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Solvent-impregnated agarose gel liquid phase microextraction of polycyclic aromatic hydrocarbons in water

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ABSTRACT

A new microextraction procedure termed agarose gel liquid phase microextraction (AG-LPME) combined with gas chromatography–mass spectrometry (GC–MS) was developed for the determination of selected polycyclic aromatic hydrocarbons (PAHs) in water. The technique utilized an agarose gel disc impregnated with the acceptor phase (1-octanol). The extraction procedure was performed by allowing the solvent-impregnated agarose gel disc to tumble freely in the stirred sample solution. After extraction, the agarose gel disc was removed and subjected to centrifugation to disrupt its framework and to release the impregnated solvent, which was subsequently withdrawn and injected into the GC–MS for analysis. Under optimized extraction conditions, the new method offered high enrichment factors (89–177), trace level LODs (9–14 ng L^{-1}) and efficient extraction with good relative recoveries in the range of 93.3–108.2% for spiked drinking water samples. AG-LPME did not exhibit any problems related to solvent dissolution, and it provided high extraction efficiencies that were comparable to those of hollow fiber liquid phase microextraction (HF-LPME) and significantly higher than those of agarose film liquid phase microextraction (AF-LPME). This technique employed a microextraction format and utilized an environmentally compatible solvent holder that supported the green chemistry concept.

1. Introduction

Conventional extraction methods, such as liquid-liquid extraction (LLE) or solvent extraction, that consume large quantities of organic solvents generate environmentally hazardous waste. This approach contradicts the concept of green chemistry, which places an emphasis on chemical processes or technology that improves the environment and quality of life [1]. Microextraction techniques, such as solid phase microextraction (SPME) and liquid phase microextraction (LPME), have emerged as potential alternative green techniques to replace solid phase extraction (SPE) and LLE.

LPME has been the most versatile sample preparation technique since single drop microextraction (SDME) was first demonstrated in 1996 [2,3]. SDME promotes the reduction of hazardous solvents in the extraction and analysis of trace-level analytes from various matrices and offers superior analyte enrichment. Hollow fiber liquid phase microextraction (HF-LPME) has been developed to overcome the instability of the solvent droplet that is formed in SDME [4]. The extraction solvent or acceptor phase in HF-LPME is well-protected in the impregnated polypropylene hollow fiber. However, the solvent dissolution problems still occur, especially when extractions are conducted at high agitation speeds or with long extraction times [5,6]. The loss of extraction solvent contributes to false positive or negative results, which causes high uncertainty. The ongoing development of different types of solvent holders and interfaces has been reported to address this shortcoming. Polypropylene hollow fiber has the most commonly used interface because it has been proven to provide superior analyte enrichment, low cost extraction and effective sample cleanup [4–6]. Other solvent holders and interfaces that have been applied to a limited extent include polypropylene and polyethylene membrane bags [7,8], nylon membrane [9], PTFE polymeric membrane [10,11] and silica monolith [12]. Recently, knitting wool has been applied as a solvent holder for LPME, and the approach can withstand high agitation speeds and long extraction times without the solvent dissolution problem [13].

Solvent-impregnated resin (SIR) has been extensively applied as a sample preparation tool to extract trace metals from environmental samples [14–20]. SIR is a combination of LLE and ion exchange

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extraction [14] where the liquid ion exchanger is dissolved in solvent and immobilized within the resin to function as an extractant. The method enhances the solute extraction when the solute forms a complex with the extractant, and it eliminates the loss of extractant into the organic phase when LLE is used [21,22]. The application of SIR has been extended to the analysis of organic compounds such as organic acids [21], α-phenylglycine [23], aldehyde [22], phenol [24,25], and herbicides [26]. Various materials, namely Si-MCM-41 [18], Amberlite XAD [15,21–23,27], montmorillonite clay [16], modified PE hollow fiber membrane [17], activated carbon [19], and organogel [20] have been utilized as resins to hold the extractant. To the best of our knowledge, most of the SIR and LPME solvent holders and interfaces are synthetic polymers or thermoplastics; the economic and environmental benefits of using these materials are debated in the scientific community. Therefore, identifying an alternative material to protect the acceptor phase in LPME is important.

Agarose, a natural polymer consisting of alternating D-galactose and 3,6-anhydro-L-galactose, is extracted from seaweed [28]. It is thought to be a "green" polymer because it is biodegradable and environmentally friendly. Its chemical inertness and flexible pore size have enabled its widespread applicability. It is especially popular as a gel electrophoresis medium [28], pervaporation membrane for the dehydration of organics [29], and optical sensor supporting material [30]. Recently, agar–agar powder has been modified and employed as an adsorbent in SPE [31]. A new innovative technique termed agarose film liquid phase microextraction (AF-LPME) has also been demonstrated, in which the agarose film was employed as an interface between the donor and acceptor phases in LPME [32]. These techniques offered inexpensive and selective approaches for the enrichment of analytes and they fulfilled green chemistry requirements.

