Handbook of Smart Materials
in Analytical Chemistry
Handbook of Smart Materials in Analytical Chemistry

Volume I

Edited by

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Preface

Analytical chemistry was dramatically changed when in the middle of the last century classical analytical methods were replaced by instrumental ones. A general complaint emerged about the absence, or strong reduction, of chemical behavior in the new methodologies and it is practically true that the advance of spectrometry and electroanalytical methods drastically reduced the use of reagents and moved to another scale of sensitivity, thus confirming the advantages of relative methods of analysis ahead of classical procedures based on stoichiometric reactions.

However, one century on, despite tremendous advancements, the new instruments do not provide the sensitivity we are looking for, nor the capability for multi-analyte determinations in a single sample. Moreover, there is a social demand for improved sensitivity and selectivity of measurements. So, nowadays we are forced to look again in our chemistry books to focus on the fundamentals of extraction, pre-concentration, and matrix removal to be able to lower the limit of detection values for the determination of target analytes. Additionally, we must search for new materials capable of producing extraordinary improvements of selectivity and sensitivity, as compared with direct measurements, and that means a return to consideration of chemical reactions at the molecular level. Thus, once again, chemistry is in the spotlight of our analysis.

Probably, some readers were a little confused on reading the title of this book and its context. For clarity, we have decided to extend the concept of smart materials and not only consider as smart those for which their characteristics and properties could be modulated by changes in external parameters like pH, ionic strength, temperature, or pressure. In fact, other materials, like enzymes, antibodies, molecularly imprinted polymers, restricted access materials, metal–organic frameworks, or aptamers, have been considered together with other nanomaterials, polymers, and composites due to the tremendous possibilities that they offer regarding analyte specific interactions, electronic properties, high surface area, magnetic behavior, size exclusion, signal enhancement, or robustness.

The main objective of this book is to explore the exciting possibilities offered by the new generation of materials capable of improving the performance of analytical determinations. New available reagents, obtained from natural sources or produced based on accurate selection and modification of raw ones, pave the way for the development of new platforms of analysis in which a balance is made between the use of instrumental techniques for detection and a series of reactions selected to create, or modify, smart materials in order to enhance the analytical features of methods.
The editors would like to acknowledge the positive response of all the invited authors which has made it possible to have 80 scientists with different areas of expertise collaborating across 20 different countries. It has been great to work with many people whose works are well known in international journals and further literature, even though in some cases we did not have the opportunity to meet them before writing this book. The main reason for this is the decision to select invited authors of chapters based on the author’s authority in their field and not on reasons of vicinity or friendship. However, we must confess that after collaborating on this project, we wish to meet all the authors and continue this fruitful cooperation in our everyday tasks and do not hesitate to view this project as just the beginning of a long story of cooperation in order to contribute to excellent analytical chemistry.

The present *Handbook of Smart Materials in Analytical Chemistry* is divided for practical reasons into two volumes; the first is devoted to the presentation of new materials for sample preparation and analysis, and the second is devoted to analytical processes and applications. Volume I is a small compendium of smart materials presently available always considering them in terms of their analytical chemistry advantages and uses. In this first volume we aim to give readers as complete an idea as possible about the new reagents as well as the advanced possibilities offered by the older ones. Thus, materials such as ionic liquids, porous monoliths, surfactants, molecularly imprinted polymers, enzymes and immunosorbents, nanomaterials, quantum dots, carbon based nanomaterials, restricted access materials, polymer membranes, and metal–organic frameworks are presented and evaluated through the 15 chapters. Volume II of the present handbook consists of a discussion of the role of smart materials in the improvement of analytical processes and applications. The first part of second volume depicts the use of novel materials in typical analytical procedures employed for both sample treatment and analytical determination, while the second part is focused on the presentation of the main applications of smart materials in different fields like environmental, food, clinical, and forensic. The editors hope that all the chapters included in the book provide plenty of ideas suitable to be employed in the laboratories of readers, to open up new ways in method development and application. Hence, we hope that the *Handbook of Smart Materials in Analytical Chemistry* will become a reference text in the field and that the efforts of all those who contributed to the book will be useful for you, the reader.

Finally, we would like to acknowledge the support and excellent work of the team of John Wiley & Sons who have helped us during all the steps of production of this book from the initial proposal to the final edition. Elsie Merlin, Emma Strickland, and Jenny Cossham, we are very happy to have had the opportunity to work with you.

