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Preparation and evaluation of solid-phase microextraction fibers based on monolithic molecularly imprinted polymers for selective extraction of diacetylmorphine and analogous compounds

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Abstract

All of the studies on solid-phase microextraction based on molecularly imprinted polymers up to now have been carried out on the synthesis of the polymer on the surface of the fiber which is brittle and the polymer coating strips during handling. The objective of this study was to develop a method for fabrication of a monolithic and robust solid-phase microextraction fiber on the basis of molecularly imprinted polymer for selective extraction of diacetylmorphine and its structural analogues followed by their GC or GC/MS analysis. A fiber was produced by copolymerization of methacrylic acid–ethylene glycol dimethacrylate imprinted with diacetylmorphine. The effective factors influencing the polymerization have been investigated and are detailed here. Also, the influences of pH, extraction time and temperature on the extraction efficiency of analytes were investigated. The prepared fiber was thermally stable up to 300 °C which has vital importance in SPME coupled with GC or GC/MS. The adsorption isotherm modeling was performed by fitting the data of studied compounds to bi-Langmuir isotherm model. The evaluated equilibrium constants for diacetylmorphine were 0.011 and 1824.72 μM^{-1}, and the number of binding sites was 170.37 and 4.64 nmol g^{-1}, respectively. This fiber was successfully used for extraction of template molecule from aqueous solution and further analysis with GC or GC/MS. The high extraction efficiency was obtained for diacetylmorphine, 6-monoacetylcodeine, and 6-monoacetylmorphine, yielding the detection limits of 300, 47, and 1 ng mL^{-1}, respectively.

Keywords: Gas chromatography; Solid-phase microextraction; Molecularly imprinted polymer; Diacetylmorphine

1. Introduction

Solid-phase micro extraction (SPME) was first introduced by Pawliszyn's group, it offers solutions to many sampling problems [1]. This is a powerful, simple, fast and solvent-free extraction and/or sampling method. It represents a further important advancement in the efficient extraction of various organic compounds at trace levels from liquid, solid, and gaseous samples. SPME has also been successfully used as a device for sampling compounds from environmental [2,3], pharmaceutical [4–6], biological [7–9], forensic [10], and food [11] samples in various analytical methods such as chromatographic analysis. Owing to the extraction mechanism, chemical and physical characteristics of fibers such as the nature of matrix, porosity and surface area have large and decisive roles in extraction efficiency, selectivity, durability, and reproducibility. To improve some of these parameters for a selective extraction, a considerable part of the research has focused on the preparation of various fibers [12–22].

Over the past 10 years considerable progress has been made on molecularly imprinted polymers (MIP). Molecular imprinting is a technique for the preparation of synthetic polymers with predetermined selectivity for a desired template. The selectivity originates from template molecules which direct the spatial orientation of the polymer building blocks (*i.e.*, the functional and cross-linking monomers) during the polymerization. The template molecules are extracted after the polymerization, leaving complementary recognition sites in the polymer network. Interest in the molecular imprinting technique has increased considerably and this is reflected in the number of excellent papers and reviews which have been published in recent years [23–25]. Among the variety of biomimetic recognition schemes utilizing supramolecular approaches, MIPs have proven their potential as synthetic sorbents in numerous applications. Their inherent

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advantages include reusability, simplicity, low cost, high affinity and selectivity for the target molecule, physical and chemical stability over a wide range of experimental conditions and solvents. The materials on the basis of MIPs have gained a widespread acceptance in many areas such as analytical chemistry [26,27]. Many publications have dealt with use of MIPs for specific purposes, *e.g.* as stationary phases for liquid chromatography [28], capillary electrochromatography [29], electrochemical sensors [30], quartz crystal microbalance [31], biomimetic sensors [32], solid-phase extraction [33–35], and membrane separation [24].

The first example of a MIP material use in SPME was reported by Mullett et al. [36]. The MIP stationary phase, imprinted for propranolol, was immobilized inside a capillary and used for a selective on-line in-tube SPME of propranolol and related β-blockers. Koster et al. [37] reported the first work dealing with the use of MIP coatings on SPME fibers. A silica SPME fiber was silanized, followed by in-situ synthesis of the MIP on the external surface of the fiber. They prepared the MIP using clenbuterol as a template and demonstrated the possibility of selective extraction of brombuterol. This fiber is brittle and the MIP coating strips during withdrawal of the fiber in the needle.

Despite emerged interests in the technique, there are no publications about SPME based on MIPs, followed by gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS).

