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Capsule Phase Microextraction: The Total and Ultimate Sample Preparation Approach

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Abstract

Although analytical instrument has enjoyed unprecedented improvements in recent years, resulting in miniaturization, enhanced sensitivity, robust control systems as well as extended separation and detection capability, analytical and bioanalytical sample preparation still remain as the most challenging and time-consuming step in the analytical workflow. Collection of a representative sample is generally followed by a series of operations, collectively known as sample preparation and often include filtration, centrifugation, protein precipitation, analyte extraction, elution in organic solvent, solvent evaporation, and sample reconstitution. Many of these steps are carried out manually that ultimately prolongs the overall analysis time. Capsule Phase Microextraction (CPME), a green and new generation sample preparation technique, has been developed to streamline current state-of-the-art of sample preparation practices. It exploits the advanced material properties of inorganic-organic hybrid sorbents, integrates the filtration and sample diffusion mechanism into the device, and provides the independence of sample preparation both in the laboratory and in the field without sacrificing the convenience of the analyst and the quality of the analytical data. The article describes the development of CPME and explains its advantageous features to the current and future analytical chemists and separation scientists.

Keywords: Capsule phase microextraction; Microextraction capsules; Sol-gel sorbents; Microextraction; Sample preparation; Green analytical chemistry

Introduction

Nowadays, a large number of analytical techniques are being used for the qualitative and quantitative determination of substances in liquid samples. Typically, prior to applying any analytical technique, the analytical chemist must render the sample to a form that is compatible to the analytical instrument. In order to achieve that, a series of steps including sample pretreatment such as filtration, centrifugation, protein precipitation; analyte extraction to isolate and preconcentrate target analytes from the sample matrix; and sample post-treatment such as solvent evaporation, derivatization, and sample reconstitution in a suitable solvent are applied. All these steps are collectively called sample preparation [1]. Sample preparation is undoubtedly the most important step in the analytical process. It is also the most time-consuming step in the analytical workflow as it accounts for at least 60% of the overall analysis time [1,2]. The large number of steps in sample preparation, many of which are carried out manually, often led to substantial analyte loss, poor reproducibility as well as questionable analytical results [3].

The phenomenal advancements of analytical instrument in recent years characterized by high resolution, enhanced sensitivity, miniaturized hardware, fast data acquisition software and other beneficial attributes that can be fully exploited when an ideal sample preparation technique complements the downstream chromatographic separation and analysis. Fortunately, a large number of scientists and researchers are working to improve the current state-of-the-art of sample preparation technologies so that it can catch up with the impressive advancements in the chromatographic instrument and mass spectrometric technology.

Classical sample preparation techniques including Solid Phase Extraction (SPE) and Liquid-Liquid Extraction (LLE) are still considered to be the most popular sample preparation techniques. Due to their relatively high consumption of toxic and hazardous organic solvent consumption, laborious and time consuming steps, inability to field deployment and many others have prompted to the invention of a number of new technologies including Solid Phase Microextraction (SPME) [4], Stir Bar Sorptive Extraction (SBSE) [5], Microextraction by Packed Sorbents (MEPS) [6], Liquid-Liquid Microextraction (LLME) [7]. Although, these techniques undoubtedly offer solutions to many problems encountered in classical SPE and LLE, they failed to deliver others such as inability to directly deal with samples with high volume of particulates, debris, blood cells, protein etc.; often require sample pretreatment steps to clean the sample matrix from matrix interferents; sample post-treatments such as solvent evaporation and sample reconstitution. The extraction sorbents are not compatible with acidic or basic sample matrices.

An ideal sample preparation technique should possess the following attributes: (1) improved sorbent coating technology that can simultaneously exploit the benefits of inorganic and organic polymer to enhance selectivity, affinity and extraction performance; (2) enhance interaction surface area for the rapid analyte-sorbent interaction, leading to shorter extraction equilibrium time; (3) field deployability, so that the entire sample preparation can be conducted in situ in the field without compromising the convenience of the analyst or data quality; (4) the ability to preconcentrate target analytes directly from the unmodified samples without any clean-up exercises; (5) resistance

to harsh chemical environments (i.e., highly acidic and basic) so that matrix pH can be adjusted to wider pH values; (6) the ability to use any organic solvent to elute the extracted analytes so that the final solution can be injected simultaneously into Gas Chromatograph (GC), High Performance Liquid Chromatograph (HPLC), and/or Capillary Electrophoresis (CE) to obtain complementary information depending on the analytical procedure; (7) equal effectiveness in field sampling and sample preparation to eliminate the burden of sample collection, transportation, storage, and sample preparation in the laboratory; and (8) ability to achieve a high preconcentration factor during the extraction so that solvent evaporation and sample reconstitution may be avoided.

In the recent years, Kabir and Furton [8,9] have managed to meet the expectations and take the sample preparation to another level with the development of Capsule Phase Microextraction (CPME). This technique has a lot of similarities with Fabric Phase Sorptive Extraction (FPSE), another very popular and green sample preparation technology invented by the same group [10,11], Stir Bar Sorptive Extraction (SBSE) [12] and Liquid Phase Microextraction (LPME) [13] as CPME is based on equilibrium driven extraction, but differs in some points that made the new technique a new generation, ideal sample preparation technique.

