

The Large ‘Tentacles’ of Liquid-Phase Microextraction

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Sample preparation is a crucial step in the analytical process, especially when determining compounds at trace (or even subtrace) levels, since it often requires both analyte concentration and sample matrix clean-up to separate potential interfering compounds. In this sense, extraction techniques play an important role, since both concentration and clean-up operations are achieved in one single step. Among them, the traditional liquid-liquid extraction (LLE), based on the transfer of the target compounds from an aqueous sample to a water-immiscible solvent, has been widely employed. However, the large amounts of organic solvents used, usually toxic and expensive, led, in the mid-to-late 90's the appearance of the so-called liquid-phase microextraction (LPME), where not only lower amounts of organic solvents were used but also higher preconcentration factors were achieved. It could be argued that LPME is a miniaturization of the traditional LLE, in a similar way solid-phase microextraction (SPME), developed by Prof. Pawliszyn in 1990, constitutes a miniaturization of the traditional solid-phase extraction (SPE). In fact, in LPME the organic acceptor phase volume is extremely reduced up to the μL range.

It should be mentioned that, at first, LPME was not very popular due to the difficulty in handling the initially proposed approaches. It was not until 1996 when Jeannot and Cantwell, trying to emulate SPME, proposed what is known today as single drop microextraction (SDME), in which a droplet of a few microlitres of a water-immiscible organic solvent is hung from the tip of a syringe needle. As in SPME, the droplet can be directly immersed (DI) into the sample solution or suspended in the headspace (HS), so that once the extraction is accomplished the drop is retracted into the syringe needle and transferred to the analytical instrument. However, the instability of the drop often causes its loss into the sample during extraction, and also limits the volume of the extracting solvent. To solve this drawback, sheltering the extracting organic solvent into a tubular porous hollow-fiber clamped in the syringe needle was proposed, so that the fiber protected mechanically the ‘drop’. In this sense, the solvent stays into the lumen and also in the pores of the fiber, thus forming the so-called supported liquid membrane (SLM). Moreover, three- phases systems can also be found, where compounds are extracted from the aqueous solution, through an organic solvent forming the SLM, and further back-extracted into another aqueous solution, conveniently pH- adjusted, located at the lumen of the hollow-fiber. This approach, using hollow-fibers, was termed hollow-fiber liquid-phase microextraction (i.e., HF-LPME). Once at this point, it should be said that there are other membrane-based LPME approaches, such as the use of a bag-shaped membrane, a membrane replacing the septum of an injection vial agitated by orbital rotation or a stirred membrane, which are all grouped under the term of membrane-assisted liquid-phase microextraction (MALPME). However, these techniques usually suffer from higher extraction times, and often equilibrium state is not usually reached, mainly due to the low contact area between the donor and acceptor phases.

Nevertheless, the most currently popular LPME technique, due to the high enrichment factors obtained, besides its speed and easy to handle features, is that known as dispersive liquid-liquid microextraction (DLLME), proposed in 2006 by Assadi and co-workers. In its original form, it is based on a ternary component solvent system, where a

few microlitres of the water-immiscible extracting organic solvent are mixed with a water-miscible solvent, named ‘disperser solvent’. Subsequently, this extracting-disperser solvent mixture is injected into the sample rapidly, forming the ‘cloudy solution’, where the extracting solvent forms thousands of fine droplets. This makes that the contact area between the extracting solvent and the sample is extremely large, so the equilibrium state is quickly achieved. After extraction, phase separation is performed by centrifugation.

Similarly, the so-called homogeneous liquid-liquid microextraction (HLLME) is also based on a ternary solvent system, composed of the extracting and the ‘auxiliary solvent’ (miscible in both extracting and sample) and the sample, but in such amounts needed to form a homogenous mixture, which is further broken by, for example, the addition of salt, a change in the pH or the addition of an ion-pairing agent. Based on the same principle of DLLME, but avoiding the use of the disperser solvent, the use of ultrasounds has been proposed to accelerate the extraction process as a consequence of fragmentation of the extracting phase in submicron droplets and simultaneously increasing the temperature and pressure in the proximity of the cavitation collapses. This results in what is known as ultrasound-assisted emulsification-microextraction (USAEME). Recently, ultrasound-assisted dispersive liquid-liquid microextraction (USA-DLLME), i.e., DLLME followed by ultrasounds application to improve the extraction efficiency, has been also proposed. Nevertheless, in order to avoid the use of ultrasounds, which could degrade some compounds, vortex agitation has been also proposed in the so-called vortex-assisted liquid-liquid microextraction (VALLME).

On the other hand, it should be emphasized that in the last years, ionic liquids (IL), which are organic salts in the liquid state, are being widely used in LPME techniques as an alternative to conventional organic solvents. Their unique physicochemical properties, that can be read elsewhere, make them very good candidates to be used in LPME. In this sense, different IL-based LPME techniques (IL-LPME) have been proposed based in the above-mentioned ones, such as IL-SDME, IL-HF-LPME, IL-DLLME, IL-USAEME, IL-USA-DLLME and IL-VALLME. We can also find articles describing a type of IL-HLLME, that is known as in situ solvent formation microextraction (ISFME), where a water-miscible IL is solvated into the sample and then a water-soluble salt is added to form (in situ) a non-soluble IL by cation exchange.

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Nevertheless, other new approaches exploiting the properties of IL have arisen. In this sense, an approach similar to IL-DLLME, termed temperature-controlled ionic liquid dispersive liquid-liquid microextraction (TC-IL-DLLME) has been proposed. In this case the extracting solvent is dispersed by heating, and afterwards the cloudy solution is obtained by cooling. In another one, considered as a type of IL-HLLME, but termed ionic liquid cold-induced aggregation microextraction (IL-CIAME), the IL is dissolved by adding a surfactant, and the cloudy solution is obtained after cooling, as in the previous approach. In another one, named ionic liquid cold-induced aggregation dispersive liquid-liquid microextraction (IL-CIA- DLLME), which is born from the mixture of IL-CIAME and IL-DLLME, the IL is dissolved in the preheated sample by using a disperser solvent, and the cloudy solution is also obtained by cooling. Finally, it should be said that when

a high content of salt is present, the performance of these approaches decreases, as IL solubility increases. To overcome this problem, a modification of both IL-CIAME and IL-CIA-DLLME, termed ionic liquid modified cold-induced aggregation microextraction (IL-M-CIAME) and ionic liquid modified cold-induced aggregation dispersive liquid-liquid microextraction (IL-M-CIA-DLLME), respectively, have been proposed by adding a salt with the counter-ion of the IL, which reduces its solubility by means of the common-ion effect.

After reading this short editorial, showing the 'tentacles' of LPME, one should realize the great development that LPME is accomplishing in these last years to improve the performance of the analytical methods dealing with trace analysis, and thus, the author would humbly like to encourage researchers to continue working on this amazing field.