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Short communication

# Microextraction of non-steroidal anti-inflammatory drugs from waste water samples by rotating-disk sorptive extraction



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## ABSTRACT

In this study, six non-steroidal anti-inflammatory drugs (NSAIDs) were extracted from water samples using the rotating-disk sorptive extraction (RDSE) technique. The extraction disk device contains a central cavity that allows for the incorporation of a powdered sorbent phase (Oasis™ HLB). The analytes were extracted from water and pre-concentrated on the sorbent to reach the extraction equilibrium, and then they were desorbed with solvent, derivatized and determined by gas chromatography–mass spectrometry (GC–MS). The variables for the extraction were studied using high performance liquid chromatography with a diode array detector (HPLC–DAD) to avoid the derivatization step, and the optimum values were as follows: 60 mg of Oasis™ HLB, a rotation velocity of 3000 rpm, a pH of 2, a sample volume of 50 mL, and an extraction time of approximately 90–100 min. The recoveries ranged from 71 to 104%, with relative standard deviations (RSD) between 2 and 8%. The detection limits ranged from 0.001 to 0.033  $\mu\text{g L}^{-1}$ .

The described method was applied to the analysis of influents and effluents from wastewater treatment plants (WWTP) in Santiago, Chile. The concentrations of the detected drugs ranged from 1.5 to 13.4  $\mu\text{g L}^{-1}$  and from 1.0 to 3.2  $\mu\text{g L}^{-1}$  in the influents and effluents, respectively. The samples were extracted by solid phase extraction (SPE). No significant differences were observed in the determined concentrations for most of the NSAIDs, indicating that RDSE is an alternative method for the preparation of water samples.

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## 1. Introduction

Over the past two decades, persistent organic pollutants and heavy metals were the primary focus of environmental monitoring. Consequently, the decontamination policies applied by industrialized nations have resulted in drastic reductions of their environmental concentrations.

Today, the “emerging” or “new” unregulated contaminants have become an environmental concern. These compounds are mainly derived from products used in large quantities in everyday life, such as pharmaceuticals for human use, veterinary products, personal care products, industrial plasticizers and additives [1,2]. Emerging pollutants do not need to be persistent in the environment to cause negative effects because their high transformation and removal rates can be compensated by their continuous introduction into the environment [1].

Regarding pharmaceuticals, the primary pollution sources are through human and animal excretion in their native form or as metabolites, as well as through the disposal of unused or expired products. Unfortunately, the current processes used in WWTP are inefficient for the removal of these products [3]. Particularly, NSAIDs are commonly used in human and animal health care, and consequently, they are among the most frequently detected drugs in the environment. Due to their hydrophilicity and stability, NSAIDs can remain in the aqueous phase and are frequently detected in surface waters. According to the literature, these compounds have been detected at concentrations ranging from  $\text{ngL}^{-1}$  to  $\mu\text{gL}^{-1}$ . In addition to the presence of NSAIDs in rivers and seawater, recent studies have shown that they can even enter (at  $\text{ngL}^{-1}$ ) drinking water sources from groundwater [3]. Concentrations of up to 1.5  $\mu\text{g L}^{-1}$  for naproxen and 85  $\mu\text{g L}^{-1}$  for ibuprofen were determined in WWTP effluents [4]. Some WWTP have detected diclofenac with a low removal efficiency (between 15 and 69%), as reported by several researchers [5–8].

Recently, efforts have been directed to performing risk assessments of pharmaceuticals present in the environment and determining the effects they may cause to living beings. Previous

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studies suggest the need for future regulations for the disposal of these compounds. Some drugs are being considered by the United States Environmental Protection Agency (USEPA) as potential candidates to be included in the list of priority organic pollutants in drinking water, such as diclofenac [9].

Despite their considerable variations in structure, NSAIDs share a common mechanism, acting as antipyretics, anti-inflammatories and analgesics to relieve swelling and pain. After administration, these compounds are metabolized and excreted as a mixture of the parent compound and metabolites [10–12].

The compounds investigated in this study correspond to six NSAIDs, which are considered emerging contaminants: ibuprofen, naproxen, ketoprofen, diclofenac, acetylsalicylic acid and mefenamic acid. These drugs are derivatives of aromatic carboxylic acids, with dissociation constants ( $pK_a$ ) ranging from 3 to 5. According to their  $\log K_{ow}$  values (between 3 and 5), all of these compounds, except acetylsalicylic acid ( $\log K_{ow}=1.2$ ), are non-polar, even though they are relatively soluble in water [13–18]. The low value for the Henry's law constant indicates that the compounds are non-volatile and should remain in the aqueous phase [19].

Modern sample preparation trends promote efficiency and green technology [20]. Solid phase microextraction (SPME) [21] is a solvent-free technique that uses fused silica fibers coated with a polymeric adsorbent. This method has allowed for the development of new extraction techniques that improve the extraction efficiency by increasing the volume of the polymeric phase and the surface area to volume ratio. In this regard, new sorption techniques have been described, including stir bar sorptive extraction (SBSE) [22], silicone rod extraction (PDMS-rod extraction) [23], microextraction with a thin sheet of PDMS (thin film PDMS) [24,25] and RDSE [26,27]. The advantage of these techniques is that they reduce the amount of solvent used and are rapid as well as efficient. In a recent review [28] a critical comparison among extraction techniques reported for the analysis of synthetic pyrethroids in water has been carried out, in which the merits of the modern extraction techniques are clearly highlighted.

