Application of new approaches to liquid-phase microextraction for the determination of emerging pollutants

Cristina Mahugo-Santana, Zoraida Sosa-Ferrera, Mª Esther Torres-Padrón, José Juan Santana-Rodríguez

Liquid-liquid extraction (LLE) has been widely used as a pre-treatment technique for separation and preconcentration of organic analytes from aqueous samples. Nevertheless, this technique has several drawbacks, mainly in the use of large volumes of solvents, making LLE an expensive, environmentally-unfriendly technique.

Miniaturized methodologies [e.g., liquid-phase microextraction (LPME)] have arisen in the search for alternatives to conventional LLE, using negligible volumes of extracting solvents and reducing the number of steps in the procedure. Developments have led to different approaches to LPME, namely single-drop microextraction (SDME), hollow-fiber LPME (HF-LPME), dispersive liquid-liquid microextraction (DLLME) and solidified floating organic drop microextraction (SFODME).

This overview focuses on the application of these microextraction techniques to the analysis of emerging pollutants.

Keywords: Dispersive liquid-liquid microextraction; Emerging pollutant; Environmental sample; Hollow-fiber liquid-phase microextraction; Liquid-liquid extraction; Liquid-phase microextraction; Pre-treatment; Single-drop microextraction; Solidified floating organic drop microextraction; Water sample

Cristina Mahugo-Santana, Zoraida Sosa-Ferrera, Mª Esther Torres-Padrón, José Juan Santana-Rodríguez*
Departamento de Química, Facultad de Ciencias del Mar, Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Spain

*Corresponding author.
Tel.: +34 928452915;
E-mail: jsantana@dqui.ulpgc.es

1. Introduction

Liquid-liquid extraction (LLE), based on the transfer of analytes from an aqueous sample to a water-immiscible solvent, is widely employed for sample preparation. Nevertheless, some shortcomings (e.g., emulsion formation and use of large sample volumes and toxic organic solvents) make LLE expensive, time-consuming and environmentally unfriendly.

Another popular sample-preparation approach is solid-phase extraction (SPE), which is based on selective retention of the target analytes in a solid sorbent that can then be eluted with an organic solvent. Several SPE materials have been developed, from the conventional alkyl-modified silica materials (C-18 non-polar phase) to the new materials based on polymer sorbents that improve the retention of polar compounds [1]. Although this technique uses much less solvent than LLE, the volume can still be considered significant. Moreover, an extra step of concentrating the extract to a small volume is needed. The demand to reduce solvent volumes and to avoid using toxic organic solvents in LLE and SPE has led to substantial efforts to adapt existing sample-preparation methods to the development of new approaches.

Miniaturization has been a key factor in the pursuit of these objectives. The introduction of solid-phase microextraction (SPME) by Pawliszyn and co-workers [2] initiated interest in microextraction techniques in analytical chemistry. With the SPME technique, target analytes are extracted from aqueous or gaseous samples onto a solid polymeric fiber [3]. This method is portable, simple to use, and relatively fast, and can be automated and coupled online to analytical instrumentation. However, the coated fibers are generally expensive and have limited lifetimes.

CLASSIFICATION OF LIQUID PHASE MICROEXTRACTION

Liquid-phase microextraction (LPME)

- Single-drop microextraction (SDME)
  - Direct inmersion (DI-SDME)
  - Headspace (HSSDME)
  - Liquid—liquid—liquid microextraction (LLLME)
  - Continuous flow microextraction (CFME)
- Hollowfiber (HFL-PME)
- Dispersive liquid—liquid microextraction (DLLME)
- Directly-suspended droplet microextraction (DSDME)
- Solid drop microextraction (SDLPME)

Figure 1. Classification of liquid-phase microextraction.

To reduce cost and to simplify the extraction procedure, new techniques have been developed, [e.g., liquid-phase microextraction (LPME), which has become an alternative miniaturized sample preparation approach]. LPME is rapid and inexpensive, and uses minimal volumes of solvent with negligible exposure to toxic organic solvents. LPME is normally performed between a small volume of a water-immiscible solvent and an aqueous phase containing the analytes of interest. The acceptor phase can be immersed directly in or suspended above the sample for headspace extraction. The volume of the receiving phase is in the µL or sub-µL range, which allows high enrichment factors. From the introduction of the first paper on LPME in 1996 [4] until now, different approaches to LPME have been developed [5]. A classification of these approaches is presented in Fig. 1.

We give an overview of the applications of these LPME approaches to the determination of emerging pollutants in this work. These compounds are not currently covered by existing water-quality regulations and are thought to be potential threats to environmental ecosystems and human health, since many of them exhibit endocrine-disrupting properties [6]. Emerging pollutants are used in large quantities in everyday life and include a diverse group of compounds [e.g., pharmaceutical compounds from different therapeutic classes, personal-care products (PCPs), flame retardants and industrial additives]. Fig. 2 shows a classification of the emerging pollutants mentioned in this overview. These contaminants do not need to persist in the environment to cause negative effects due to their continual introduction into the environment.

EMERGING POLLUTANTS

Emerging pollutants

- Pharmaceuticals
  - Analgesic and anti-inflammatory drugs
  - Antibiotics
  - Psychiatric drugs
  - Beta-blockers
  - Lipid regulators
  - Steroids and hormones
- Personal care products
  - UV filters
  - Antiseptics
  - Sintetic musk fragances
- Flame retardants
  - Polybrominated diphenyl ethers
  - Organophosphate esters
- Industrial additives
  - Pthalathe esters
  - Alkylphenols

Figure 2. Emerging pollutants.