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Electromembrane surrounded solid phase microextraction using electrochemically synthesized nanostructured polypyrrole fiber

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ABSTRACT

Electromembrane surrounded solid phase microextraction using conductive polymers as the sorbent is carried out for the first time for extraction of two antidepressants including amitriptyline (AMI) and doxepin (DOX), as model analytes. The polypyrrole coating was prepared and utilized as both cathode and SPME sorbent. Different variables such as the conditions for preparation of polypyrrole fiber, pH of the donor and the acceptor phases, applied voltage, and extraction time were optimized. Under the optimized conditions, figures of merit of the proposed method were investigated in human whole blood and urine samples. Intra- and inter-assay precisions ranged between 3.1–7.5% and 7.6–12.3%, respectively were obtained in different extraction media. Detection limits of 0.15 and 0.05 for AMI and 0.3 and 0.1 ng mL^{-1} for DOX were achieved in the urine and blood samples, respectively. Linearity of the method was studied up to 50.0 ng mL^{-1} for both analytes and coefficients of determination better than 0.9966 were achieved. Regardless of the high sample cleanup, which makes the proposed method suitable for analysis of drugs from complicated matrices, clean chromatograms were obtained. Finally, the proposed method was applied for analysis of AMI and DOX in different real samples and reasonable data were obtained.

1. Introduction

Sample preparation is an important issue in analytical chemistry which is often a bottleneck for chemical analysis. As a consequence, a series of steps is required to remove interfering substances, preconcentrate the analyte and increase the sensitivity. Traditionally, liquid–liquid extraction (LLE) has been used for pre-treatment of biological samples, but LLE is laborious and requires environmentally toxic solvents. Due to several advantages, solid-phase extraction (SPE) has become more popular [1] compared to LLE, but it also requires an organic solvent for elution of analytes, solvent evaporation step prior to final analysis, relatively high cost of SPE cartridges and their blockage during extraction procedure. In recent years, modern trends in analytical chemistry are towards simplification, miniaturization, automation, and minimization of organic solvent used in sample preparation.

Stir-bar sorptive extraction (SBSE) [2], solid-phase microextraction (SPME) [3], and liquid phase microextraction methods (LPME) are miniaturized techniques [4], which have been developed for sample preparation. SPME and SBSE are simple and solventless methods. However, the major disadvantages of SPME are its high cost, sample carry-over, fiber fragility, and limited lifetime of the fiber [5]. SBSE needs relative long extraction (30–120 min) and desorption time, and also have carry-over problems [6]. According to the literature over different liquid phase microextraction techniques (LPME), dispersive liquid–liquid microextraction (DLLME) and hollow fiber-based liquid phase microextraction (HF-LPME) have attracted more interests among analytical research community around the world [7,8].

DLLME is a simple and fast method and provides high preconcentration factors. HF-LPME provides high preconcentration factors and produces clean extracts without any need for solvent evaporation and re-constitution as required for LLE and SPE [9]. Also, sample carry-over can be avoided in HF-LPME because the hollow fibers are inexpensive enough to be disposed after each use. Because the LPME tolerates a wide pH range, it can be used in applications, which would not be suitable for SPE or SPME.

However, these techniques have some drawbacks; DLLME is only efficient for simple matrices, so that it creates crowded chromatograms for extracts from complex matrices, especially biological fluids. This intensifies distinguish among peaks of

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interferences and analytes. Therefore, sample pretreatment is an unavoidable step for this technique. Moreover, automation of this technique is difficult. For HF-LPME, the extraction time needed is usually high and common extraction times of 30–50 min have been reported [10,11].

Recently, Pedersen-Bjergaardet et al. introduced a novel microextraction technique called electromembrane extraction (EME) [12]. In EME, the driving force for the extraction is a DC electrical potential defrayed over the supported liquid membrane (SLM) and the analytes are extracted by electrokinetic migration. Sufficient ionization of the target analytes in both the sample and the acceptor solution are therefore essential. The ionized compounds are migrated in an electrical field from the sample solution across the SLM into the aqueous phase [13–17]. The use of an electrical potential difference as the driving force reduces the extraction time. Other advantages are high sample cleanup and preconcentration factors [18,19]. There are some difficulties in coupling of EME with gas chromatography (GC) since the acceptor phase is an aqueous solution and direct injection of water to GC may cause some damages. This is while GC is faster, simpler, and less expensive than high performance liquid chromatography (HPLC) and it can easily be coupled with different types of sensitive detectors [20].