We hope you enjoy the handbook.
Let our Analytical Chemistry become smart by working together.

*Miguel de la Guardia and Francesc A. Esteve-Turrillas*
Valencia, April 2018
1

Smart Materials

Made on Measure Reagents

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1.1 Role of Smart Materials in Analytical Chemistry

Analytical chemistry can be considered, from an applied pragmatic point of view, as the development and application of chemical methods to find an appropriate answer to social and research and development challenges by solving underlying analytical problems [1]. Thus, analytical chemistry is a multidisciplinary science in continuous evolution that must be adapted to face new problems and limits. Modern analytical chemistry must be focused to provide validated methods and tools to fulfill solutions to present and future issues, in a rapid and efficient way without any reduction of the main figures of merit of available methods while reducing human and economic consumed resources, without forgetting to be environmentally conscientious. In this sense, the conception of Green Analytical Chemistry considers in its 12 principles aspects such as: (i) direct analytical techniques instead of sample treatment, (ii) sample and residue reduction, (iii) automatization and miniaturization, and (iv) multianalyte determination methods [2]. Improvements in current analytical instrumentation have allowed achievement of many of these milestones, but their use in combination with smart materials has allowed us to go a further step.

A specific definition of smart materials is that they have some properties that can be modulated significantly in a controlled way through external stimuli such as stress, temperature, pH, moisture, electric, or magnetic fields [3, 4]. However, in this book we have focused on the analytical process and define as smart materials those tailored, task-specific, or designed materials that provide tremendous enhancements of practical properties, at any level of sample preparation and analytical determination, such as their selectivity, sensitivity, easy automation, or speediness. Consequently, their use can incorporate added value to well-established analytical methods. Discoveries of novel functional materials have played very important roles in improving conventional analytical methods and in developing novel technologies and procedures, giving huge improvements in terms of sensitivity, selectivity, ease of use, rapidity, and miniaturization of modern analytical methods.
In recent years, the application of smart materials has attracted the attention of researchers, as shown by the high increase in published papers related to analytical determination using smart materials (Figure 1.1). Nanoparticles, carbon-based materials, ionic liquids (ILs), quantum dots (QDs), antibodies, immunomaterials, aptamers, metal–organic frameworks (MOFs), and molecularly imprinted polymers (MIPs) are among these new tools suitable for modifying the characteristics of analytical methods. These smart materials have been applied in different steps of an analytical process, affording high efficacy sorbents in sample treatment, improved stationary phases in chromatography, main molecular recognizing components of electrochemical sensors and portable systems, among other functions. In this chapter and throughout both volumes of the **Handbook of Smart Materials in Analytical Chemistry** the main advantages and uses of these special reagents will be analyzed in detail.

### 1.2 Smart Materials for Sample Treatment

Usually, an analytical procedure has been considered as a succession of steps systematically organized, like a chain made up of several links, with the treatment of samples being the most crucial step, and also the weakest, link (see Figure 1.2). Moreover, it has been quantified that sampling and sample treatment steps involve 67% of the analysis time, but most importantly they give rise to 60% of error sources [5]. Sample preparation generally involves the clean-up of the sample matrix and the enrichment of target analytes to provide an interference-free signal enhancement. Consequently, both the sensitivity and selectivity enhancement of the method are the main challenges.

---

**Figure 1.1** Evolution of the number of articles published in per-reviewed journals related to analytical determination using smart materials, such as nanoparticles, carbon nanotubes (CNTs), graphene, ionic liquids (ILs), quantum dots (QDs), antibodies, immunomaterials, aptamers, metal–organic frameworks (MOFs), and molecularly imprinted polymers (MIPs). Source: Scopus (Elsevier B.V., Amsterdam, Netherlands).
In particular, sample preparation is the most critical step in the analysis of biological matrices, due to the complexity of the matrix and the presence of multiple interferents at diverse concentrations, such as protein, polypeptides, lipids, fatty acids, sugars, etc., together with analyte related species such as metabolites [6]. In this sense, the development and use of novel smart materials with improved properties for sample treatment is considered one of the most promising strategies to improve practical aspects and, in particular, to decrease analysis time and labor, together with an increase in the efficacy, selectivity, simplicity, and speed of the treatment. Obviously, the final analytical properties of the method not only depend on the sample treatment, they are strongly related to the employed separation method (liquid and gas chromatography, or capillary electrophoresis) and the detection technique. Thus, chromatography techniques coupled to mass spectrometry provide high selectivity and sample treatment is based on a simple clean-up of extracts or sample matrix directly to remove macromolecules and proteins using inexpensive and low selective sorbents; while using detection systems with relatively low selectivity, such as UV–visible, fluorescence, or ion mobility spectrometry, the use of sorbents with high selectivity toward target analytes is required. Thus, the application of smart materials for sample treatment can be summarized as: (i) increased selectivity in the target analyte retention and pre-concentration, (ii) high adsorption capacity due to the improved surface area to volume ratio, (iii) extension of novel chemical analyte–sorbent interactions with high extraction efficacy, and (iv) easy handling of materials and speed of processes related to the use of magnetic materials. On the other hand, the aforementioned advances provided by smart materials in the separation and determination steps focus on the improvement of selectivity including specificity in chiral analysis or the separation of strongly related chemical forms. In this sense, the use...
of smart materials for building column or capillary materials together with their use as mobile phases have been exciting possibilities in clinical, environmental, and food analysis.

