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Rapid on-line microextraction of neutral analytes in plastic-bottled beverages through ultrasound-assisted push/pull perfusion hollow-fiber liquid–liquid–liquid microextraction ☆

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ABSTRACT

In this study we developed a rapid sample cleanup and enrichment procedure combining ultrasound-assisted push/pull perfusion technique and hollow-fiber liquid–liquid–liquid microextraction for online extraction of neutral analytes in liquid samples. To overcome the problems of long extraction times for neutral analytes and fluid loss or gain across the porous hollow fiber membrane to or from the donor phase, we used an ultrasonic probe to accelerate the mass transfer and a push/pull syringe pump as the driving source to perfuse the acceptor phase and decrease the perfusion pressure, permitting on-line coupling of hollow-fiber liquid–liquid–liquid microextraction to HPLC. We tested the extraction of three low- to transitional-molecular-weight phthalate esters as model neutral compounds from plastic-bottled waters and plastic-bottled functional beverages. Good linearity existed in the range 0.1–100 ng mL^{-1} with a precision of less than 5.8% and limits of detection in a range 0.01–0.02 ng mL^{-1}. This developed micro-extraction method allowed the sensitive, simple, and rapid determination of target phthalate esters in bottled drinks with a sampling time of just 2 min.

1. Introduction

Sample preparation is a key step and a major challenge in the development and application of any analytical method. In general, this step consists of the cleanup and preconcentration of target analytes from a sample matrix.

Although liquid–liquid extraction (LLE) is a versatile sample preparation technique for the determination of trace levels of contaminants in a sample, it can be a time-consuming, tedious, multistage operation. Over the last 10 years, the surge in interest in miniaturization in analytical chemistry has led to the development of several miniaturized approaches to LLE, with resultant savings in the consumption of solvent and sample [1–4]. Hollow-fiber liquid–liquid–liquid microextraction (HF-LLLME), a miniaturized version of LLE, is a fairly new method for sample pretreatment [5]. It employs a single porous hollow fiber (HF) made of polypropylene supporting a hydrophobic solvent (only several microliters) in the pores [a so-called supported liquid membrane (SLM)] for the extraction of target analytes [6]. The porosity of the HF increases the interfacial area between the solvent and the aqueous sample, thereby increasing the extraction efficiency [7]. The principles and the analytical applications of HF-LLLME have been described in several reviews [7–10]. The advantages of the HF-LLLME method are low cost, little solvent consumption, strong cleanup, and high enrichment factors; its main drawbacks are difficulty in online operation and the requirement for considerable time and manual operation, with few solutions having been developed until recently [8].

To date, most reports of HF-LLLME have been based on passive diffusion and the migration of analytes across the SLM; these time-consuming processes have typically taken 15–120 min [11]. In an attempt to improve the extraction kinetics and the extraction yields of HF-LLLME, pH gradients, carrier-mediated transport, and electromembrane extraction (EME) have all been examined, where extraction is promoted by a strong concentration/level gradient of protons or counter ions or by an electrical potential across the SLM driving the target analytes through the interfaces between the sample solution and the SLM and between the SLM and the acceptor solution [7]. Experimental data have confirmed that EME is much faster than conventional HF-LLLME; the extraction times required for EME are basically in the range 5–15 min [12]. In 2010, Eibak and coworkers decreased this time requirement to the level of 1 min for the extraction of antidepressants from human plasma while achieving detection limits

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in the range 0.4–2.43 ng mL^{-1} [13]. EME and the other two modified approaches mentioned above are expected to be interesting options for sample preparation when integrated with final chemical analyses. The extraction modes of these modified HF-LLLME approaches are limited, however, to basic or acidic analytes featuring ionizable functionalities [7]. Thus, the need remains to develop generic HF-LLLME methods for the analyses of neutral molecules to minimize their extraction times.

Much recent effort at modifying liquid-phase microextraction (LPME) has focused on the development of on-line methods to lessen the degree of manual handling of samples and, thereby, minimize the risk of errors, such as transfer losses or contamination of samples [14]. Several recent publications have described the on-line operation of LPME, including techniques such as on-line dispersive liquid–liquid microextraction [15] and on-line single-drop microextraction [16]. Nevertheless, despite effective cleanup and high enrichment through pretreatment, the on-line coupling of extraction devices with analytical instruments has generally remained incompatible with HF-LLLME applications [8]. The implementation of on-line HF-LLLME is currently impeded by both the thickness of the wall and the microporosity of the HFs. The on-line coupling of a regular HF-LLLME device requires two important factors to be considered: (i) the thick contact wall of the HF will potentially necessitate long extraction times, which would result in low sample throughput in on-line applications, for target analytes; (ii) and the acceptor-to-donor/donor-to-acceptor fluid pressure caused by the flowing acceptor phase stream in the HF lumen can potentially lead to fluid loss or fluid gain across the porous membrane (Fig. 1), thereby decreasing the collection of the extracted acceptor phase or diluting the extracted acceptor phase. To the best of our knowledge, no previous reports have described the successful on-line coupling of HF-LLLME to any analytical instrument over short sampling times without fluid loss or gain.

