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Recent advances and future trends in new materials for sample preparation

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ABSTRACT

The analysis of chemical compounds present at very low concentrations in complex matrices (e.g., residues and contaminants in food samples) usually requires a complex analytical approach, involving sampling, sample preparation, analyte isolation and qualitative and quantitative determination. Most analysts consider sample preparation to be the Achilles' heel, because it is usually time consuming, presents low yields, is prone to introducing contamination, and is more difficult to automate than other steps. Recently, a strong movement towards utilization of greener analytical methods stimulated development of microextraction techniques. Most of these microextraction techniques are based upon sorption processes, making the development of novel sorptive materials one of the most active research areas in this field. In the present work, we present a review on the new materials recently developed for sample preparation in line with the concept of green analytical chemistry. We also review the techniques using them and their main applications.

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Abbreviations: β-CD, β-cyclodextrin; β-NSA, β-naphthalenesulfonic acid; γ-MPTS, γ-mercaptopropyltrimethoxysilane; ADS, Alkyl-diol silica; APTES, 3-amiopropyltriethoxysilane; APTMS, (3-aminopropyl)trimethoxysilane; ASE, Accelerated solvent extraction; BIN, Barrel-insert needle; BSA, Bovine serum albumin; CAR, Carboxen; CE, Capillary electrophoresis; CNF, Carbon nanofiber; CNT, Carbon nanotube; CW, Carbowax; DAD, Diode-array detector; DLLME, Dispersive liquid-liquid microextraction; DVB, Divinylbenzene; ECD, Electron-capture detector; EF, Enrichment factor; FAAS, Flame atomic absorption spectrometer; FLD, Fluorescence detector; G, Graphene; GAC, Green analytical chemistry; GC, Gas chromatography; GMA, Glycidyl methacrylate; GO, Graphene oxide; GPTMS, (3-glycidyloxypropyl)trimethoxysilane; HF-LPME, Hollow-fiber liquid-phase microextraction; HPLC, High-performance liquid chromatography; HS, Headspace; ICP, Inductively-coupled plasma; IIP, Ion-imprinted polymer; IL, Ionic liquid; LC, Liquid chromatography; LLE, Liquid-liquid extraction; LOD, Limit of detection; LOQ, Limit of quantification; LVI, Large-volume injection; MAA, Methacrylic acid; MALDI, Matrix-assisted laser desorption/ionization; MEPS, Microextraction by packed sorbent; MIM, Molecularly imprinted monolith; MIP, Molecularly imprinted polymer; MNP, Magnetic nanoparticle; MPTMS, (3-mercaptopropyl)trimethoxysilane; MS, Mass spectrometry; MS/MS, Tandem mass spectrometry; MSPD, Matrix solid-phase dispersion; MSPE, Magnetic solid-phase extraction; MTMOS, Methyltrimethoxysilane; MTMS, Methyltrimethoxane; OES, Optical emission spectrometry; OH-PDMS, Hydroxy-terminated polydimethylsiloxane; PA, Polyacrylate; PAD, Pulsed amperometric detection; PAH, Polycyclic aromatic hydrocarbon; PDMS, Polydimethylsiloxane; PEG, Polyethylene glycol; PHEMA, Poly(2-hydroxyethyl methacrylate); PIL, Polymeric ionic liquid; PPy, Polypyrrole; PTMS, Phenyltrimethylsiloxane; PT-SPE, Pipette-tip solid-phase extraction; PVA, Polyvinyl alcohol; RAM, Restricted access material; RSD, Relative standard deviation; SBSE, Stir-bar sorptive extraction; SCSE, Stir-cake sorptive extraction; SDME, Single-drop microextraction; SFE, Supercritical fluid extraction; SOX, Soxhlet; SPE, Solid-phase extraction; SPME, Solid-phase microextraction; SWE, Subcritical water extraction; TAP, Thiamphenicol; TBOT, Tetrabuthoxytitanium; TEOS, Tetraethoxysilane; TMOS, Tetramethoxysilane; ToF, Time of flight; VBC, Poly(vinylbenzylchloride).

