

# A novel hollow-fibre microporous membrane liquid–liquid extraction for determination of free 4-isobutylacetophenone concentration at ultra trace level in environmental aqueous samples

Saioa Zorita<sup>\*</sup>, Thær Barri, Lennart Mathiasson

*Division of Analytical Chemistry, University of Lund, PO Box 124, SE-22100 Lund, Sweden*

Received 13 March 2007; received in revised form 23 April 2007; accepted 2 May 2007

Available online 16 May 2007

## Abstract

In this study, a method was developed for determination of the free concentration of 4-isobutylacetophenone, a toxic degradation product of ibuprofen, in river and sewage water samples from Sweden. Sample preparation and analysis were performed by a hollow-fibre microporous membrane liquid–liquid extraction (HF-MMLLE) set-up and gas chromatography–mass spectrometry (GC–MS), respectively. In this novel approach, only the liquid in the membrane pores is utilised for non-depleting extraction. Several parameters were studied, including: type of organic solvent, sample pH, and salt and humic acid content. The optimised method allowed the determination of the analyte at the  $\text{ng L}^{-1}$  level in river and sewage water. A linear plot gave a correlation coefficient better than 0.992 and resulted in a limit of detection of 7 and 14  $\text{ng L}^{-1}$  for river and sewage water, respectively. The enrichment factor was over 2000 in the fibre and over 300 after dilution. The repeatability and reproducibility were better than 5% and 10%, respectively. For the first time, 4-isobutylacetophenone was found at free concentrations of 40  $\text{ng L}^{-1}$  or below in sewage waters, while it could not be quantified in a river downstream from a municipal sewage treatment plant.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Hollow-fibre microporous membrane liquid–liquid extraction; 4-Isobutylacetophenone; Sewage water; Free dissolved concentration

## 1. Introduction

During the last years, an increased concern about the effects of pharmaceuticals on the environment has been raised in the scientific community [1–5]. Many studies have accordingly been performed to study different aspects as occurrence, fate and toxicology of diverse drug families in water. One of the most studied pharmaceutical groups has been nonsteroidal anti-inflammatory drugs (NSAIDs), particularly ibuprofen. This compound is highly consumed worldwide [1] and therefore, it has been one of the most detected pharmaceuticals in the environment, with concentrations up to micrograms per litre, together with clofibrac acid and diclofenac [6]. In the environment, the major degradation products of ibuprofen are the same as in human body metabolism, namely 2-hydroxyibuprofen and carboxyibuprofen [7–9]. Furthermore, 13 ibuprofen degradation products have

been identified in oxidation and photodegradation studies [10]. At least two of these have shown to be toxic, one of them being 4-isobutylacetophenone (4-IBAP). The effects that this compound causes in the central nervous system are well known [11–14]. To our knowledge, no data is available about the presence of 4-IBAP in environmental waters, *e.g.* in sewage or river water.

Generally, solid-phase extraction (SPE) has been used for sample preparation of environmental aqueous samples containing different pharmaceuticals [15–18] since it is a relatively robust technique offering low limit of detection (LOD) in the low  $\text{ng L}^{-1}$  range, using chromatographic techniques for the final analysis. However, this common technique is time consuming, because clean-up is often required. The demand to reduce the amount of organic solvents used in SPE has led to the use of other solvent-free techniques, such as solid-phase microextraction (SPME). In some few occasions, SPME has been applied for drug analysis [19–21]. Nevertheless, the LODs obtained combining this technique with chromatography are often somewhat high for analysis of pharmaceuticals in water, which are often present in the low  $\text{ng L}^{-1}$  level [3]. For instance, in the analysis

<sup>\*</sup> Corresponding author. Tel.: +46 46 222 0369; fax: +46 46 222 4544.  
E-mail address: [saioa.zorita@analykem.lu.se](mailto:saioa.zorita@analykem.lu.se) (S. Zorita).

of ibuprofen by SPME [19,20], with a derivatization step and analysis by GC–MS, the obtained LOD was above  $100 \text{ ng L}^{-1}$ . However, the LOD obtained by SPME was recently improved with values below  $15 \text{ ng L}^{-1}$  for some NSAIDs in Milli-Q water [21], which is of course a non-complex matrix compared to the environmental samples containing, *e.g.* humic substances.

Membrane-based extraction techniques, such as: supported liquid membrane (SLM) extraction or microporous membrane liquid–liquid extraction (MMLLE), are attractive alternatives to SPE or SPME. SLM is a three-phase extraction system with an organic phase immobilised in a porous membrane separating two aqueous phases. MMLLE is a two-phase membrane extraction technique with one aqueous donor phase (sample) and another organic acceptor phase separated by a microporous membrane, where the same organic liquid is immobilised in membrane pores. SLM is mainly used for compounds that are easily protonated and often have low  $\log K_{ow}$  [22–24], while MMLLE is preferably used for neutral and/or more hydrophobic organic compounds [25,26]. The main advantages of membrane-based extraction techniques, such as SLM or MMLLE, are high analyte capacity (collection in a liquid instead of using adsorption), very low organic solvent consumption, easy handling, and low analysis costs.