In the present paper, a very simple approach has been developed for the fabrication of SPME fiber from diacetylmorphine-imprinted polymers which were subsequently used for extraction of diacetylmorphine and then analyzing with GC and GC/MS. This fiber is monolith and flexible enough to be placed in a home-made syringe and inserted to GC and/or GC–MS injection port. In general, adequate removal of the template molecule is difficult to achieve, which results in a slow release of the template molecule from the imprinted polymer during experiments. In this way, complete removal of template takes place by thermal desorption. So, the main goal of this study is to prepare of a new monolithic and thermally stable SPME fiber for selective extraction of diacetylmorphine from aqueous samples and then analyzing by GC/MS.

2. Experimental

2.1. Chemicals

Methacrylic acid (MAA) and ethylene glycol dimethacrylate (EDMA), acetonitrile and 2,2′-azobis-isobutyronitrile were from Merck (Darmstadt, Germany); diacetylmorphine (DAMO), morphine (MO), 6-monoacetylmorphine (6-MAMO), and 6-monoacetylcodeine (6-MACO) as hydrochloride salts were from United Nation Drug Controlled Program (Amsterdam, Netherlands) (Fig. 1).

2.2. Equipments

Monitoring of the analytes was performed using a gas chromatograph (Shimadzu 2014, Kyoto, Japan), equipped with a FID and a hydrogen generator (model OPGU 1500S, Shimadzu). A

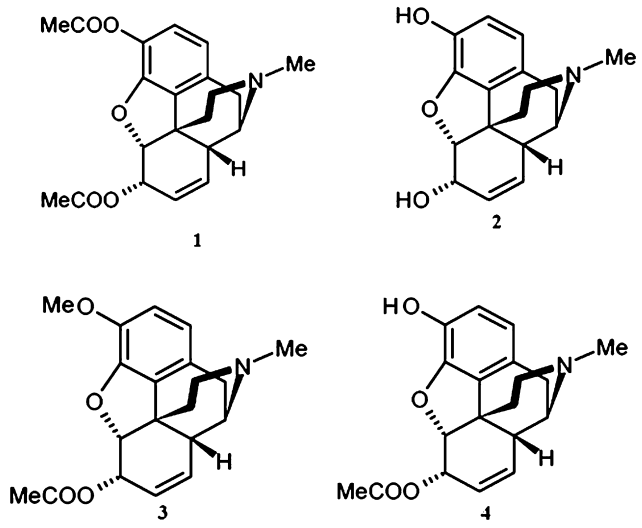

Fig. 1. Structure of (1) diacetylmorphine, (2) morphine, (3) 6-monoacetylcodeine, and (4) 6-monoacetylmorphine.

capillary column of 30 m × 0.25 mm i.d. coated with a 0.25 μm film thickness (CPB-1, Supelco, Dorset, UK) was used. The column temperature was programmed from 80 °C at 10 °C min^{-1} to 220 °C, then until 280 °C at 5 °C min^{-1} and the final temperature was held for 2 min. Analyte desorption from fiber was performed in a split/splitless mode at a temperature of 270 °C for 1 min. Detector temperature was optimized at 280 °C. The helium velocity as carrier gas was 25 cm s^{-1} and make-up gas flow was 30 mL min^{-1}.

Recognition of diacetylmorphine and its analogues was performed by Varian GC (model 3200, Palo Alto, USA) coupled to a mass spectrometer (model 2000, Varian). The chromatographic column used for GC–MS was CP-Sil8-CB, 30 m × 0.25 mm i.d. (Chrompack, Palo Alto, USA).

Pre-polymer solution was stirred in an ultrasonic bath (Grant, Cambridge, England) for 5 min, also polymerization was carried out in a water bath (Grant) at 60 °C. Thermal conditioning of the fibers was conducted in a Carbolite furnace (Bemaford, Sheffield, England).

Extraction of the analyte was performed in a vial sealed with a silicone-rubber septum cap (Supelco) and contained a Teflon stirring bar. Samples were agitated during SPME by a magnetic stirrer (Gerhardt, Konigswinter, Germany) operated at 600 rpm.

Surface characteristic studies of the prepared fibers were performed by scanning electron microscopy (LEO 440I, UK).

2.3. Polymer preparation

The MIP was prepared through the thermal radical copolymerization of MAA and EDMA in the presence of DAMO as described in literature for preparation of MIP for similar template [38]. For this purpose, 2 mmol DAMO hydrochloride and 30 mmol MAA were dissolved in 30 mL acetonitrile and were stirred in ultrasonic bath for 5 min. Then 120 mmol EDMA and 280 mg of 2,2′-azobis-isobutyronitrile were added. 1 mL of this pre-polymer solution was poured into test tube and was bub-