A. Martin-Esteban, Anal. Chim. Acta 482 (2003) 165.
[72] C. Alexander, H.S. Andersson, L.I. Andersson, R.J. Ansell, N. Kirsch, I.A. Nicholls, J. O'Mahony, M.J. Whitcombe, J. Mol. Recogn. 19 (2006) 106.
[73] I. Chianella, M. Lotierzo, S.A. Piletsky, I.E. Tothill, B.N. Chen, K. Karim, A.P.F. Turner, Anal. Chem. 74 (2002) 1288.
[74] L.Q. Wu, B.W. Sun, Y.Z. Li, W.B. Chang, Analyst 128 (2003) 944.
[75] I. Chianella, K. Karim, E.V. Piletska, C. Preston, S.A. Piletsky, Anal. Chim. Acta 559 (2006) 73.
[76] M. Pascale, A. De Girolamo, A. Visconti, N. Magan, I. Chianella, E.V. Piletska, S.A. Piletsky, Anal. Chim. Acta 609 (2008) 131.
[77] F. Lanza, B. Sellergren, Anal. Chem. 71 (1999) 2092.
[78] Q.Z. Zhu, K. Haupt, D. Knopp, R. Niessner, Anal. Chim. Acta 468 (2002) 217.
[79] B. Dirion, Z. Cobb, E. Schillinger, L.I. Andersson, B. Sellergren, J. Am. Chem. Soc. 125 (2003) 15101.
[80] F. Navarro-Villoslada, B. San Vicente, M.C. Moreno-Bondi, Anal. Chim. Acta 504 (2004) 149.

[81] M.T. Koessdjojo, H.T. Rasmussen, A.M. Fermier, P. Patel, V.T. Remcho, J. Comb. Chem. 9 (2007) 929.
[82] A.R. Khorrami, S. Mehrseresht, J. Chromatogr. B 867 (2008) 264.
[83] K. Tang, S. Chen, X. Gu, H. Wang, J. Dai, J. Tang, Anal. Chim. Acta 614 (2008) 112.
[84] B. Claude, P. Morin, M. Lafosse, A.S. Belmont, K. Haupt, Talanta 75 (2008) 344.
[85] P.S. Sharma, D. Lakshmi, B.B. Prasad, Biomed. Chromatogr. 21 (2007) 976.
[86] A. Beltran, E. Caro, R.M. Marce, P.A.G. Cormack, D.C. Sherrington, F. Borrull, Anal. Chim. Acta 597 (2007) 6.
[87] F. Puoci, G. Cirillo, M. Curcio, F. Iemma, U.G. Spizzirri, N. Picci, Anal. Chim. Acta 593 (2007) 164.
[88] J. Yang, Y. Hu, J.B. Cai, X.L. Zhu, Q.D. Su, Y.Q. Hu, F.X. Liang, Food Chem. Toxicol. 45 (2007) 896.
[89] S. Le Moullec, L. Truong, C. Montauban, A. Begos, V. Pichon, B. Bellier, J. Chromatogr. A 1139 (2007) 171.
[90] M.M. Ariffin, E.I. Miller, P.A.G. Cormack, R.A. Anderson, Anal. Chem. 79 (2007) 256.
[91] C. Schirmer, H. Meisel, J. Chromatogr. A 1132 (2006) 325.
[92] G. Theodoridis, M. Lasakova, V. Skerikova, A. Tegou, N. Giantsiou, P. Jandera, J. Sep. Sci. 29 (2006) 2310.
[93] L. Ding, H. Li, F. Tang, S. Yao, Anal. Lett. 39 (2006) 2373.
[94] Y. Xiong, H. Zhou, Z. Zhang, D. He, C. He, Analyst 131 (2006) 829.
[95] E. Caro, R.M. Marce, P.A.G. Cormack, D.C. Sherrington, F. Borrull, J. Sep. Sci. 29 (2006) 1230.
[96] F. Breton, P. Euzet, S.A. Piletsky, M.T. Giardi, R. Rouillon, Anal. Chim. Acta 569 (2006) 50.
[97] L.Q. Lin, J. Zhang, Q. Fu, L.-C. He, Y.-C. Li, Anal. Chim. Acta 561 (2006) 178.
