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 μg 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 μg L^{-1} and from 1.0 to 3.2 μg 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.

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 ngL^{-1} to μgL^{-1}. In addition to the presence of NSAIDs in rivers and seawater, recent studies have shown that they can even enter (at ngL^{-1}) drinking water sources from groundwater [3]. Concentrations of up to 1.5 μg L^{-1} for naproxen and 85 μg 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

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. This drugs are derivatives of aromatic carboxylic acids, with dissociation constants (pKa) ranging from 3 to 5. According 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 μg L^{-1} and from 0.16 to 0.22 μg 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 (fenoprop 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 mg L^{-1}) and the surrogate standard (20 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 mg L^{-1}) was prepared in ethyl acetate from Merck (Darmstadt, Germany). The pH was adjusted with 37% p.a. hydrochloric acid (0.1 L^{-1}) and p.a. sodium hydroxide (0.1 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-butyldimethylsilyl-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 mm × 4.6 mm × 5 μm, Atlantis) was used. A 20 μL aliquot of the methanol extract was injected into the HPLC system with the mobile phase acetonitrile: 5 mmol L^{-1} potassium dihydrogen phosphate (pH 4.5) (1:1 v/v) under isocratic conditions at a flow rate of 1 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 m × 0.25 mm id; 0.25 μm 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 °C. The initial oven temperature schedule was 100 °C, which was maintained for 1 min followed by heating to 280 °C at a rate of 50 °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 °C, an ionization source temperature of 200 °C, and a carrier gas flow rate of 1 mL min^{-1}. A dwell time of 0.1 s was employed for each $m z^{-1}$. 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.

Table 1
Retention times and quantification and qualifier ions ($m\,z^{-1}$) selected for each analyte.

Analyte	Retention time (t_R)	$m\,z^{-1}$	
		Quantification ion	Qualifier ion
Hexachlorobenzene (IE)	19.21	284	286
Acetylsalicylic acid	20.57	195	237
Ibuprofen	21.78	263	264
Salicylic acid	24.00	309	310
Fenoprop (SE)	26.07	253	281, 327
Naproxen	30.35	287	288
Ketoprofen	32.64	311	312
Mefenamic acid	32.75	224	298
Diclofenac	34.28	352	354
Meclofenamic acid (SE)	35.57	243	244, 352

*Salicylic acid was included because it is one of the main metabolites of acetylsalicylic acid.
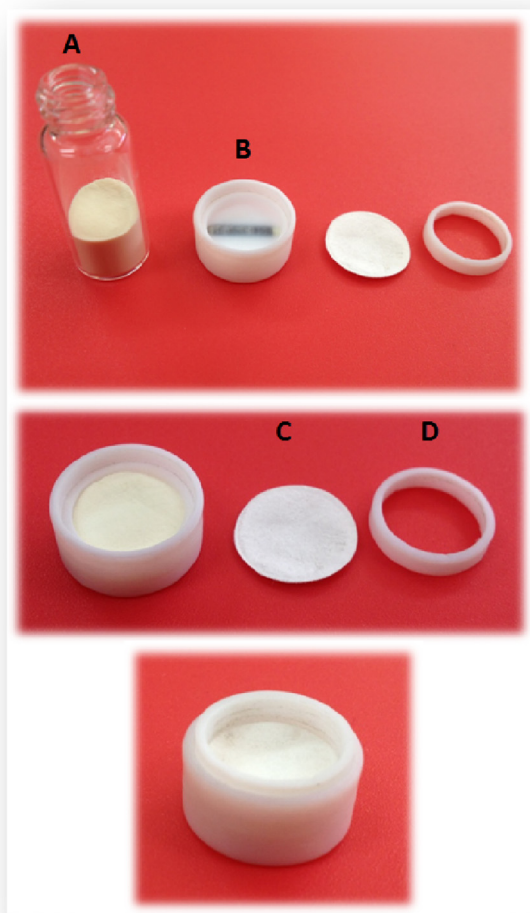

Fig. 1. Rotating disk with Oasis™ HLB sorbent used in this study. (A) powder phase; (B) rotating disk; (C) fiberglass filter; and (D) Teflon ring.

