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Electroenhanced solid-phase microextraction of methamphetamine with commercial fibers

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ABSTRACT

Electroenhanced solid-phase microextraction (EE-SPME) method with gas chromatographic mass spectrometric analysis was investigated for the determination of methamphetamine in urine sample with commercial fibers. In this approach, commercial SPME fibers were used in direct immersion mode with an applied potential to extract methamphetamine. EE-SPME was more effective in the extraction compared to conventional SPME (i.e. application of potential). The method was simple to use, and avoided the need for alkalization and derivatization of methamphetamine. Experimental conditions were optimized to achieve better extraction performance. Various conditions including applied potential, sample pH, extraction and desorption time were investigated. Based on the optimized conditions, EE-SPME achieved a higher enrichment factor of 159-fold than conventional SPME. The calibration plot under the best selected parameters was linear in the range of 0.5–15 ng/mL ($r = 0.9948$). The feasibility of EE-SPME was demonstrated by applying it to the analysis of human urine samples. The limit of detection of methamphetamine was 0.25 ng/mL with a satisfactory relative standard deviation of 6.12% ($n = 3$) in human urine.

1. Introduction

Methamphetamine (MA) is a central nervous system stimulant that produces euphoria, hallucinations, increased alertness and wakefulness [1]. It is among the commonly abused drugs in the US and throughout the world [2]. Unfortunately in recent times, Southeast and East Asia has appeared as a global center for methamphetamine production and trafficking [3]. Methamphetamine has been considered to be one of the most consumed illicit drugs among abusers [4]. Therefore, there is a need for rapid, reliable and sensitive detection methods for the quantification of methamphetamine which is especially of importance to law enforcement agencies.

MA exists as the ionic form (MA^+) in aqueous form, making them highly soluble and thus difficult to extract by solid phase microextraction (SPME) at low concentrations from complex samples. SPME is an established sample preparation technique that has many advantages over classic sample preparation technique because it integrates sample extraction, concentration and introduction into a single step [5]. There are three different modes of SPME – direct immersion SPME for polar analytes [6], headspace-SPME for non-polar analytes [7] and membrane protected-SPME for polar analytes from complex samples [8]. Recently, electroenhanced-SPME (EE-SPME) methods using modified fibers have been reported, for example, using pencil lead fibers [9], Nafion-coated fibers or molecularly imprinted polypyrrole/multi-walled carbon nanotubes (MWCNTs) fibers [10,11] and activated carbon fiber [12]. These methods gave better performance than other SPME modes. However, preparation of EE-SPME fibers can be too complicated and life time of the fiber is not suitable for multiple extractions.

The other commonly used extraction methods for methamphetamine are liquid–liquid–liquid microextraction) [13], solid-phase extraction [14], electromembrane extraction [15] and single drop microextraction [16]. After extraction, analyses are usually carried out by gas chromatography–mass spectrometry [12,14,17,18], liquid chromatography coupled with mass spectrometry [19,20] or ultraviolet detection [15,21,22] and capillary electrophoresis [13,23,24].

While the extraction of analytes on SPME is based on passive partitioning, an application of an electrical potential on it gives more effective extraction efficiency [9]. This is because when an electrical potential is applied on the SPME system, the charged analytes are attracted to the surface of the fiber via electrophoresis at a rate faster than passive partitioning [10].

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Our objective in the present work was to investigate EE-SPME for the determination of methamphetamine in human urine samples using commercial SPME-fibers without any complicated derivatization procedures. The technique is simple to use without any SPME fiber modification and has the potential being developed further in which battery operated devices can be realized for portable sample preparation in clinical applications. The work may be of interest to illegal-drug monitoring institutions. Several important factors influencing EE-SPME efficiency were investigated including the type of SPME fiber coating, stirring speed, extraction time and the pH of the sample solution. EE-SPME and GC–MS conditions were optimized and the procedure was applied to spiked genuine urine samples.

2. Experimental

2.1. Chemicals and materials

MA was provided by the Health Sciences Authority (HSA, Singapore). A 200 mg/mL stock solution of MA was prepared with ultrapure water to suitable concentration. All standard solutions used for SPME were prepared to the required concentration by diluting the stock solution with ultrapure water. Ultrapure water used for preparing stock solutions was generated by a Milli-Q water purification system (Millipore, Bedford, MA, USA). A commercial SPME fiber holder and 100 μm polydimethylsiloxane (PDMS), 85 μm polyacrylate (PA), 65 μm polydimethylsiloxane/divinylbenzene copolymer (PDMS/DVB) and 85 μm Carboxen/PDMS (CAR/PDMS) fibers were obtained from Supelco (Bellefonte, PA, USA). Prior to use, the fibers were conditioned in the GC injection port, in accordance with the manufacturer's recommendation. A variable voltage DC adapter was bought from a local market. Two cable wires, with a crocodile clip at each end, and a platinum wire with a diameter of 0.5 mm were fabricated in-house.

2.2. Urine samples

Urine samples were collected from a drug-free volunteer. The treated urine samples were directly spiked at various concentrations of MA and used for the experiments.