[98] J. Yang, Y. Hu, J.B. Cai, X.L. Zhu, Q.-D. Su, Anal. Bioanal. Chem. 384 (2006) 761.
[99] G. Karasova, J. Lehotay, J. Sadecka, I. Skacani, M. Lachova, J. Sep. Sci. 28 (2005) 2468.
[100] E. Caro, R.M. Marce, P.A.G. Cormack, D.C. Sherrington, F. Borrull, Anal. Chim. Acta 552 (2005) 81.
[101] E. Caro, R.M. Marce, P.A.G. Cormack, D.C. Sherrington, F. Borrull, J. Sep. Sci. 28 (2005) 2080.
[102] X. Zhu, J. Yang, Q. Su, J. Cai, Y. Gao, J. Chromatogr. A 1092 (2005) 161.
[103] R. Carabias-Martinez, E. Rodriguez-Gonzalo, E. Herrero-Hernandez, J. Chromatogr. A 1085 (2005) 199.
[104] E. Caro, R.M. Marce, P.A.G. Cormack, D.C. Sherrington, F. Borrull, J. Chromatogr. B 813 (2004) 137.
[105] E. Blahova, J. Lehotay, I. Skacani, J. Liq. Chromatogr. Rel. Technol. 27 (2004) 2715.
[106] P.D. Martin, G.R. Jones, F. Stringer, I.D. Wilson, J. Pharm. Biomed. Anal. 35 (2004) 1231.
[107] B. San Vicente, F. Navarro-Villoslada, M.C. Moreno-Bondi, Anal. Bioanal. Chem. 380 (2004) 115.
[108] E. Caro, R.M. Marce, P.A.G. Cormack, D.C. Sherrington, F. Borrull, J. Chromatogr. A 1047 (2004) 175.
[109] N.M. Maier, G. Buttinger, S. Welhartizki, E. Gavioli, W. Lindner, J. Chromatogr. B 804 (2004) 103.
[110] F. Chapuis, V. Pichon, F. Lanza, B. Sellergren, M.C. Hennion, J. Chromatogr. B 804 (2004) 93.
[111] W. Cummins, P. Duggan, P. McLoughlin, Anal. Chim. Acta 542 (2005) 52.
[112] R.G.C. Silva, F. Augusto, J. Chromatogr. A 1114 (2006) 216.
[113] H.S. Wei, Y.L. Tsai, J.Y. Wu, H. Chen, J. Chromatogr. B 836 (2006) 57.
[114] H. Bartels, B. Prijs, Adv. Chromatogr. 11 (1974) 115.
[115] S.L. Chong, D. Wang, J.D. Hayes, B.W. Wilhite, A. Malik, Anal. Chem. 69 (1997) 3889.
[116] Z. Wang, C. Xiao, C. Wu, H. Han, J. Chromatogr. A 893 (2000) 157.
[117] F. Zhou, X. Li, Z. Zeng, Anal. Chim. Acta 538 (2005) 63.
[118] J. Yu, L. Dong, C. Wu, L. Wu, J. Xing, J. Chromatogr. A 978 (2002) 37.
[119] A.L. Lopes, F. Augusto, J. Chromatogr. A 1056 (2004) 13.
[120] L. Yun, Anal. Chim. Acta 486 (2003) 63.
[121] Z. Zeng, W. Qiu, Z. Huang, Anal. Chem. 73 (2001) 2429.
[122] L. Cai, J. Xing, L. Dong, C. Wu, J. Chromatogr. A 1015 (2003) 11.
[123] M. Liu, Z. Zeng, B. Xiong, J. Chromatogr. A 1065 (2005) 287.
[124] Y.-L. Hu, Y.-L. Fu, G.-K. Li, Anal. Chim. Acta 567 (2006) 211.
[125] M. Liu, Z. Zeng, Y. Tian, Anal. Chim. Acta 540 (2005) 341.
[126] H. Bagheri, E. Babanezhad, F. Khalilian, Anal. Chim. Acta 616 (2008) 49.
[127] J. Zeng, J. Chen, Z. Lin, W. Chen, X. Chen, X. Wang, Anal. Chim. Acta 619 (2008) 59.
