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Application of electro-enhanced solid phase microextraction combined with gas chromatography–mass spectrometry for the determination of tricyclic antidepressants in environmental water samples

Ruyi Xu [a], Hian Kee Lee [a,b,*]

[a] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore
[b] National University of Singapore Environmental Research Institute, 5A Engineering Drive 1, T-Lab Building #02-01, Singapore 117411, Singapore

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ABSTRACT

A fast and efficient method for the determination of tricyclic antidepressants using electro-enhanced solid phase microextraction (SPME) coupled to gas chromatography–mass spectrometry (GC–MS) has been developed. One advantage of this approach is that the mass transfer of target analytes from the sample solution to an SPME fiber can be accelerated by the electrical field, improving extraction selectivity and efficiency. In the present work, the target analytes extracted to the SPME fiber were thermally desorbed in the GC injection port after extraction. Under the optimized extraction conditions, the developed method exhibited low limits of detection (between 0.079 and 0.296 μg/L) and good linearity over the concentration range of between 1 and 500 μg/L with coefficients of determination (r^2) of between 0.993 and 0.999. The relative standard deviations were lower than 9.2% for all analytes. The proposed method was applied to extract tricyclic antidepressants in environmental water samples.

1. Introduction

Tricyclic antidepressants (TCAs) have long been used as reference for treatment of depression and psychiatric disorders like phobias and anxiety [1]. They perform as inhibitors of the reuptake of the neurotransmitter norepinephrine (as in the case of desipramine, nortriptyline and protriptyline secondary amines) or serotonin (as in the case of amitriptyline, imipramine, clomipramine and doxepine tertiary amines) in the central nervous system [2]. These drugs are used extensively especially in developed countries and can enter the aquatic environment mainly through human excretion [3]. Many TCAs cannot be completely removed or degraded during the sewage treatment process and therefore it is important to develop methods to determine their concentrations for the purpose of monitoring their presence in environmental samples [4].

Gas chromatography–mass spectrometry (GC–MS) [1,5–9], high-performance liquid chromatography (HPLC) [10–14], HPLC-tandem mass spectrometry (MS/MS) [15–17], and capillary electrophoresis (CE) [4,18–22], have been applied to the analysis of TCAs in different matrices including serum, whole blood, urine, plasma and waste water [4,6,14,15,22–26] after sample pretreatment or preconcentration, which is a crucial step to obtain good selectivity and sensitivity when determining TCAs in biological fluids or environmental samples using the techniques mentioned above. Compared to conventional techniques like solid-phase extraction (SPE) and liquid–liquid extraction (LLE), microextraction methods such as solid-phase microextraction (SPME) or liquid phase microextraction (LPME) have been favored in the last few years due to their advantages such as low or no consumption of organic solvent and speed of processing. SPME, introduced in 1990 [27], combines preconcentration and extraction in one step. It is a solvent free approach, compatible with GC–MS, since the compounds extracted to the thin polymeric layer can be thermally desorbed in the GC injection port. However, normally the whole process of SPME is relatively long, ranging from 30 min to 1 h or even several hours, much longer compared to techniques like dispersive liquid–liquid microextraction (DLLME) [6,9] or electromembrane extraction (EME) [28,29].

* Corresponding author at: Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore. Tel.: +65 65162995; fax: +65 67791691.
E-mail address: chmleehk@nus.edu.sg (H.K. Lee).

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EME is a microextraction technique based on analyte migration from a sample solution to an acceptor solution (extract) with electrical potential as the driving force. The speed of the extraction is dependent on the characteristics of the analytes and the magnitude of the electrical potential. In Davarani's work, it took 20 min to extract imipramine and clomipramine under 200 V [5]. However, 200 V is relatively large and may cause electrical accidents if not handled properly. Recently, some reports indicated that low voltage EME could also give satisfactory results [30–32]. A limitation of EME is that since the acceptor solution is aqueous (because the target analytes should be in their ionized forms in both donor and acceptor phases), only reversed phase HPLC and CE can be used for analysis. It would be advantageous if compounds could be analyzed with GC–MS after EME, and this might expand the applicability of EME. It has been reported that the application of a potential to an SPME fiber could accelerate the migration of some analytes with a charge opposite to that of the fiber, therefore enhancing extraction efficiencies and permitting the use of GC–MS as the determination technique at the same time [33]. So far, there have been a few reports on electro-enhanced (EE)-SPME [33–37].

