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Metal-organic frameworks as novel sorbents in dispersive-based microextraction approaches

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ABSTRACT

This review provides a critical overview on the current state of the use of MOFs as sorbents in dispersive-based microextraction methods, not only classifying the different MOFs used in these methods and highlighting the advantages of these materials in terms of stability, analytical performance, and reuse in some cases; but also insightfully describing the analytical applications reported. A description of the current methods described in literature to prepare bare MOFs, hybrid/functionalized MOFs, and different magnetic composites based on MOF, is also included.

1. Introduction

Nowadays, the analytical monitoring of trace compounds still requires the utilization of adequate extraction and preconcentration strategies [1,2], which undoubtedly constitute the bottleneck of any analytical method. Despite the impressive advances in detection systems, it is fair to recognize that direct trace analysis of complex samples is hardly achieved [2,3]. Besides, the use of pretreated samples favors the reduction of time (and associated cost) needed to maintain instruments [4]. Sample preparation is thus devoted to minimize the sample complexity and to eliminate most matrix interferences, while ensuring proper preconcentration. In this sense, current efforts in Analytical Chemistry have been shifted to improve highly sample preparation methods, particularly in terms of miniaturization, greenness, simplification, and reduction of time [5].

Solid-phase extraction (SPE) is the most frequently used sample-pretreatment technique in laboratories worldwide. This miniaturized version of the classical liquid chromatography (LC) technique is a beneficial alternative to classical liquid–liquid extraction (LLE) because it features high preconcentration factors, rapid phase separation, low organic solvent consumption compared to LLE, simplicity, and easiness of automation [1,6]. Despite the clear advantages of SPE, it is still far to be considered a green technique given the organic solvent consumption required. Miniaturized versions of SPE (μSPE) imply the use of sorbent amounts lower than 500 mg, ensuring in this way a further consumption decrease of organic solvents required during elution. This greener μSPE mode is particularly useful when performed in its dispersive version (D-μSPE), because it allows an efficient transfer of analytes to the sorbent material given the strength of the interaction during the microextraction. The dispersion of the sorbent through the sample solutions using magnetic (or manual) stirring, vortex, or ultrasounds, provides high contact area analyte-sorbent [6]. In this mode, it has also been described the use of specific devices containing the sorbent, devices that are properly dispersed into the sample solution to attain this high contact sample-sorbent. The D-μSPE method can also be improved by incorporating magnetic materials as sorbent, in the so-called magnetic (and dispersive) – based μSPE mode (M-D-μSPE). In this interesting approach, the magnetic material containing the extracted analytes can be easily separated from the remaining non-extracted components of the aqueous sample by application of an external magnetic field (*i.e.* a strong magnet, normally with

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strengths varying from 0.2 to 0.9 T). The M-D-μSPE mode avoids the necessity of centrifugation and/or separation steps to isolate the material from the aqueous sample, thus decreasing extraction times and sources of error. Fig. 1 summarizes main modes of dispersive μSPE.

1.1. Novel sorbent materials in dispersive-based microextraction methods

Together with improvements in dispersive μSPE strategies, there has been a trend in searching of novel materials, useful not only for this sample preparation technique but also for achieving green analytical goals simultaneously. Several of the requirements that an ideal sorbent material needs to meet include: adequate chemical and mechanical stability under extraction (and desorption) conditions, ability to establish interactions with target analytes through the different mechanisms (absorption, adsorption, or both), ability to ensure quantitative sorption and elution of target analytes, fast kinetics, high capacity of dispersion in liquid samples, large specific surface area (~400 m^2 g are considered adequate for successful solid sorbents), and proper reuse, among others [6,7]. A number of materials has been introduced as novel sorbents in SPE and its diverse microextraction versions, with the purpose of achieving such ideal characteristics. Among them, molecularly-imprinted polymers (MIPs) and nanoscale materials merit citation [1,8].

MIPs have recognition sites in their structure able to embrace specific molecules. High selectivity is obtained during the synthesis of a MIP, by utilizing a template (the imprint molecule), which is chosen in accordance with the target analyte or structurally-related class of compounds [2,4]. Success of MIPs in sample preparation is undoubtedly linked to their impressive selectivity [4,9,10].