[128] J. Zhou, F. Yang, D. Cha, Z. Zeng, Y. Xu, Talanta 73 (2007) 870.
[129] K. Farhadi, R. Mamaghanian, R. Maleki, J. Hazard. Mater. 152 (2008) 677.
[130] S.S. Segro, Y. Cabezas, A. Malik, J. Chromatogr. A 1216 (2009) 4329.
[131] A. Oliveira, C. Silveira, S. Campos, E. Campos, E. Carasek, Chromatographia 61 (2005).
[132] A. Oliveira, C. Silveira, S. Campos, E. Campos, E. Carasek, Talanta 66 (2005) 74.
[133] C. Silveira, A. Oliveira, S. Campos, E. Campos, E. Carasek, Colloid Surf. A 259 (2005) 15.
[134] D. Budziak, E. Mardendal, E. Carasek, J. Chromatogr. A 1187 (2008) 34.
[135] D. Budziak, E. Mardendal, E. Carasek, J. Sep. Sci. 31 (2008) 2875.
[136] D. Budziak, E. Mardendal, E. Carasek, J. Chromatogr. A 1158 (2008) 54.
[137] D. Budziak, E. Mardendal, E. Carasek, Anal. Chim. Acta 629 (2008) 92.
[138] H. Chen, X.-J. Liu, C. Yang, J. Gao, C.-W. Ye, X.-J. Li, Chromatographia 70 (2009).
[139] W. Zhang, Y. Sun, C. Wu, J. Xing, J. Li, Anal. Chem. 81 (2009) 2912.
[140] R. Maleki, K. Farhadi, R. Tahmasebi, Chromatographia 69 (2009) 775.
[141] M. Azenha, M. Ornelas, A. Fernando-Silva, J. Chromatogr. A 1216 (2009) 2302.
[142] F. Bianchi, F. Bisceglie, M. Careri, S. di Bernardino, A. Mangia, M. Musci, J. Chromatogr. A 1196 (2008) 15.
[143] F. Bianchi, M. Careri, A. Mangia, M. Mattarozzi, M. Musci, J. Chromatogr. A 1196 (2008) 41.
[144] A.F.P. Biajoli, F. Augusto, Anal. Sci. 24 (2008) 1141.
[145] Z. Zeng, W. Qiu, M. Yang, X. Wei, Z. Huang, F. Li, J. Chromatogr. A 934 (2001) 51.
[146] X. Li, Z. Zeng, J. Zhou, Anal. Chim. Acta 509 (2004) 27.
[147] X. Li, Z. Zeng, M. Hu, M. Mao, J. Sep. Sci. 28 (2005) 2489.
[148] X. Li, Z. Zeng, J. Zhou, S. Gong, W. Wang, Y. Chen, J. Chromatogr. A 1041 (2004) 1.
[149] Y.L. Fu, Y.L. Hu, J. Zeng, G.K. Li, J. Sep. Sci. 29 (2006) 2864.
[150] J. Yu, C. Wu, J. Xing, J. Chromatogr. A 1036 (2004) 101.
[151] T.P. Gbatu, K.L. Sutton, J.A. Caruso, Anal. Chim. Acta 402 (1999) 67.
[152] V.G. Zuin, A.L. Lopes, J.H. Yariwake, F. Augusto, J. Chromatogr. A 1056 (2004) 21.
[153] R.C. Silva, V.G. Zuin, J.H. Yariwake, M.G. Eberlin, F. Augusto, J. Mass Spectrom. 42 (2007) 825.
[154] R.G.C. Silva, F. Augusto, J. Chromatogr. A 1072 (2005) 7.
[155] T.Y. Kim, A. Alhooshani, A. Kabir, D.P. Fries, A. Malik, J. Chromatogr. A 1047 (2004) 165.
[156] X. Li, J. Gao, Z. Zeng, Anal. Chim. Acta 590 (2007) 26.
[157] M. Azenha, P.J. Nogueira, A.F. Silva, Anal. Chem. 78 (2006) 2071.
[158] M. Azenha, P. Nogueira, A. Fernando-Silva, Anal. Chim. Acta 610 (2008) 205.
[159] D. Budziak, E. Martendal, E. Carasek, J. Chromatogr. A 1164 (2007) 18.