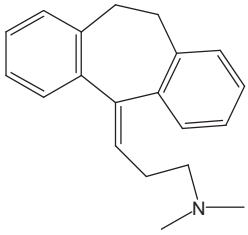
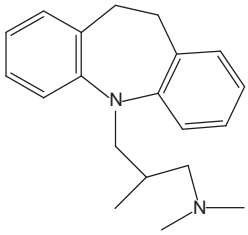
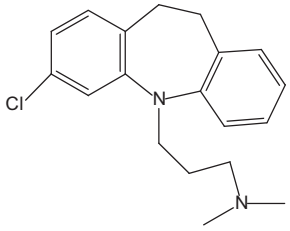
In this study, EE-SPME followed by GC–MS was applied to determine TCAs in environmental water samples. The mass transfer of target analytes from the sample solution to an SPME fiber was accelerated by the electrical field, to improve extraction selectivity and efficiency. Extraction conditions such as SPME fiber type, pH value of the sample solution, voltage applied, extraction time, stirring speed, desorption temperature were evaluated. The procedure was then tested on environmental water samples.

2. Experimental

2.1. Reagents and materials

The TCAs, trimipramine, amitriptyline hydrochloride, and clomipramine hydrochloride were purchased from Sigma–Aldrich (St. Louis, MO, USA). Their structures and characteristics are shown in Table 1. Sodium hydroxide (NaOH) was obtained from Chemicon (Temecula, CA, USA). Hydrochloric acid was bought from Merck (Darmstadt, Germany). Ultrapure water was produced from a Nanopure water purification system (Barnstead, Dubuque, IA, USA), and the magnetic stirrer plate was purchased from Heidolph (Kelheim, Germany).

Table 1
Characteristics of TCAs.

Analytes	Molecular mass	Molecular structure	pK_a
Amitriptyline	277.41		9.42 ± 0.37
Trimipramine	294.43		9.38 ± 0.28
Clomipramine	314.30		9.49 ± 0.28

2.2. Apparatus

The commercial SPME fiber holder and fibers coated with polydimethylsiloxane (PDMS, 100 μm); polydimethylsiloxane/divinylbenzene (PDMS/DVB, 65 μm); Carboxen/polydimethylsiloxane (CAR/PDMS, 85 μm); polyacrylate (PA, 85 μm); and divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50 μm) were bought from Supelco (Bellefonte, PA, USA). Prior to use, the fibers were conditioned in the GC injection port as recommended by the supplier. A voltage adaptor which was used to control the electrical field (from 3 to 15 V, direct current) and a voltmeter were bought from the local market. A platinum wire with a diameter of 0.5 mm was used as the positive electrode.

Analysis was performed with a Shimadzu (Kyoto, Japan) QP2010 Ultra GC–MS system, equipped with a Shimadzu AOC-2000 autosampler and a DB-5 MS (J&W Scientific, Folsom, CA, USA) fused silica capillary column (30 m × 0.25 mm internal diameter, 0.25 μm film thickness). Helium (purity 99.9999%) was employed as the carrier gas at a flow rate of 1.0 mL/min. The injection port temperature was set as 240 °C, and the GC–MS interface temperature was set as 250 °C. For chromatography, the GC oven was initially held at a temperature of 80 °C for 3 min, programmed to 240 °C at 30 °C/min, held for 5 min, and further programmed to 280 °C at 20 °C/min and held at the final temperature for 3 min. Samples were injected in splitless mode and sampling time was set as 3 min. The TCAs were analyzed in selective ion monitoring (SIM) mode. Based on selectivity and sensitivity concerns, the monitored ions were selected as follows: amitriptyline, *m*/*z*, 58, 202, 193; trimipramine, *m*/*z*, 58, 193, 249; clomipramine, *m*/*z*, 58, 85, 269.

2.3. Sample preparation

Standard solutions were prepared by diluting stock solutions (containing 1000 mg/L of each analyte) with methanol. Working solutions were prepared by spiking ultrapure water with the analytes at known concentrations in volumetric flasks. All the solutions were kept in the refrigerator at 4 °C before use, and working solutions were prepared daily.

Tap water was collected from our laboratory and reservoir water was collected from the MacRitchie Reservoir, Singapore. These genuine water samples were collected using pre-cleaned glass bottles and kept in the dark at 4 °C until use. No pretreatment was conducted on them.

2.4. EE-SPME procedure

Fig. 1 shows the set-up of the EE-SPME procedure. An aliquot of 10 mL aqueous sample solution (pH 4.0) was introduced into a glass vial. A platinum wire was used as the positive electrode and inserted into the sample solution. The immersed stainless needle sleeve of the SPME holder served as the negative electrode. The electrical voltage was applied using the adaptor and the extraction was carried out for 10 min, at a stirring rate of 500 rpm. After extraction, the fiber was retracted into the needle and immediately inserted into the GC injection port for thermal desorption of the analytes at 240 °C for 3 min.