Nanomaterials (NMs) are also quite unique D-μSPE sorbents. Their behavior is totally linked to their particle size, which is accompanied by a high superficial area, interesting thermal and mechanical properties, together with an easy functionalization of their surface (which in turns facilitate the modification of the material pursuing an increase of its selectivity) [6,8,11]. Successful NMs nowadays include carbon-based (fullerenes, graphene, and single- and multi-walled carbon nanotubes) and metallic

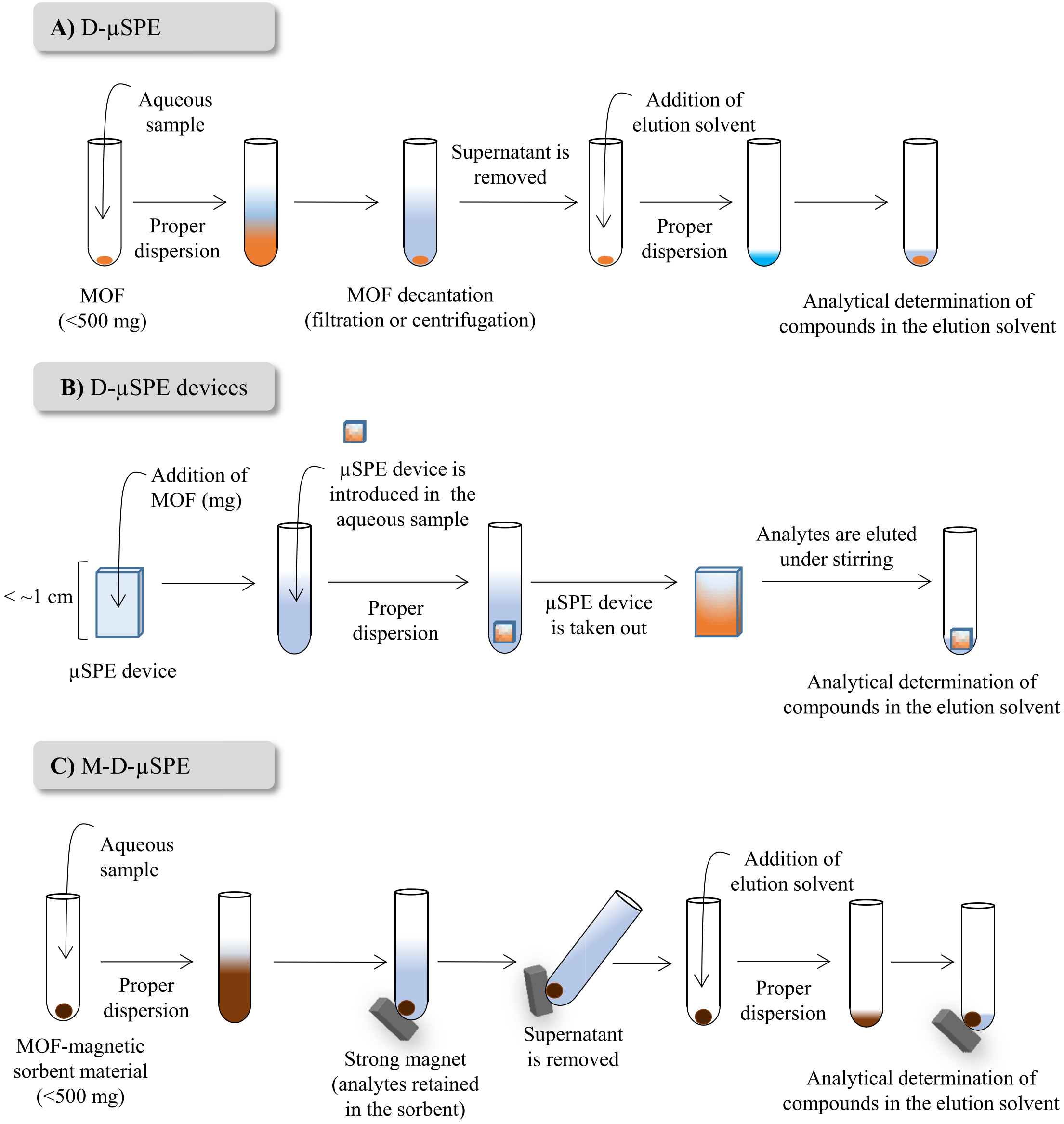

Fig. 1. Summary of the different modes to perform dispersive μSPE using MOFs.