Design and Fabrication of Microextraction Capsules

CPME utilizes a specially designed and built device known as Microextraction Capsules (MEC). Microextraction capsules are built in different sizes: 1 cm, 2 cm and 3 cm for different volumes of sample (from 1 mL to 100 mL) and can be reused many times. Figure 1 demonstrates different sizes of microextraction capsules.

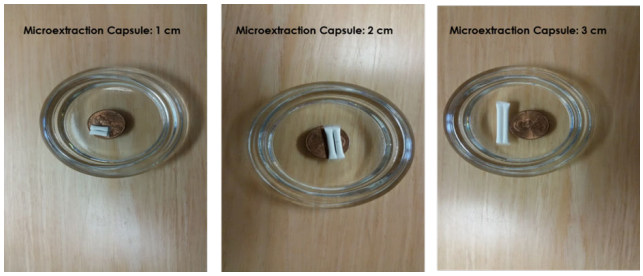

Figure 1: Microextraction capsules of different sizes.

Microextraction capsules consist of three parts: a sol-gel hybrid inorganic-organic sorbent coated fiber (usually made of cotton and a sorbent adsorbed on the fiber such as polyterahydrofuran, polyethylene glycol, polydimethylsiloxane), a cylindrical magnet and a permeable microporous membrane. Figure 2 presents the images of the building blocks used in fabricating the microextraction capsules.

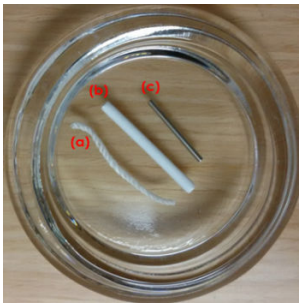

Figure 2: Building blocks of microextraction capsules: (a) sol-gel polytetrahydrofuran coated cellulose fiber segment; (b) microporous polypropylene protective filtration medium; and (c) a cylindrical bar magnet.

The polypropylene microporous membrane works as a protective sheath to minimize the sol-gel sorbent coated extracting fiber segment from potential contamination by particulates, biomasses, proteins and another matrix interferents. The microporous membrane has a porosity of 200 nm (0.2 μm), which is even finer that a typical filter with 450 nm (0.45 μm) pore size. In addition, a cylindrical bar magnet, which is encapsulated into one of the two conjoined porous tubular membranes, gives the main advantage of the extraction device by providing the ability to stir magnetically without the use of an external magnetic rod, thus reducing the time and cost of the sample preparation. Figure 3 presents the photograph of the hollow microporous membrane and the scanning electron microscopy image, revealing the surface morphology of the membrane.

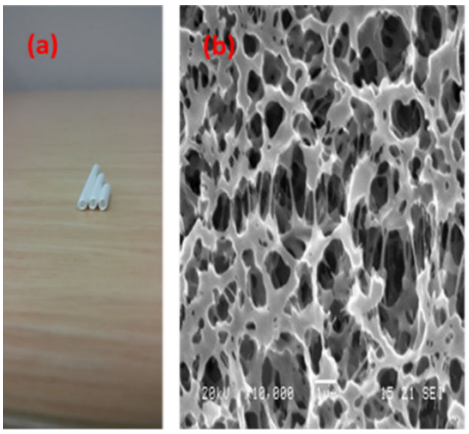

Figure 3: Microporous polypropylene tubes used in microextraction capsules: (a) image of empty tubes; (b) scanning electron microscopy image at 10,000x magnification of polypropylene tubes demonstrating micro pores of the protecting tubes.

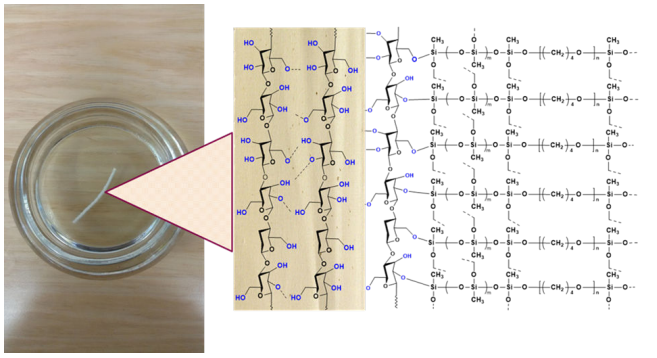

Figure 4: Sol-gel polytetrahydrofuran coated fiber segment used in microextraction capsules.

One of the most advantageous features of microextraction capsules is the sorbent coating technology. The sol-gel coating technology used to create a thin film of sponge-like hybrid inorganic-organic polymeric coating on the surface of a fiber, is indeed a highly controllable chemical coating process that substantially reduces the batch-to-batch variability and provides a pathway to load higher amounts of sorbent on the fiber surface. Due to the chemical nature of the hybrid sorbents, they are very stable in a wide range of pH and provides unprecedented solvent stability. Figure 4 demonstrates a sol-gel polyterahydrofuran coated fiber segment.

