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Determination of non-steroidal anti-inflammatory drugs in urine by hollow-fiber liquid membrane-protected solid-phase microextraction based on sol–gel fiber coating

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ABSTRACT

A new rapid, simple and effective cleanup procedure is demonstrated for the determination of ibuprofen, naproxen and diclofenac in urine samples by using hollow-fiber liquid membrane-protected solid-phase microextraction (HFLM-SPME) based on sol–gel technique and gas chromatography–flame ionization detector (GC–FID). In this technique, a sol–gel coated fiber was protected with a length of porous polypropylene hollow fiber membrane which was filled with water-immiscible organic phase. Subsequently the whole device was immersed into urine sample for extraction. Poly(ethylene glycol) (PEG) grafted onto multi-walled carbon nanotubes (PEG-g-MWCNTs) was used as extraction phase to prepare the sol–gel SPME fiber. Important parameters influencing the extraction efficiency such as desorption temperature and time, organic solvent, extraction temperature and time, pH, stirring speed and salt effect were investigated and optimized. Under the optimal conditions, the method detection limits (S/N = 3) were in the range of 0.03–0.07 ng mL^{-1} and the limits of quantification (S/N = 10) between 0.08 and 0.15 ng mL^{-1}. Relative standard deviations for intra-day and inter-day precisions were 4.8–9.0% and 4.9–8.1%, respectively. Subsequently, the method was successfully applied to human urine fractions after administration of ibuprofen, naproxen and diclofenac.

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1. Introduction

Non-steroidal anti-inflammatory drugs (NSAIDs) are the mainstay of drug therapy for the inflammation and pain associated with various forms of arthritis. In the case of long-term NSAIDs therapy, a high incidence of severe side effects, including gastrointestinal ulcer and nephrosis, has been reported, especially in rheumatoid arthritis therapy [1–3]. Hence, it is considered that the monitoring of NSAIDs is of importance in order to improve the toxicological management of long-term NSAID therapy.

Solid-phase microextraction (SPME) technique, introduced by Pawliszyn and coworkers [4,5], is a convenient and solvent-free extraction method which combines extraction, concentration and sample introduction in one step. This technique has important advantages over conventional extraction techniques due to its ease of use, being rather rapid, easy-to-automate, portable and solvent-free. Up to now, several SPME technique coupled with gas chromatography (GC) have been developed for the analysis of NSAIDs [6–11] and high performance liquid chromatography (HPLC) [12–14].

In spite of the advantages of this technique, the lack of proper chemical bonding of the extraction phase coating and the relatively high thickness of the conventional fibers seem to be responsible for some drawbacks of the commercial fiber such as: low thermal and chemical stability, the stripping of coating and short lifetime [15].

Sol–gel chemistry can overcome this problem by providing efficient incorporation of organic component into the inorganic polymeric structure in solution under very mild thermal conditions [16]. The porous structure of the sol–gel coating offers a high surface area; allowing high extraction efficiency and the coating composition can be altered with a relative ease to give different selectivity characteristics. Strong adhesion of the coating onto the support due to chemical bonding is a very important characteristic which increases the coating stability toward organic solvents and high desorption temperatures [15].

Compared with other materials used for SPME, nanomaterials offer a significant higher surface area-to-volume ratio that promises much greater extraction capacity and efficiency. Carbon nanotubes (CNTs), with large accessible specific surface area, the ability to establish π–π interactions, excellent chemical, mechanical and thermal stability, etc., are a new type of carbon nanomaterial first found in 1991 by Iijima [17]. Carbon nanotubes as a kind of effective sorbent nanomaterials have been successfully used as the SPME fiber coating for analyzing organic compounds [18–22].

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In this work, poly(ethylene glycol) (PEG) grafted onto multi-walled carbon nanotubes (PEG-g-MWCNTs) were used as coating material. Polymer functionalization with PEG is adopted to improve the solubility of MWCNTs in organic solvents, selectivity and their viscidity, which could be good for coating.

The main drawback of silica based sorbents is the narrow range of pH stability. Under extreme pH conditions, silica-based materials become chemically unstable, and their sorptive properties may be compromised. Therefore, the development of alternative materials possessing superior pH stability and better mechanical strength should provide SPME with additional ruggedness and versatility. Recently, titania has attracted interest in separation science due to its superior pH stability and mechanical strength compared with silica. A number of reports have also recently appeared in the literature on the use of titania based hybrid organic–inorganic sol–gel sorbents in SPME [23–25].

The complexity of the sample can affect the recovery of the analytes, and also the analytical method precision, the accuracy, and the sample compatibility with a subsequent chromatographic technique [26]. Furthermore, for samples containing both non-volatile target analytes and high-molecular weight interfering compounds, the application of direct or headspace SPME may be challenging.

In 1999, Pedersen-Bjergaard and Rasmussen introduced an extraction technique that reduced solvent consumption, termed hollow-fiber liquid-phase microextraction (HF-LPME) [27]. HF-LPME combines extraction, concentration and sample clean-up in one step. The disposable nature of the hollow fiber totally eliminates the possibility of sample carryover and ensures reproducibility. In addition, the small pore size prevents large molecules and particles present in the donor solution from entering the accepting phase and, at the same time, most macromolecules do not enter the hollow fiber because they are not soluble in the organic phase present in the pores, thus yielding very clean extracts. Additional advantages of HF-LPME are its tolerance to a wide pH range, as well as its application in assays that are not suitable for silica-based SPE or SPME.

