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The potential of new solvents and materials in the context of green analytical chemistry

The need to increase the eco-sustainability of chemical processes and reduce their impact on the health of humans and ecosystems is nowadays widely recognized as an essential point to consider during the establishment and development of academic and industrial processes and methodologies. As expected, and as it should be, this consideration also applies to the analytical practice, as evidenced by the definition and increasing adoption of the principles of green analytical chemistry [1] and, more recently, green sample preparation [2]. These principles recognized already well-established trends, such as miniaturization, hyphenation, automation, on-site and direct determination, and the minimization of the use of reagents. But they also introduced other new concepts and aspects to improve the sustainability of the analytical practice, thus stimulating further development in particular study areas. This consideration would be applicable, among others, to research on the development of materials and solvents with safer and/or improved features compared to conventional options. The synthesis of sorbents with enhanced loading capacities, improved selectivity or the capacity to simplify the isolation of challenging-to-analyze compounds remains an extremely active research field. The outcomes of this research often have practical applications in both the sample preparation step and the instrumental separation and determination of the investigated analytes. Similarly, the interest for developing safe and tailored solvents, and the evaluation of alternative, green and sustainable solvents has steadily increased during the last decades, and it is becoming a highly desirable feature for novel analytical methods developed by both the scientific community and industry.

This Special Issue of *Advances in Sample Preparation (Adv. Sample. Prep.)* reviews and highlights many advances and developments that contribute to approach the principles of green analytical chemistry and green sample preparation, with special focus on the use and characterization of novel sorbents and solvents developed to enhance the safety and sustainability of the considered analytical processes. Although special attention has been paid to the analysis of liquid samples, i.e. environmental waters and biological fluids, the knowledge and background associated with most of the topics covered in this Special Issue are also applicable to other types of matrices and application studies.

The articles compiled in this Special Issue discuss modern solventless techniques for the characterization and comparison of fragrance and flavor components in psilocybin and non-psilocybin mushrooms [3], as well as for the determination of chlorophylls and carotenoids in environmental waters [4] with minimal sample manipulation.

Recent relevant advances and applications involving aptamer-functionalized magnetic supports for sample preparation have been reviewed [5], while a tutorial outlines the procedure for on-line coupling between aptamer-based solid-phase extraction and capillary electrophoresis (CE)-mass spectrometry for the determination of protein biomarkers in biological fluids and food [6]. Continuing along the path of selective sorbents, the influence of the template ion/monomer proportion on the properties of an ion-imprinted polymer has been illustrated using Ra(II) as target and natural waters as study matrix [7]. Additionally, a proof-of-concept of the potential of *in situ* formed ferrite nanoparticles to remove inorganic arsenic species from waters has been provided [8]. This material was also employed as core substrate for a magnetic multiwalled carbon nanotube-polypyrrole nanomaterial, which was used for the dispersive micro-solid phase extraction of four PDE-5 inhibitors from a variety of human, beverages and food matrices with minimal sample and reagents consumption [9]. This miniaturized extraction technique has been demonstrated to be an ideal approach for the fast and selective isolation of microcontaminants and impurities from different types of environmental and food samples using newly designed sorbents. This was exemplified by functionalized nanostructured silica modified with C8 for the preconcentration of polycyclic aromatic hydrocarbons from environmental waters [10], and mesostructured magnetic silica functionalized with β-cyclodextrin for the extraction of opium alkaloids from poppy seed infusions [11]. The feasibility of a homemade silica-based mixed-mode ion-exchange sorbent for the determination of drugs of diverse nature and polarity in environmental waters has been evaluated [12]. Alternatively, a number of application studies have involved metal-organic frameworks as advanced materials for the efficient retention of various pollutants using different extraction formats. These formats range from batch extraction, applied for the determination of colored azo dyes in contaminated textile industry wastewaters [13], to paper-based extraction of synthetic cannabinoids from oral fluids [14], and solid-phase microextraction of organophosphorus pesticides from tomato samples [15]. Other authors have illustrated how to take advantage of the special selectivity provided by specific state-of-art chromatographic sorbents to achieve challenging separations [16,17].

Regarding the use of novel, green and tailored solvents, one review paper has discussed the current use of supramolecular solvents for multitarget and matrix-independent sample preparation [18], while another article provided an overview of emerging procedures, including the use of new solvents, for the pre-treatment of biological matrices [19]. The potential of CE as an alternative approach for the determination of deep eutectic solvents viscosity with minimum sample consumption has also been demonstrated [20]. Finally, a couple of application studies used these solvents to green the determination of trace levels of toxic elements from class 1 in drugs samples [21], and priority polychlorinated biphenyls in fatty foodstuffs [22], all while still fulfilling the analytical requirements specified in current legislations for these types of

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determinations.

Altogether, the articles included in this Special Issue provided an updated overview of the current usage and topics of interest regarding the development and application of novel sorbents and solvents and their potential to enhance the eco-friendless of the different steps of the analytical process. In all instances, the proposed methodologies have demonstrated their effectiveness and validity for the intended determination through rigorous analytical validation and satisfactory comparison with more conventional and widely accepted procedures. However, these examples also underscore the persistent need for further research across various study and application areas. Additionally, they play a role in persuading readers that sample preparation continues to be a challenging but also active and stimulating research area.

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