2.3. EE-SPME

A 5 mL sample solution containing methamphetamine was placed in a 10 mL sample vial with a magnetic stir bar. A platinum wire was inserted into the sample solution. Both the platinum wire and SPME fiber holder were clamped tightly as shown in Fig. 1. The platinum wire and needle of the SPME fiber holder were connected via cable wires to the DC adapter. For EE-SPME, the fiber was immersed in the sample solution. The tip of the SPME holder needle was also immersed in the sample (to a depth of ca. 0.4 cm) to complete the circuit with the platinum wire. (It should be noted that CAR is a carbon-based material and thus CAR/PDMS is also a conductive sorbent.) A negative voltage was applied to the needle during the experiments. A voltmeter was connected to the circuit to monitor the voltage during the experiments. The entire assembly was placed on a magnetic stirrer which was operated at 1000 rpm during EE-SPME. After the extraction was complete, the fiber was introduced into the GC injection port for analyte desorption at 250 °C for 3 min. The fiber was regenerated for another extraction after heating it at 250 °C in the injector port of the GC for 3 min.

A comparison was made between EE-SPME and conventional SPME. The latter was similarly set up as described above except for the electrical apparatus.

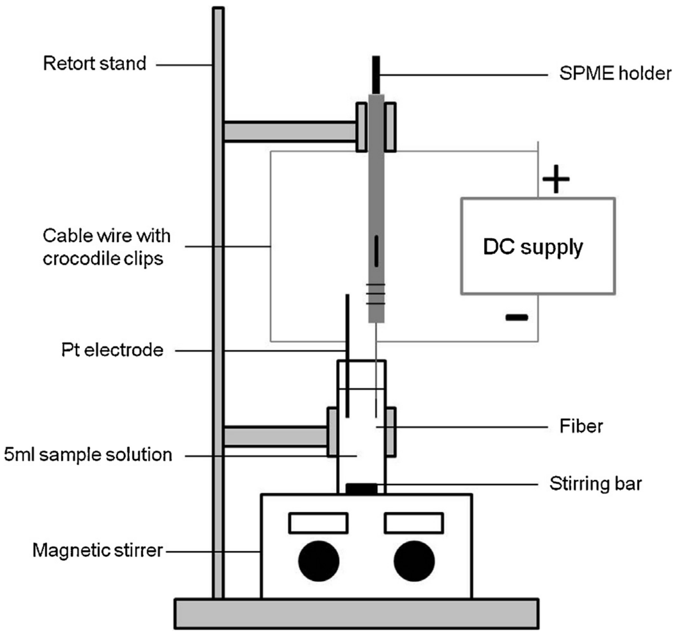

Fig. 1. Schematic of EE-SPME.

2.4. GC–MS analysis

Analysis was carried out on a Shimadzu QP2010 (Kyoto, Japan) GC–MS system with a DB-5ms fused silica capillary column (30 m × 0.25 mm I.D., film thickness 0.25 μm) (J&W Scientific, Folsom, CA, USA). Helium was employed as the carrier gas at a flow rate of 1.7 mL/min. The GC injector temperature was set at 250 °C. Prior to analysis, the fiber was conditioned on the injector port according to the manufacturer instructions. After each analysis, the fiber was conditioned on the injector port for 3 min. The GC oven temperature was programmed from 100 °C to 260 °C at 20 °C/min. The GC–MS interface was maintained at 280 °C. The solvent cut off time was 1 min. All injections were in splitless mode. Selective ion monitoring (SIM) mode was adopted for quantitative determination of MA (*m*/*z* 58, 91). The masses monitored by the detector were set to be within a retention time under of between 4 and 5 min. The identification of MA was confirmed by the mass spectral library. Fig. 2 shows a chromatogram of an extracted water sample spiked with 10 ng/mL of MA.

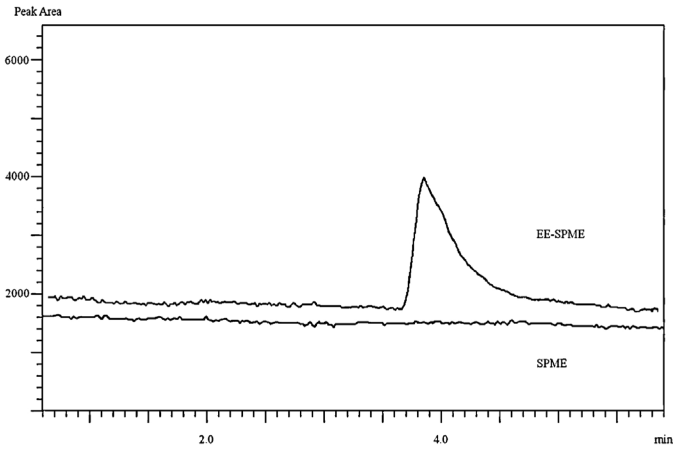

Fig. 2. GC–MS-SIM trace analysis of an extracted water sample containing MA using EE-SPME compared to SPME (analyte spiked at 10 ng/mL).