2.3. Preparation of the rotating disks

The extraction device used (Fig. 1) included a Teflon disk (1.5 cm diameter) containing an embedded miniature magnetic stirring bar (Teflon-coated Micro Stir bar from VWR International).

The disk has a 0.44 cm³ cavity on one of its surfaces, in which 60 mg of the Oasis™ HLB sorbent was loaded. The cavity was covered with a fiberglass filter (1.4 cm diameter, 3 μm mean pore size) and sealed with a Teflon ring. Before extraction, the Oasis™ HLB phase was conditioned with ethyl acetate, methanol and Milli-Q water for five minutes each.

2.4. Analytical procedure

A 50 mL aliquot of standard or the water sample was poured into a beaker and adjusted to pH 2.0 with 0.1 M HCl. A 500 μL aliquot of 2 mgL^{-1} surrogate standard (containing both fenoprop and meclofenamic acid) was added to the real samples.

The rotating disk containing the Oasis™ HLB phase was placed inside the beaker, and the disk rotated at 3000 rpm for 90–100 min at room temperature. After extraction, the disk was placed into a 10 mL beaker containing 5 mL methanol as a desorbing solvent and was stirred for 10 min at 2000 rpm twice. The methanol extract containing the concentrated analyte was then evaporated under a N$_2$ stream to dry. The extract was re-dissolved into 500 μL of methanol or ethyl acetate, depending on whether the determination method was HPLC or GC, respectively. The methanol extract was directly injected into the HPLC. The ethyl acetate extract was derivatized for 60 min at 60 °C with the addition of 20 μL of MTBSTFA. Prior to the injection into the GC–MS, 20 μL of 20 mg L^{-1} HCB was added as an internal standard.

2.5. Real sample analysis

To evaluate the applicability of the method in a real sample, samples from two WWTPs from Santiago, Chile, were analyzed using the proposed method. These samples were collected from the influent of each plant and then stored in polypropylene bottles and frozen until analysis. Next, 200 mL samples were collected and adjusted to a pH of 2. The sample was then divided into four 50 mL aliquots. Two aliquots were spiked with a concentration of 20 μg L^{-1} NSAIDs using a multi-standard. Subrogate standards were added to all aliquots. A sample of effluent from a treatment plant was obtained and analyzed in the same manner as the samples of the influent.

Some of the samples were also analyzed by SPE following the protocol described by Santos et al. [37] and compared with the results obtained by RDSE.

3. Results and discussion

3.1. Study of variables

Different chemical and preconcentration factors were evaluated to obtain the highest extraction efficiency of the drugs investigated. Optimization studies were conducted using only ketoprofen, naproxen, diclofenac and ibuprofen as model compounds. HPLC-DAD was the selected technique in the study of the variables because it was not necessary to perform the derivatization step. In addition, the variables were studied in deionized water spiked with a known concentration of NSAIDs; consequently, the selectivity of the technique was able to assess the behavior of each variable.

The effect of pH on the analytical signal of NSAIDs was studied between pH 2–10. The pH of the sample affects both the dissociation of the analytes (pKa=4–5) and the protonation of the lactam moiety of the sorption polymer (pKa 7.4 approx.) [38]. Fig. 2 shows the sorbent phase at pH values lower and higher than the pKa of the lactam moiety. Fig. 3 conveys that NSAIDs can be extracted
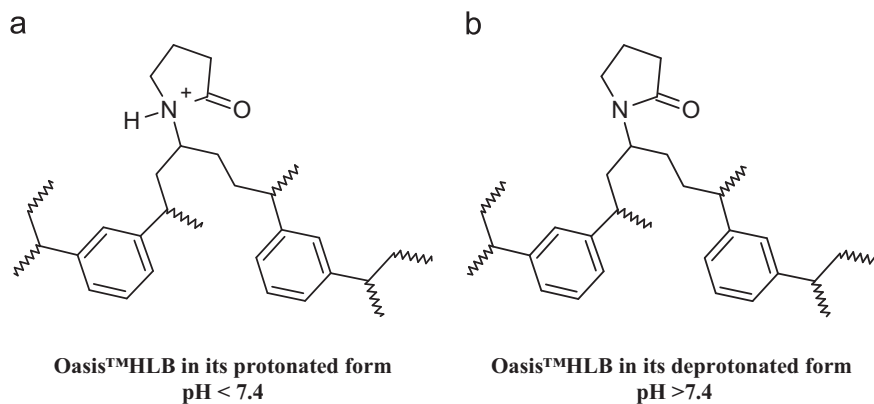
a