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1. Introduction

In the analytical chemistry universe dealing with the determination of mixtures of analytes present at very low concentrations in complex matrices, every single step in the analytical workflow is relevant. From the sampling procedure up to the final data-processing, every step might introduce errors compromising the quality of the final analytical result [1]. Due to the need to assure the quality, the reproducibility and the integrity of the data, in some application areas (e.g., food chemistry and pharmaceutical analysis), international regulatory agencies require several procedures, including method validation and comprehensive statistical data treatment in order for the results to be considered acceptable. Unfortunately, in spite of the tremendous evolution of the analytical instrumentation that has occurred in recent decades, especially in chromatography and mass spectrometry (MS), complex sample analysis still cannot achieve the desired results if the samples are introduced directly into the analytical instrument without a sample-pre-treatment step. As a result, more extended methods have been developed to fulfill regulatory and analytical requirements, resulting in methodologies that involve several independent, complex steps.

A typical analytical workflow widely for the analysis of residue and contaminants in food matrices (e.g., veterinary drugs in meat and pesticides in fruits) employs a sample preparation step after the sampling procedure [2]. Sample preparation aims to minimize the sample complexity and to eliminate most matrix interferences before introduction into the analytical instrument (usually a chromatograph) in order to facilitate improved isolation of the target analytes before they are introduced into the detector. Nowadays, a mass spectrometer – single (MS) or in tandem (MS/MS) – is becoming the standard detector in this application area. By following the analytical workflow described, the inclusion of a sample-preparation step (usually involving an extraction technique) after the sampling step simplifies the complexity of the extract to facilitate the separation of the desired analytes from other components in the analytical column. As a result, fewer and purer analytes are introduced into the MS or MS/MS detector thus making their identification and quantification less demanding.

Even considering that all described steps are without doubt important in any analytical process, sample preparation is the step most likely to cause problems and difficulties (e.g., consumption of time, cost, contamination, poor reproducibility and low extraction yields) [3,4].

In the past five decades, several extraction techniques have been utilized for sample preparation. Soxhlet (SOX) and pressurized solvent extraction techniques [e.g., supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) and subcritical water extraction (SWE)] gained preference for solid sample analysis. For the sample preparation step when dealing with liquid samples, large-bore open-tubular glass liquid chromatographic (LC) columns operating at gravity pressure and liquid-liquid extraction (LLE) were the dominant techniques.

In the 1970s, solid-phase extraction (SPE), a miniaturized version of the classical LC technique, was introduced and shortly became one of the preferred substitutes for LLE. Although SPE represented a considerable advance over the previously utilized techniques by lowering the amount of organic solvent utilized for sample preparation, it was far from being a “green” extraction technique due to the relatively large amounts of organic solvents still utilized [5]. Even considering that some efforts were directed to miniaturize further the sorption-based extraction, as in the open-tubular-trap approach by Cramers et al. [6], this picture started to change only during the last decade of the twentieth century with the development of SPME by Pawliszyn et al. [7]. SPME may be considered a miniaturized version of SPE. A sorption-based approach, SPME inaugurated the era of the so-called microextraction techniques.

Shortly after the success of this technique, Cramers, Sandra et al. [8] proposed another sorption-based extraction technique, termed stir-bar sorption extraction (SBSE), a modification of the SPME technique, described in the PhD thesis of their student Baltussen [9]. Coating a polydimethylsiloxane (PDMS) film thicker than those utilized in SPME over a small magnetic bar, SBSE presented extraction yields not achieved by SPME for some analytes possessing low K_{ow} values. However, for several years, the only commercially-available sorbent for SBSE was PDMS, which limited its use to the extraction of low- and slightly medium-polarity analytes.

Meanwhile, a further miniaturization of SPE, termed microextraction by packed sorbent (MEPS), was developed [10] and commercially introduced. The conventional polymeric cartridge utilized in SPE techniques to hold the sorbent was substituted by a stainless-steel, miniaturized version termed the barrel insert and needle (BIN), which could contain any of a large number of sorbents, such as those utilized in SPE.

The main feature of these and similar techniques has been to decrease or to eliminate organic solvents during the extraction procedure, thus moving the sample preparation step towards the concept of green analytical chemistry (GAC). Several solvent-based miniaturized extraction techniques were also developed in recent decades, including dispersive liquid-liquid microextraction (DLLME), single-drop microextraction (SDME) and hollow-fiber liquid-phase microextraction (HF-LPME), which were recently reviewed by Spietelun et al. [11].

Among the several micro-techniques available nowadays for sample preparation, those based upon the use of sorptive materials are by far the most utilized. The development of new materials as sorbents in sample preparation has been widely exploited in order to achieve more selective materials with higher adsorption capacity, and to expand the availability of cheaper, more easily synthesized sorbents.

The use of micro-techniques combined with more selective sorbents allows a GAC approach based on the concept of the three Rs