Figure 1.3 shows the most promising smart materials employed as sorbents for selective and non-specific sample treatments. Smart materials employed for the selective extraction of target analytes include antibodies and aptamers, from biological sources, but also synthetic materials like MIPs, MOFs, and RAMs. In the case of non-specific sorbents, many sample treatment approaches have been developed using materials like graphene, carbon nanotubes (CNTs), silica nanomaterials and monoliths, surfactant-based compounds, or ionic liquids, which offer high extraction efficacies and could be also improved by the incorporation of modified surface activities for the selective extraction of target analytes. In fact, all the aforementioned smart materials have gained the attention of researchers to be employed as sorbent in different extraction techniques [7].

1.2.1 Solid-Phase Extraction

Worldwide, one of the most frequently used sample treatment techniques in laboratories is solid-phase extraction (SPE), where the target analytes are transferred to a solid sorbent from a liquid or dissolved sample; the analytes are released in a later step using elution solvents. SPE provides as main advantages simplicity, versatility, efficacy, low-cost, and high recoveries. Traditional SPE sorbents are based on adsorption, reversed phase, normal phase, and ion exchange interactions, using silica gels with chemically bonded stationary phases or porous polymers. The development of novel sorbents for SPE has played an important role in recent decades, in order to improve extraction efficiency and selectivity [8].

The use of carbon-based materials as SPE sorbents was introduced following the discovery of fullerene (C_{60}) in 1985, with the use of materials like single- and multi-walled CNTs, nanohorns, nanocones, nanofibers, graphene oxide, or graphene [9]. CNTs have been widely employed in recent years because of their π–π interactions with aromatic...
compounds, as well as their interesting properties like high surface area, easy functionalization, wide accessibility, and relatively low price [10]. The uses of graphene as SPE sorbent are reduced due to its lower water dispersibility. However, graphene oxide has gained great attention due to the surface incorporation of a wide range of functional groups like hydroxyls, carbonyls, or ketones, which improve the extraction efficacy [11]. Moreover, surface-modified graphene oxides promote van der Waals interactions that allow the retention of both hydrophilic and polar analytes [12].

SPE support selectivity was increased by the linking of enzymes to solid supports and can be greatly enhanced by using antibody-based materials, and also so-called immunosorbents, which involve antigen–antibody interactions that provide a selective extraction of target analytes with a minimal coextraction of sample matrix [13]. Antibodies are usually covalently coated, via amino, carboxyl, or thiol groups, to materials like carbohydrate polymers, as agarose and cellulose, or synthetic acrylamide, polymethacrylate, and polyethersulfone polymers [14]. Immunosorbents have been employed for the robust, quantitative, and selective SPE of a wide variety of antibiotics, hormones, pesticides, and mycotoxins in complex samples such as urine, soil, or food [15, 16]. Additionally, some selective immunoaffinity materials are nowadays commercially available for mycotoxin extraction from R-Biopharm AG (Darmstadt, Germany) and Merck (Darmstadt, Germany).

MIPs are cross-linked synthetic polymers, with a three-dimensional macromolecular structure, obtained by the co-polymerization of a functional monomer and a cross-linker in the presence of a template molecule. MIPs are considered as artificial biomimetic receptors with a high selectivity in the same range as that of antibodies and other biological receptors, but with an improved stability at extreme temperature and pH conditions, easy and low cost synthesis, and reusability [17]. The first reported use of MIPs, as selective sorbent for SPE, was made in 1994 [18]. Since then a rising number of MIPs have been synthetized for versatile use in sample preparation [19], including environmental [20] and food applications [21]. In fact, MIP-based SPE sorbents are widely established in current analytical methods, and they are commercially available from standard supply companies like Merck (Darmstadt, Germany) or Affinisep (Petit Couronne, France).