Since 1976, polycyclic aromatic hydrocarbons (PAHs) have been known mutagens or carcinogens [33]. PAHs enter the food chain through the contamination of vegetables and drinking water. SPE and LLE are frequently applied to extract PAHs from water samples, although both techniques consume large amounts of chemicals and organic solvents [34–37]. Conversely, microextraction techniques are used less frequently, most likely because they have not been recognized as standard methods of analysis by many regulatory agencies. Micro solid phase extraction (μ-SPE) involves the utilization of a porous polypropylene membrane as a filtration device to exclude interferences and to protect the sorbent [38,39]. Solid phase microextraction (SPME) employs minute amounts of sorbent that are in direct contact with the analytes during extraction [40]. Both μ-SPE and SPME permit trace analysis and have greatly reduced the consumption of organic solvents [38–40]. Ferrofluid-based LPME applies solvent that is confined within the pores of silica coated magnetic particles to extract PAHs from river water samples [41]. The technique has simplified the sample preparation procedure and can potentially be applied as an on-site extraction tool [41]. Stir bar sorptive extraction (SBSE) with a home-made portable stirrer has been demonstrated as an on-site extraction and sampling device [42]. The technique was beneficial for high sample throughput extraction with greatly improved detection limits [42]. In summary, microextraction techniques have been applied as promising alternatives to SPE and LLE, which are less congruent with green chemistry practices.

This work describes, for the first time, the feasibility of solvent-impregnated agarose gel liquid phase microextraction (AG-LPME) for the preconcentration of analytes prior to gas chromatography–mass spectrometry (GC–MS) detection. The AG-LPME approach is a combination of SIR and LPME, where the agarose gel disc functions as a three-dimensional solvent holder to protect the acceptor phase that is immobilized within its framework. In this study, the analytical performance of AG-LPME was compared to that of HF-LPME and AF-LPME in analyzing selected polycyclic aromatic hydrocarbons (PAHs) in water.

2. Experimental

2.1. Chemicals and reagents

Polycyclic aromatic hydrocarbons (PAHs) were selected as model compounds. Fluorene (FLU), phenanthrene (PHE), fluoranthene (FLA) and pyrene (PYR) were obtained from Sigma–Aldrich (St. Louis, MO, USA). Stock solutions (500 mg L^{-1}) were prepared separately by dissolving the analytes in acetonitrile (for PHE and PYR) and methanol (for FLU and FLA). Working standard solutions were prepared diluting the stock solutions with methanol, and the solutions were stored at 4 °C when not in use. 1-Octanol and absolute ethanol (analytical grade), methanol, acetonitrile and acetone (HPLC-grade) were purchased from Merck (Darmstadt, Germany). Agarose (molecular grade) was obtained from Promega (Madison, USA). Deionized water was obtained from a Milli-Q water system (Millipore, USA).

2.2. Materials

Accurel Q3/2 polypropylene hollow fiber membrane (600 μm I.D. × 200 μm wall thickness and 0.2 μm pore size) was purchased from Membrana GmbH (Wuppertal, Germany). For HF-LPME, the hollow fiber was cut into 2.2 cm lengths and sonicated in acetone for 5 min to remove impurities and then air-dried before use. A 10-μL SGE HPLC microsyringe (Melbourne, Australia) was used to introduce the acceptor phase and support the hollow fiber during extraction. A hot plate stirrer (Favorit, Malaysia) and a magnetic stir bar (12 mm × 4 mm) were used to stir the sample during extraction. For AF-LPME, a tiny glass tube (40 mm × 2 mm I.D., 1 mm wall thickness) with an agarose film attached at the lower end of the tube was used to hold the acceptor phase [34]. For AG-LPME, a similar glass tube (50 mm × 2 mm I.D., 1 mm wall thickness) was used as the agarose gel mold.

2.3. Chromatographic conditions

PAHs were analyzed using a HP 6890 Series Plus gas chromatograph (Agilent Technologies, Milan, Italy) equipped with a MSD 5973 mass spectrometer (Agilent Technologies, Milan, Italy). Helium was used as the carrier gas at a constant flowrate of 1 mL min^{-1}. Splitless injection (sample volume of 1 μL) was performed at 250 °C. The chromatographic separations of PAHs were performed on a HP5 MS column (30 m × 0.25 mm I.D., 0.25 μm film thickness) from Agilent Technologies. The oven temperature profile was programmed at 150 °C for 3 min, and then increased to 250 °C at 10 °C min^{-1}. The transfer line and the ion source temperatures were fixed at 280 °C. Electron impact mass spectra were recorded at 70 eV and the detector voltage was set at 1.0 kV. Data were collected and quantified in the selected ion monitoring (SIM) mode using the mass values corresponding to the molecular ions of the PAHs. Chromatographic data were processed using MSD Chemstation software.

2.4. Preparation of solvent impregnated agarose disc

Approximately 0.80 g agarose was accurately weighed and added to 100 mL deionized water. The mixture was brought to a boil to completely dissolve the agarose. A warm solution of the mixture was poured into a glass tube (50 mm × 2 mm I.D.) that was sealed with Parafilm at one end. The 2 mm I.D. glass tube was used to produce a low volume disc to enhance the analyte enrichment.