In this paper, we report the on-line coupling of ultrasound-assisted push/pull perfusion (UPP) HF-LLLME and HPLC. In this approach, we used an ultrasonic probe and a push/pull syringe pump to accelerate the mass transfer of neutral analytes and minimize fluid loss and/or fluid gain. We employed three low- to transitional-molecular-weight phthalate esters (LTPAEs) as model neutral compounds to evaluate the potential of the proposed method and optimized several parameters affecting the performance of the system. The wider application of this method would potentially expand the application of HF-LLLME as a routine technique for analyses of real samples.

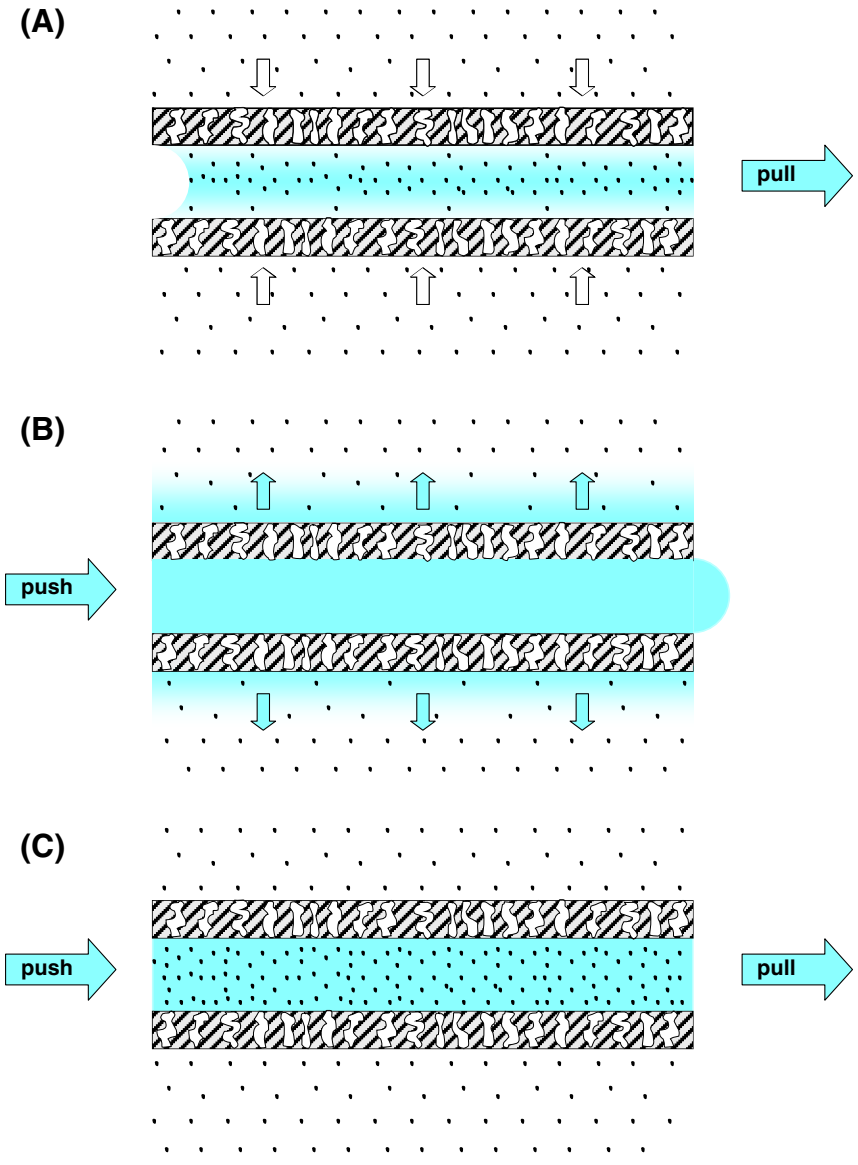

Fig. 1. Fluid leakage in HFs caused by different types of perfusion.