b

Oasis™HLB in its protonated form
pH < 7.4

Oasis™HLB in its deprotonated form
pH >7.4

Fig. 2. Chemical modification of the structure of the Oasis™ HLB polymer according to pH.
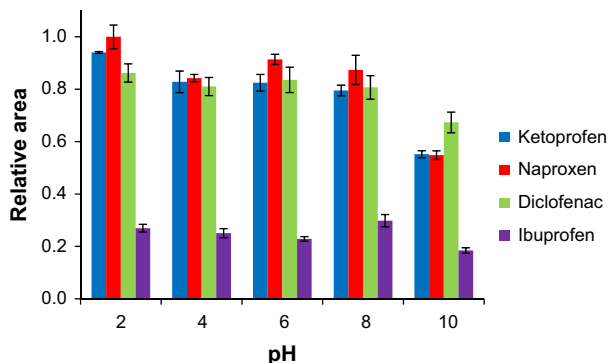

Fig. 3. Effect of pH on the extraction of NSAIDs.

into the Oasis™ HLB within a pH range of 2–10; however, at a pH of 2, extraction is favored for most of the compounds, and whenever the pH is higher than 8, the extraction efficiency decreased. At a pH lower than the pKa of NSAIDs, these compounds are sorbed into Oasis™ HLB by π–π stacking and hydrogen bonding between the H of the carboxylic acid and the C$=$O of the lactam. At a pH higher than the pKa of NSAIDs but lower than the lactam pKa, the H of the carboxylic acid is lost and these compounds should be sorbed by ionic interaction between the carboxylate of the analytes and the cation centered on the nitrogen of the lactam group as well as by π–π stacking. However, a disfavored sorption at a pH over 8 occurs because the only interaction between the analyte and the sorbent is though π–π stacking.

Matrix modifiers are usually tested in microextraction techniques because they can enhance the extraction efficiency of a given analyte, depending on the polarity. For semi-polar and polar analytes, the presence of salt, through the salting-out effect, increases the extraction, making the analyte insoluble in water and increasing its affinity for the organic phase [39]. In contrast, for apolar analytes (log $K_{ow} > 3.5$), the addition of salt reduces the extraction efficiency [40]. In the present case, salt was studied in the interval of 0–15% w/v, and the highest extraction efficiency was obtained in the absence of salt (see Supplementary material, Fig. S1). Most likely, the increase in the viscosity of the sample with the addition of salt decreased the analyte mass transfer and slowed the extraction.

Methanol is a commonly used organic modifier, particularly for the extraction of apolar analytes (with a log - $K_{ow} > 5.0$), because it prevents the adsorption of these analytes on the walls of the vial [40,41]. In the current case, the analytes have log K_{ow} values between 3 and 5; subsequently, it was observed that as the percentage of methanol in the extraction solution increased in the interval 0–15% v/v, the NSAIDs exhibited very similar responses (see Supplementary material, Fig. S2). Therefore, further studies were performed without methanol.

It is know that an increase in extraction temperature results in a higher rate of transfer of the analyte from the water to the solid phase [29,31]. In the present case, increasing temperature in the interval 20–50 °C resulted in similar sensitivity of the method (see Supplementary material, Fig. S3). Temperatures higher than 50 °C were discarded because vapor bubbles that formed on the phase surface prevented mass transfer of the analytes. In addition, over this temperature filter paper of the extraction device deteriorates causing leakage of phase. Therefore, room temperature was selected as optimum for further studies.

Another important hydrodynamic factor of RDSE is the rotation velocity of the disk. Efficient stirring of the sample in contact with the extraction phase is necessary to achieve the partition equilibrium as quickly as possible because the mass transfer of the analyte through the boundary layer that contacts the surface of the phase in microextraction techniques is the rate-determining step for its extraction. Consequently, in this study, this factor was studied between 200 and 3000 rpm. The dependence of the extraction efficiency on this factor was linear, and 3000 rpm was selected as the optimum value (see supplementary material, Fig. S4). At this rotation velocity, the Reynolds number (Re) is approximately 16,500, indicating that under this condition, the hydrodynamic extraction into the rotating disk occurs through turbulent flow.

