New materials and trends in sorbents for solid-phase extraction

Fabio Augusto, Leandro W. Hantao, Noroska G.S. Mogollón,
Soraia C.G.N. Braga

In this article, we outline and discuss some of the most recent tendencies on the research related to novel sorbent materials for solid-phase extraction (SPE). Hemimicelles and admicelles are structures formed from solutions of ionic surfactants, which can be sorbed on the surfaces of active solids, resulting in sorbents capable of simultaneously extracting a wide range of analytes with extremely varied polarity. The performance of another important class of new SPE materials is based on molecular recognition, which mimics the selective or specific affinity of several biomolecules towards their target compounds: these sorbents include molecularly-imprinted materials, immunosorbents and aptamer-modified surfaces. Finally, there is also a growing interest on sorbents based on nanostructured materials (e.g., electrospun nanofibers and carbon nanotubes).

Keywords: Affinity; Aptamer; Carbon nanotube (CNT); Electrospun nanofiber (NF); Immunosorbent; Ionic surfactant; Molecularly-imprinted polymer (MIP); Molecular recognition; Solid-phase extraction (SPE); Sorbent

Fabio Augusto*,
Leandro W. Hantao,
Noroska G.S. Mogollón,
Soraia C.G.N. Braga
Institute of Chemistry and
Instituto Nacional de Ciência e
Tecnologia em Bioanalítica
(INCTBio), University of
Campinas (Unicamp), CP 6154,
13084-971 Campinas,
São Paulo, Brazil

1. Introduction

The main objectives of any analytical chemists – whatever their field of work – has been to pursue techniques, protocols and devices to improve the sensitivity and the selectivity of the analytical methods, without compromising the reliability of the results, the overall speed of the procedures and their cost. This is a formidable task, demanding deep comprehension of chemical and physico-chemical processes involved in all steps of methodologies and an increasing need for knowledge of the principles and the application of chemometric and computational tools to optimize laboratory routines, and to process and to decipher results. In some cases, the discovery of analytes previously unknown in particular matrices requires the development of analytical methods for their detection and quantitation {e.g., 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone, later known as MX, was first found at ng/L levels as a disinfection by-product after water chlorination [1]}. Subsequently, this compound and other similar halofuranones were found to be powerful mutagenic agents, and, since then, considerable effort has been devoted to their detection and determination at very low levels in water and related environmental matrixes. Also, some compounds whose presence in food and environmental matrixes has been well known for some time, or that already were of concern but as environmental pollutants, were formerly overlooked as food contaminants or considered unimportant in this context. These species turned into relevant analytes due to novel information related to their presence in the food and environmental matrixes or to their action on humans and animals. Such emerging food contaminants include, but are not limited to, perfluorinated compounds, polybrominated diphenyl ethers (PBDEs), nanomaterials, pharmaceutical residues and marine biotoxins [2]. Along with new analytes, other causes for continual development in analytical sciences may be the sudden increase in the demand for results on traditional areas {e.g., the efforts to ensure so-called ''homeland security'' after the 2001 terrorist attacks on USA included a renewal of interest in fast, simple methods

*Corresponding author.
Tel.: +55 19 3521 3057;
Fax: +55 19 3521 3023.;
E-mail: augusto@iqm.unicamp.br,

0165-9936/$ - see front matter © 2012 Elsevier Ltd. All rights reserved. doi:http://dx.doi.org/10.1016/j.trac.2012.08.012

to determine species associated with chemical warfare [3–5]}.

Finally, novel fields of application are always emerging, pushing for research on faster and more reliable procedures {e.g., the ''omics'' sciences – from proteomics to metabolomics – demand fast analytical procedures that may handle trace quantities of frequently unstable analytes contained on highly complex biological matrixes [6]}. The achievement of faster, more dependable methods with suitable sensitivity and selectivity depends on enhancements to all steps regularly included in analytical methods – from sampling to data processing and interpretation. During the sample-preparation stages, the inclusion of one or more operations involving extraction of the target analytes, potential interferents or matrix macroconstituents prior final separation, detection and quantitation is frequent (and sometimes mandatory) [7]. Frequently, problems related to loss of accuracy or precision are associated with these extraction and clean-up operations, which are also usually the slower steps in any analytical process. Among any other issues, improvement in extraction technologies is therefore a recurrent topic in current research in analytical chemistry.