For the first time, Basheer and Lee [28] proposed a SPME procedure with the polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber protected by a polypropylene hollow fiber membrane. The method was effective for protection of SPME fiber in “dirty” samples.

In a previous study [29], a silica-based sol–gel PEG-g-MWCNTs coated fiber was found to be very effective in extracting nonpolar analytes when coupled to GC analysis. In this study, we report the preparation of the titania based hybrid organic–inorganic sol–gel sorbents from a precursor, titanium(IV) isopropoxide, and a sol–gel-active polymer (PEG-g-MWCNTs). For the first time, we introduced a new method, which combines the advantages of SPME based sol–gel, CNTs and HF-LPME for extraction and preconcentration of ibuprofen, naproxen, and diclofenac in urine samples. This new method is termed hollow-fiber liquid membrane-protected solid-phase microextraction (HFLM-SPME). In this method, a titania based sol–gel PEG-g-MWCNTs coated fiber was protected by a hollow fiber impregnated with a water-immiscible organic phase. The performance of the proposed method was evaluated by comparing with the results of DI-SPME and HF-LPME.

2. Experimental

2.1. Chemicals and materials

Trifluoroacetic acid (TFA, 99%), poly(ethylene glycol) (PEG, MW 6000), tetrahydrofuran (THF), thionyl chloride ($SOCl_2$) and sodium chloride were purchased from Merck (Darmstadt, Germany). Titanium(IV) isopropoxide was obtained from Aldrich (Sigma–Aldrich, Germany). The drugs, ibuprofen (99.9%), naproxen (99.9%), and diclofenac (99.9%), were obtained from Daana pharmaceutical Co. (Tabriz, Iran). These drugs were provided in powder form. The MWCNTs (outer diameter 10–20 nm, length range of 5–15 μm, purity >95%, specific surface area >40–300 $m^2\ g^{-1}$) were purchased from Shenzhen Nanotech Port (Shenzhen, China). Hydrochloric acid (37% (w/w), Merck, Darmstadt, Germany) was used for modification of sample pH.

Methanol, 2-octanone and toluene with Suprasolv quality were obtained from Merck (Darmstadt, Germany). 1-Octanol was purchased from Fluka (Buchs, Switzerland). The porous membrane used to support the organic phase and for protecting the sol–gel fiber was an accurel Q 3/2 polypropylene hollow fiber membrane (Membrana, Wuppertal, Germany). The wall thickness of the fiber was 200 μm, the inner diameter was 600 μm, and the pore size was 0.2 μm.

2.2. Instrumentation

A Chrompack CP9001 gas chromatography system equipped with a split/splitless injector and flame ionization detector (FID) was employed for the SPME-GC experiments. Helium (99.999%, Sabalan Co., Tehran, Iran) was employed as carrier gas and its flow rate was adjusted to 1 mL min^{-1}. The separation was performed with a CP-Sil 24CB (50% phenyl, 50% dimethylsiloxane) capillary column, WCOT Fused silica, 30 m × 0.32 mm ID with 0.25 μm stationary film thickness (Chrompack, Middelburg, The Netherlands). The column temperature was programmed as follows: initial oven temperature 80 °C for 3 min, increasing to 260 °C at 20 °C min^{-1} then holding for 10 min. The optimum desorption temperature was selected as 280 °C and optimum desorption time was 5 min. The detector temperature was held at 300 °C.

The surface characteristics of the created sol–gel PEG-g-MWCNTs coating were studied by scanning electron microscopy (SEM) (LEO, model 1450VP, Germany).

A VELP Scientifica heating magnetic stirrer, model ARE (Milano, Italy) was employed for stirring and heating samples during the extraction. To mix various solution ingredients, a ultrasonic bath (Branson 1510, Branson Ultrasonics Co., Danbury, CT), was employed at a frequency of 42 kHz.

2.3. Fiber preparation

The titania based sol–gel PEG-g-MWCNTs coated fiber was prepared using the exact same procedure used for the sol–gel silica based PEG-g-MWCNTs coating [29]. However, instead of using methyltrimethoxysilane, titanium(IV) isopropoxide was used as the sol–gel precursor. Before being used, the MWCNT-g-PEG sol–gel fiber was conditioned at the GC injection port under helium gas, at 100 °C for 30 min, then 200 °C for 1 h, and finally 300 °C for 1 h.

2.4. Sample preparation

Stock standard solutions of ibuprofen, naproxen and diclofenac (100 mg L^{-1}) were prepared by dissolving proper amounts of each drug in methanol and stored in the dark at 4 °C. The urine samples were collected from drug-free healthy volunteers. When HFLM-SPME or HF-LPME was applied, do not require any further pre-treatment steps. But for DI-SPME, urine samples were filtered through a 0.22 μm membrane (Millipore) and diluted 10 times with deionized water.

The urine samples were stored at −20 °C prior to use. Spiked urine samples with ibuprofen, naproxen and diclofenac were prepared from the stock solutions freshly prior to analysis. When

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