The extraction time for each analyte was determined under the selected experimental conditions for a 50 mL sample. The samples were extracted by RDSE at various times ranging from 5 to 180 min and the extraction profile was then obtained. Fig. 4 shows the extraction profile for ketoprofeno and ibuprofeno as representative analytes. Diclofenac and naproxen profiles are not shown because their behavior is very similar to ketoprofen. The extraction time affects the amount of analyte concentrated in the Oasis™ HLB phase, as shown in Fig. 4. The extraction yield increases with the extraction time until equilibrium is reached after approximately 90–100 min. The recoveries were higher than 80% under these conditions, except for that of ibuprofen, which was approximately 60%.

It has been previously observed [30] that the extraction time is directly related to the sample volume. In this case, for sample volumes of 100 mL with constant analyte concentrations in the solution, it was observed that equilibrium was not attained within the range studied, although the preconcentration factor increased for the same extraction time. In this context, if more sensitivity is desired, the sample volume can be increased.

Once the compounds are extracted into Oasis™ HLB, it is necessary to find a solvent that allows for the rapid desorption of the analytes with a small volume. Fig. 5 shows the various conditions in which the desorption of the extracted analytes was assessed, which consists of the use of various solvents in one and two stages of desorption with different stirring times at 2000 rpm. Higher rotation velocities were not considered because the vortex formed under this condition impedes desorption of the analytes from the sorbent. As shown in Fig. 5 in the case of desorption with methanol, two successive desorptions of 5 min are more effective than one desorption of 10 min. This is the why all of the following desorption procedures were performed in two steps. During the first desorption step, methanol most likely dissolved traces of water that remained in the disk cavity after extraction, and in the second desorption step, the solvent acted with more power in the desorption of the analytes.
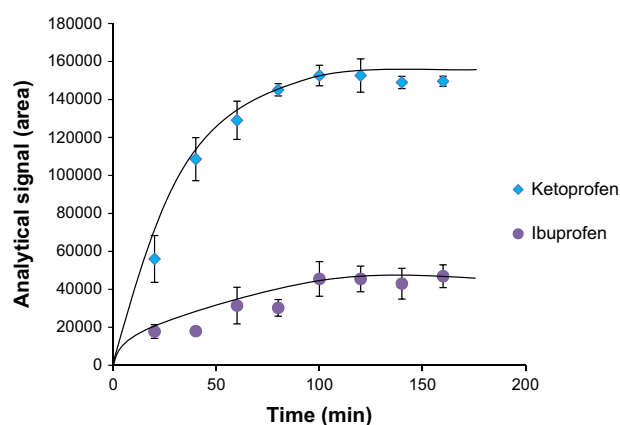

Fig. 4. Extraction profile of ketoprofen and ibuprofen as representatives for a 50 mL sample volume.
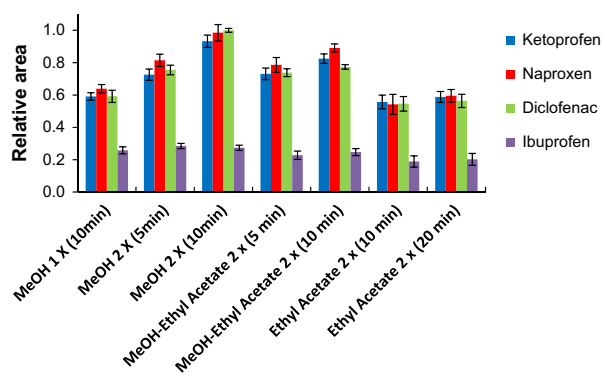

Fig. 5. Different desorptions of NSAIDs from the sorbent Oasis™ HLB.