Solid phase microextraction (SPME) was originally devised by Pawliszyn et al. as a new technique in 1989 [21]. In this technique, a small amount of extraction phase coated on a solid support, utilized to extract analytes from aqueous or gaseous samples [22,23]. However, this method faces some problems in analysis of nonvolatile or ionizable species in complicated matrices due to fiber saturation with interferences. Therefore, combination of EME and SPME was introduced for the first time in 2013 by Yamini et al. and termed electromembrane surrounded solid phase microextraction (EM-SPME). The setup they used was the same as that in the EME technique, except the cathode (the electrode inserted in the lumen of hollow fiber) was substituted by a carbonaceous pencil lead fiber. By applying electrical field, the model analytes migrated from sample solution through the SLM into an aqueous phase, which was located inside the hollow fiber lumen. The analytes were afterward adsorbed on the solid sorbent, which was also the cathode. Finally, the pencil lead was directly introduced into the GC-FID injection port. Pencil lead was chosen due to its conductive nature, thermal stability, and low cost [24]. However, this fiber contains large amounts of modifiers and these interferences make crowded chromatograms at high temperatures in the GC analysis.

In the present study, EM-SPME using conductive polymers as the sorbent was carried out for the first time for analysis of two antidepressant drugs as the model analytes. Here, AMI and DOX were selected as model compounds to present the applicability of the new coating for EM-SPME and the selectivity were not the aim of this research project. Conductive polymers with conjugated double bonds have attracted much attention as advanced materials [25–31]. Polypyrrole (PPy) is one of the most studied conducting polymers owing to its simple preparation procedure, high conductivity, and relative stability. Application of electrochemically synthesized conductive polymers may increase the extraction efficiency due to its porous structure and could result in cleaner chromatograms in comparison with previous pencil lead fiber [24,32]. Also, the fragility problem which was associated with previous pencil lead is eliminated by new fiber due to deposition of the fiber coating on an unbreakable substrate. Moreover, higher voltages could be applied in EM-SPME system, leading to enhanced extraction efficiency due to the low electrical current through the extraction system, which increases the stability of PPy fiber.

2. Experimental

2.1. EM-SPME equipment

The equipment used for the extraction procedure is shown in Fig. 1. A 10 mL glass vial was used as the sample compartment. The platinum electrode used in this work, with the diameter of 0.25 mm, was obtained from Pars Pelatine (Tehran, Iran). The electrodes were coupled to a power supply model 8760T3 with a programmable voltage in the range of 0–600 V and with a current output in the range of 0–500 mA from Paya Pajoohesh Pars (Tehran, Iran). During the extraction, the EM-SPME unit was stirred with a stirring speed in the range of 0–1250 rpm by a heater-magnetic stirrer model 3001 from Heidolph (Kelheim, Germany) using a 1.5 × 0.3 cm magnetic bar.

2.2. Chemicals and materials

AMI and DOX were purchased from Razi Pharmaceutical Company (Tehran, Iran). The chemical structure and physicochemical properties of the drugs are provided in Table 1. 2-Nitrophenyl octyl ether (NPOE) and Pyrrol (Py) were obtained from Fluka (Buchs, Switzerland). Distilled Py was prepared freshly prior to the syn-

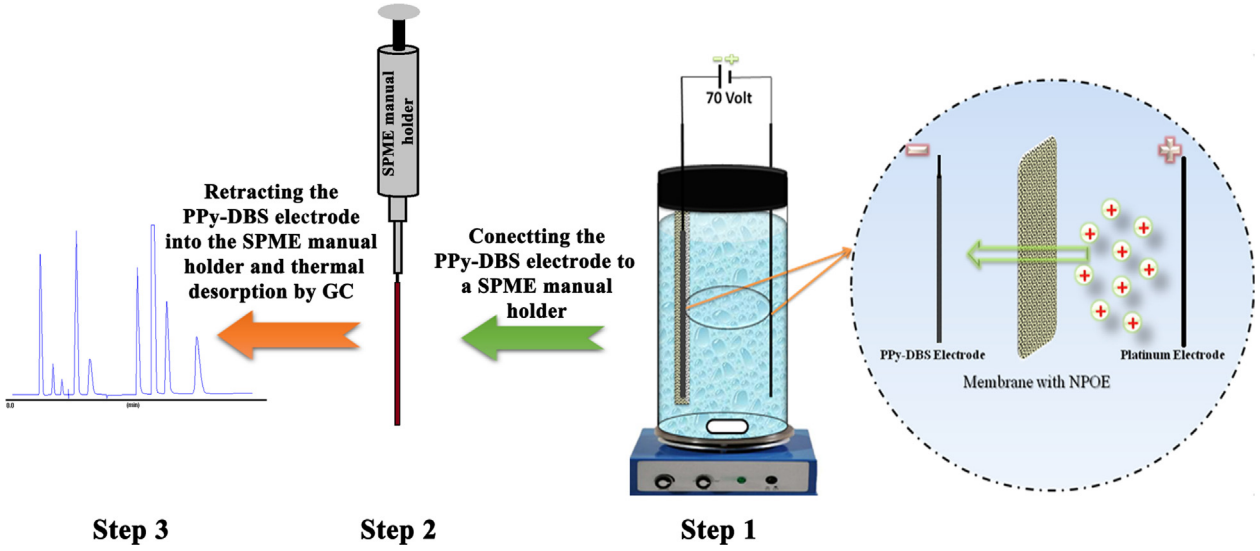

Fig. 1. Equipment used for the EM-SPME method and mechanism of transport across liquid-liquid-liquid-solid boundaries.