Last but not least, the permeable membrane, due to its high porosity, provides a high rate of extraction from the sample matrix to the sorbent allowing only the desired substances to be transferred. This can be very useful especially when dealing with a biological sample that contain high volume of protein precipitation, lipid, phospholipid and other cellular interferents.

With regards to analytical protocol development in CPME, there are three steps similar to the traditional SPE, but on a smaller scale. In the first step, called Activation, it is necessary to activate the sorbent material of MEC with a suitable solvent such as methanol or acetonitrile. This phase is very important in order to give the free-silanol groups an appropriate orientation to accept the upcoming sample. In the next phase that is called Loading, the sample is loaded into a vial holding the MEC. During this analyte extraction phase, interactions between the sample and the sorbent take place leading to the extraction of the target analytes from the sample to the sorbent. This process is more efficient due to the increased contact surface area between the analyte and the sorbent. In the third and final phase, called Elution, an organic solvent such as methanol or acetonitrile or mixture of them is used to elute the adsorbed analytes from the sorbent. The ability to use small volumes of the above solvents leads to very high recoveries of the determined substances. Also, it is of great importance that all these phases take place in a well–sealed vial avoiding solvent evaporation, but even more that both in the second and third phase, magnetic stirring is applied in order to increase the rate of extraction and elution respectively. Figure 5 represents the capsule phase microextraction process.

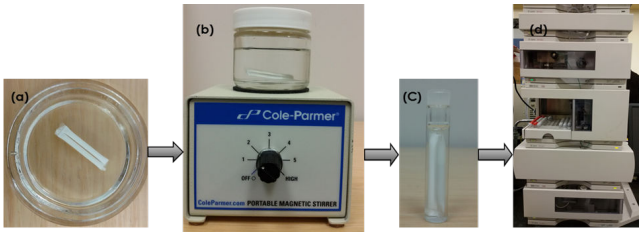

Figure 5: Capsule phase microextraction process: (a) clean microextraction capsule; (b) extraction on a battery powered magnetic stirrer; (c) back-extraction to bring extracted analytes into organic solvent; (d) chromatographic separation and analysis.

Due to the efficient integration of a filtration mechanism, stirring mechanism and the proven power of sol-gel derived advanced material systems with unique selectivity and high extraction sensitivity into a small, but innovative device, CPME opens up new opportunities in the analytical and bioanalytical sample preparation space with a wide variety of future potential applications. A large number of available sorbents including polar, medium polar, nonpolar, positive charged, negatively charged, mixed mode, and zwitterionic sorbents have made this unique sample preparation technique unparalleled to other microextraction techniques. Recent studies by the inventors CPME reveal that they can be used instantly in biological and environmental samples such as whole blood and environmental water. It is widely known that these types of samples have high volume of interferents making the sample preparation even more difficult and often requires using pretreatment techniques such as protein precipitation, centrifugation and filtration. As such, even though there are a lot of hardships in current sample preparation to overcome, CPME can be the ultimate solution to all these problems as it is capable of isolating the target analyte without any sample pretreatment exercises and provides a clean sample ready for instrumental analysis without requiring any solvent evaporation and sample reconstitution anymore.

Applications of Capsule Phase Microextraction

Due to the distinct advantages of capsule phase microextraction over classical sample preparation techniques, many academic researchers across the world are currently studying the application potential of the new technique [14,15]. As an illustration, Figure 6 demonstrates high absolute recovery values obtained for Polycyclic Aromatic Hydrocarbons (PAHs) when extracted from environmental water sample using CPME.

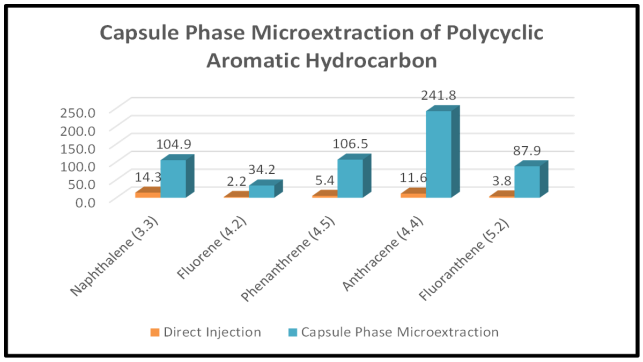

Figure 6: Chromatographic sensitivity comparison between direct injection and capsule phase microextraction followed by HPLC-UV analysis.

Conclusion

As time passes, technology evolves and new ways of addressing problems are being created. As far as analytical chemistry is concerned, there is a great hope that in the future problems related to sample preparation and the use of a suitable analytical technique will be minimized and better and faster results will be achieved. But, in the meantime, the innovation of CPME with its exquisite design and applications is only the beginning of what awaits us, and a lot of time is needed to understand what creativity and resourcefulness will continue to be the driving forces in research and development. Besides, as Peter Atkins said: "Chemistry begins in the stars. The stars are the source of the chemical elements, which are the building blocks of matter and the core of our subject". In that way, a new star "capsule phase microextraction" is born.

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