The RDSE technology has been applied for the extraction/preconcentration of various emerging pollutants from water samples [26,27,29–31] by using polydimethylsiloxane (PDMS) as the sorbent phase. Other phases, such as C18 [32] and Oasis™ HLB [33], have also been used in RDSE to extract hexachlorobenzene from water and florfenicol from porcine plasma, respectively.

SPE has been the most used technique for the extraction of NSAIDs in water [3,34] using Oasis™ HLB as the solid phase. This extraction technique minimizes the use of solvents in comparison to the traditional liquid–liquid extraction, and by using large sample volumes (100–1000 mL), high preconcentration factors can be achieved (200–2000). SBSE [35] and mixed matrix membrane (MMM) [36] have also been used as media for the extraction of NSAIDs from water, reaching limits of detection ranging from 1 to 1.7  $\mu\text{g L}^{-1}$  and from 0.16 to 0.22  $\mu\text{g L}^{-1}$ , respectively. The SBSE recoveries were relatively low because the sorptive phases (PDMS and polyurethane) have not the optimum polarity for this type of analytes. In MMM, a phase of C18 was used, and the results were comparable to the SPE method using the same sorbent [36].

In this study, the extraction of NSAIDs from aqueous samples was optimized by using a RDSE technique in which a reusable disk with a central cavity that allows for the incorporation of the Oasis™ HLB sorbent phase was used [33]. After extraction, the analytes were desorbed with a solvent and determined by HPLC-DAD only for optimization of preconcentration variables. For the analysis of real water samples, the analytes were derivatized and determined by GC-MS to increase the selectivity and sensitivity of the measurement. The method was applied to the determination

of NSAIDs in waste water samples and compared with its homolog SPE as a sample preparation technique.

## 2. Experimental

### 2.1. Reagents

Water from a Millipore Milli-Q Plus water system (Billerica, MA) was used throughout the experiment. All non-steroidal anti-inflammatory drugs (ketoprofen, ibuprofen, naproxen, diclofenac, acetylsalicylic acid and mefenamic acid) and surrogate standards (fenprop and meclofenamic acid) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). The internal standard (hexachlorobenzene) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). The standard stock solution of the analytes (50  $\text{mg L}^{-1}$ ) and the surrogate standard (20  $\text{mg L}^{-1}$ ) were prepared separately in methanol (GC-MS/pesticide analysis grade, Fisher Scientific, Fair Lawn, NJ, USA) and the internal standard solution (20  $\text{mg L}^{-1}$ ) was prepared in ethyl acetate from Merck (Darmstadt, Germany). The pH was adjusted with 37% p.a. hydrochloric acid (0.1  $\text{mol L}^{-1}$ ) and p.a. sodium hydroxide (0.1  $\text{mol L}^{-1}$ ) from Merck.

Nitrogen and helium with a purity of  $\geq 99.999\%$  were purchased from Linde (Santiago, Chile) and were used in the final extract evaporation and as the chromatographic carrier gas, respectively. Acetone, acetonitrile (HPLC grade, 99.8% purity), potassium dihydrogen phosphate (99.5% purity) and sodium chloride (99.5% purity) were all purchased from Merck. N-tert-butyl dimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) was provided by Sigma Aldrich and used as a derivatizing agent. The Oasis™ HLB extraction cartridges were obtained from Waters Corporation (Milford, MA, USA).

### 2.2. Instruments

An HPLC System equipped with a Waters 1525 binary pump, a Waters 2998 diode array detector (DAD) and a C18 HPLC column (250  $\text{mm} \times 4.6 \text{ mm} \times 5 \mu\text{m}$ , Atlantis) was used. A 20  $\mu\text{L}$  aliquot of the methanol extract was injected into the HPLC system with the mobile phase acetonitrile: 5  $\text{mmol L}^{-1}$  potassium dihydrogen phosphate (pH 4.5) (1:1 v/v) under isocratic conditions at a flow rate of 1  $\text{mL min}^{-1}$ . The chromatographic run required a total of 25 min.

A Thermo Scientific Focus gas chromatograph (Milan, Italy) coupled to a Thermo Fisher Scientific ISQ mass-selective detector (Austin, TX, USA) was used for the final determinations in the analysis of real samples. The fused silica capillary column used was a Restek RTX-5MS (Bellefonte, PA, USA) (30  $\text{m} \times 0.25 \text{ mm id}$ ; 0.25  $\mu\text{m}$  film thickness) coated with 5% phenyl–95% methylpolysiloxane. Two microliters of the derivatized sample extract was injected into the gas chromatograph using the splitless mode. The injector temperature was 250  $^{\circ}\text{C}$ . The initial oven temperature schedule was 100  $^{\circ}\text{C}$ , which was maintained for 1 min followed by heating to 280  $^{\circ}\text{C}$  at a rate of 50  $^{\circ}\text{C min}^{-1}$ . The chromatographic run required a total of 39 min with a solvent delay of 14 min, a transfer line temperature of 250  $^{\circ}\text{C}$ , an ionization source temperature of 200  $^{\circ}\text{C}$ , and a carrier gas flow rate of 1  $\text{mL min}^{-1}$ . A dwell time of 0.1 s was employed for each  $m/z$ . The ions used in the selective ion monitoring (SIM) mode for the quantification and confirmation of the compounds are shown in Table 1.

The beaker containing the sample and the rotating disk was placed on a MMS-3000 Boeco magnetic stirrer (Hamburg, Germany). The pH values were determined with a WTW Model pMX 3000 pH meter (USA). A KMC-1300V vortex mixer (Vision Scientific Co., Ltd., Korea) and an analog heatblock evaporator (VWR, USA) were employed during the extraction process.

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