Aptamers are synthetic oligonucleotides with up to 110 single stranded base pairs able to retain specifically target molecules with a high selectivity due to the combination of hydrogen bonds, van der Waals forces, and dipole interactions.

The selectivity of aptamers is comparable to that obtained with antibodies, but they can be produced in vitro, avoiding the use of experimental animals and, thus, provide relatively low cost biomaterials. Molecular recognition sorbents based on aptamers show promising properties for SPE because of their high specificity and binding affinity, low cost, good stability, and easy in-vitro synthesis [22]. Applications of aptamer-based materials for SPE include the analysis of mycotoxins, drugs, antibiotics, and even persistent organic pollutants such as polychlorinated biphenyls [23, 24].

RAMs show a dual surface; the inner layer retains small molecules by both hydrophobic and hydrophilic interactions, while the external layer exhibits a size exclusion effect over the sample matrix. Thus, it allows the simple and easy extraction of target analytes from biological fluids, avoiding the retention of macromolecules from the matrix. RAMs have been employed for SPE in biological fluids for the analysis of drugs [25] or pesticides [26], even including inorganic species like Cu(II) and Cd(II) [27].
MOFs are distinctive materials made from metal ions and organic ligands with unusual properties, like high surface area, porosity, selectivity, and thermal and chemical stability [28]. MOFs have been employed for the SPE of compounds such as non-steroidal anti-inflammatory drugs [29], naproxen and its metabolites [30], and naphthol enantiomers [31].

1.2.2 Solid-Phase Microextraction

The solid-phase microextraction (SPME) technique was proposed by Pawliszyn and Arthur in 1990. It consists of a fused silica fiber, coated with a thin layer of an extracting material, fixed inside of the needle of a syringe [32]. Analyte extraction is carried out directly from liquid or dissolved samples or after a head-space thermal treatment from liquid or solid materials. Desorption of target analytes from the fiber is usually carried out by thermal desorption, which makes it easy to couple directly to gas chromatographic systems, but analysis by liquid chromatography or capillary electrophoresis is also possible. SPME provides great advantages for sample treatments, such as simplicity, versatility, sensitivity, short extraction time, reusability, solvent-free technique, robustness, and easy automation [33].

Commercial SPME devices are mainly coated with polymeric sorbents such as polydimethylsiloxane (PDMS) and polyacrylate, alone or in combination with divinylbenzene and/or carboxen depending on the final application. Extraction efficiency and selectivity of standard devices have been improved by the use of several smart materials as fiber coating materials, such as ionic liquids, polymeric ionic liquids, graphene, CNTs, MIPs, and MOFs [34]. These materials provided enhanced properties because of their easy synthesis, sensitivity, high thermal and chemical stability, reproducibility of measurements, and wide linear range. Regarding selectivity, carbon-based materials provide a moderate selectivity toward aromatic compounds due to their p-electron-rich structure, but a tunable selectivity for different analytes can be obtained by the use of ionic liquids, polymeric ionic liquids, MIPs, and MOFs [35]. Strategies to improve the extraction efficiency of SPME have focused on the use of nanomaterials, nanostructured polymers, and monolith packing capillaries [7].

Additionally, on-line SPME techniques are based on the adsorption of target analytes at the inner surface of an internally coated capillary column that is directly coupled online to a chromatography system. The extraction properties of the method mainly depend on the thickness and nature of the sorbent. Commercially available capillary columns have been traditionally employed for in-tube SPME, but they have been replaced by new coating materials with improved properties such as MIPs, immunosorbents, ionic liquids, nanoparticle-based materials, and monolithic capillary columns [36].

1.2.3 Magnetic Extraction

Dispersive SPE is an extraction method, where the extraction is carried out directly in the bulk sample solution instead of using a column filled with a solid material. The sorbent is dispersed into the sample solution to extract the target analytes or to remove matrix interferents. This technique has gained increased attention in recent years due to its high efficacy, speed, and simplicity. Dispersive SPE avoids the loading of large volumes of sample and increases the analyte mass transfer from the sample to the