There are some published papers on the use of SLM [22,27] or MMLLE [28] for determination of drugs, such as ibuprofen, diclofenac, carbamazepine, clofibrac acid and ethinylestradiol in environmental aqueous samples. In these three membrane-related studies, the LODs for the different pharmaceuticals were equal to or below  $20 \text{ ng L}^{-1}$  with a squared correlation coefficient of the methodology's linearity better than 0.995 and RSD values varying from 3.5 to 32%.

In this work, a new, simple and precise extraction technique, based on hollow-fibre microporous membrane liquid–liquid extraction (HF-MMLLE) is reported. Traditionally, the acceptor phase comprises the organic phase in the pores as well as in the lumen inside the hollow fibre. The novelty of the extraction procedure employed in this study has been to use only the organic solvent immobilised in the pores of a hollow fibre as the acceptor phase. This set-up has been used to extract the toxic degradation product, 4-IBAP, from environmental samples, such as river and sewage waters, followed by final analysis with GC–MS.

## 2. Experimental

### 2.1. Reagents and standards

The standard of 4-isobutylacetophenone (4-IBAP) was purchased from Mikromol (Luckenwalde, Germany). 4-Butylacetophenone, used as internal standard (IS), was from Sigma–Aldrich (Steinheim, Germany). Hexane and toluene were purchased from Fluka (Buch, Switzerland) and Riedel-de Haën (Seelze, Germany), respectively, while 2-heptanone and 1-octanol were obtained from Sigma–Aldrich. All solvents were puriss. p.a. grade. Sodium chloride (NaCl) and sodium bicarbonate were obtained from Fluka, sodium hydroxide from Scharlau (Barcelona, Spain), humic acids (HAs, 35% TOC) from Sigma, and sodium carbonate anhydrous, tri-sodium

phosphate dodecahydrate, di-sodium hydrogen phosphate and sodium dihydrogen phosphate were all from Merck (Darmstadt, Germany). Ultrapure reagent water purified by a Milli-Q gradient system (Millipore, Bedford, MA, USA) was used throughout the experiments. The Q3/2 Accurel PP polypropylene hollow-fibre membranes (200  $\mu\text{m}$  wall thickness, 600  $\mu\text{m}$  inner diameter, 0.2  $\mu\text{m}$  pore size) were obtained from Membrana (Wuppertal, Germany).

Standard stock solutions of 4-IBAP and IS were prepared in hexane at  $500 \mu\text{g mL}^{-1}$ . Working solutions were prepared by appropriate dilution in hexane (for GC calibration) or a mixture of hexane:acetone (1:50, for sample spiking) and stored at  $-20^\circ\text{C}$ .

### 2.2. Sample collection

River water was collected on 18th of July 2006 at Höje River downstream the municipal sewage treatment plant of the city of Lund, Sweden. Sewage water was collected from three different points of the sewage system of the city of Kristianstad, Sweden. One of the sampling points was nearby the hospital (H samples, 11th of October 2006), the second point was downstream hospital (DH, 27–28th of June 2006) and the third one (Ö, 11th of October 2006 and 18th of January 2007) in an area with dwelling houses, schools and apartments. DH water was used for the validation of the method. The samples were kept in the dark at  $4^\circ\text{C}$  until analysis, which was performed within a week, except for DH samples, which were frozen until analysis. No filtration or any further treatment was applied in any of the samples before extraction.

### 2.3. Hollow-fibre microporous membrane liquid–liquid extraction (HF-MMLLE)

Hollow fibres were cut into pieces of 1-cm length with a porous volume of  $\sim 3.3 \mu\text{L}$  (porosity of  $\sim 66\%$ ). The fibres were cleaned with acetone by sonication and then dried. The cleaned 1-cm long fibre was completely inserted into a 25- $\mu\text{L}$  3025RN Kloehe HPLC syringe plunger (Las Vegas, NE, USA). After the fibre was impregnated with the organic phase (2-heptanone) for around 30 s, it was dipped into reagent water and then placed into the aqueous sample (500 mL) for extraction as illustrated in Fig. 1. In the optimised method, the sample containing the

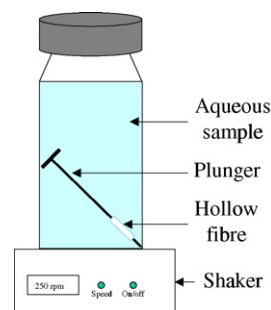


Fig. 1. Extraction set-up HF-MMLLE with a 1-cm long fibre, inserted into a syringe plunger.

Download English Version:

<https://daneshyari.com/en/article/1207008>

Download Persian Version:

<https://daneshyari.com/article/1207008>

[Daneshyari.com](https://daneshyari.com)