Several extraction techniques, ranging from classic conventional liquid-liquid extraction (LLE) and liquid-solid (Soxhlet) extraction, to more contemporary methods based on microextraction approaches are available; however, since the end of the twentieth century, certainly the most popular analytical extraction technique has been solid-phase extraction (SPE). The fundamentals of SPE, including the different available formats, aspects of method development and applicability to organic and inorganic analytical problems have been thoughtfully discussed and reviewed in the literature [8].

Among other aspects of SPE, significant efforts have been devoted to development and characterization of new, advanced sorbent materials to endeavor to improve selectivity or specificity towards target analytes, higher sorptive capacity (with consequent better sensitivities and detectabilities) and enhanced chemical or physical-mechanical stability. Of course, it is not possible to focus simultaneously on achieving all these goals, and, among them, it is possible to discern some clear trends. According to Poole [9], sorbents for SPE can be divided in three groups: inorganic oxides, low-specific sorbents, and compound-specific and class-specific sorbents. The window for new developments in the first class – adsorptive inorganic oxides [e.g., silica, alumina and Florisil (magnesium silicate)] – is obviously limited by the nature of such materials and of the analyte-adsorbent interactions. Non-specific sorbents (individually most employed as SPE media) embrace surface-modified silicas and porous polymers (e.g., polystyrene-divinylbenzene resins and carbon-based materials). Among them, surface-modified silicas have the broader range of applications but suffer from several limitations, including limited stability when submitted to aqueous samples with low or high pH; research work on this class of sorbents is usually motivated by the exploration of materials with improved stability under aggressive conditions and/or higher affinity for polar analytes [10].

Most of the analytical problems related to the food industry, and an important fraction of those related to environmental sciences, involve aqueous samples, matrixes containing a significant amount of water and other polar macroconstituents, and molecules with high molecular weight. Despite the limitations of silica-based non-selective sorbents, their use in extracting analytes with low or moderate polarity from such samples is intensive and, except for more complex matrixes or otherwise problematic samples, is usually uncomplicated. However, for problems related to the isolation of highly-polar species or macromolecules from aqueous samples – where for most conventional non-selective sorbents the partition coefficients either do not favor the transfer of the target compounds to the sorbent bed or where there is irreversible sorption – and for complex samples containing large amounts of interfering species, the use of compound-specific and class-specific sorbents may be essential. There is therefore considerable interest in novel SPE materials with high selectivity or even specificity towards such compounds and sorbents concurrently applicable to wider range of matrixes and analytes – from extremely polar to hydrophobic species.

In the following sections, we present and discuss the recent advances and applications of some of the emerging new class-specific and compound-specific sorbents for SPE.

2. Surfactant-modified sorbents

On surfactant solutions above the so-called critical micellar concentration (CMC), molecules organize themselves in micelles (spherical nanostructures formed by aggregation of surfactant molecules where the hydrophilic end of the molecule is in contact with solvent and the hydrophobic tails are in the center of the micelle). However, in concentrations slight below the CMC, molecules of ionic surfactants can be sorbed on the surface of active solids (e.g., alumina, silica, titania and iron oxides) exposed to the solution, forming monolayers or bilayers on these surfaces [11]; these structures are known, respectively, as hemimicelles and admicelles (Fig. 1). On hemimicelle-based sorbents, the hydrophobic tail of the surfactant is exposed to the sample, so the corresponding sorbents have higher affinity towards non-polar analytes. As for sorbents containing admicelles on the surface, the portion of the coacervates exposed to the solution comprises the ionic tails of the surfactant molecules, rendering the materials more