3.2. Analytical features of the method

The analytical features of the method together with the analysis of real samples were performed using GC–MS in SIM mode to increase the sensitivity and selectivity of the determination. Chromatographic and derivatization conditions were selected with consideration of previous studies [14,42–44]. The analytical curve for each analyte was constructed using concentrations of the standards ranging from 0.005 to 2 mg L^{-1}, which are 100 times lower if the preconcentration factor implicit in the method is considered. In addition of the four NSAIDs considered in the optimization studies, two other anti-inflammatory drugs were included in the following experiments: acetylsalicylic acid and mefenamic acid, as these compounds are also widely used and most likely appear in real samples.

Table 2 shows the correlation between the analyte concentrations and the signal obtained from the GC–MS, together with the detection limit, precision and recovery of the method.

The detection limits of the method were determined by following the 3-σ criteria, using 10 sample aliquots at concentrations of 0.05 μgL^{-1}, and they were sufficiently low (between 0.001 and 0.033 μg L^{-1}) for the determination of these compounds in water.

The reproducibility and recovery were determined using different extraction disks ($n=10$) with NSAID sample concentrations of 5 μg L^{-1} in a drinking water sample. Recovery values ranging between 71–104% were obtained with relative standard deviations (RSD) ranging from 2 to 8%. The precision was also determined by the sequential use of the same extraction disk (containing the same sorbent phase) for various aliquots of the same sample at 5 μg L^{-1} ($n=5$). The RSD under these conditions were between 6 and 13%, clearly indicating that the sorbent Oasis™ HLB could be re-used five times. A higher number of adsorption–elution cycles gave rise to RSD over 18%.

3.3. Real sample analysis

The optimized and validated method was applied to real water samples obtained from the influents of two waste water treatment plants in Santiago, Chile (WWTP1-I and WWTP2-I) and from the effluent of one of the plants (WWTP1-E). It was possible to quantify the six studied drugs (Table 3) with subrogate standards, as stated above. Fig. 6 shows the SIM mode chromatogram of the sample under study from WWTP1-I.

In Table 3, NSAIDs are quantified in the effluent of the treatment plant, but the concentrations decrease between 15–80%. However, NSAID compounds are reaching natural waters. Similar values were observed in countries such as Canada, USA, Italy, Spain, Germany, China, Japan and Brazil [3].

The results obtained from the proposed method were compared with their counterparts obtained by solid phase extraction (SPE) with Oasis™ HLB cartridges, following the protocol described by Santos et al. [37], which is the only extraction method reported for these analytes using this sorbent. The

Table 2
Analytical features of the method.

Analyte	Linearity (r)	Slope (μg L^{-1})$^{-1}$	Intercept	LOD (μg L^{-1})	LOQ (μg L^{-1})	Recovery (% $n=10$)	Precision (% RSD $n=10$)
Acetylsalicylic acid	0.9975	5.3581	-0.0102	0.001	0.032	90	6
Ibuprofen	0.9902	4.2971	-0.2033	0.002	0.007	87	8
Naproxen	0.9950	6.4208	-0.2047	0.007	0.024	94	4
Ketoprofen	0.9935	2.7374	-0.1762	0.011	0.036	104	4
Mefenamic acid	0.9943	5.6816	-0.1863	0.006	0.019	99	2
Diclofenac	0.9907	0.2117	-0.0098	0.033	0.109	71	2

Table 3
Concentrations of NSAIDs determined in real samples using RDSE and SPE.

Analyte	RDSE			SPE	
	WWTP1-I Concentration ($\mu g\ L^{-1}$)	WWTP2-I Concentration ($\mu g\ L^{-1}$)	WWTP1-E Concentration ($\mu g\ L^{-1}$)	WWTP1-I Concentration ($\mu g\ L^{-1}$)	WWTP1-E Concentration ($\mu g\ L^{-1}$)
Ibuprofen	2.1 ± 0.3	6.7 ± 0.5	1.43 ± 0.05	3.0 ± 0.5	1.8 ± 0.1
Acetylsalicylic acid[a]	2.8 ± 0.5	11.4 ± 0.4	1.0 ± 0.1	2.5 ± 0.5	0.8 ± 0.2
Naproxen	3.9 ± 0.3	4.7 ± 0.3	1.44 ± 0.07	3.5 ± 0.2	1.05 ± 0.02
Ketoprofen	13.4 ± 0.6	5.2 ± 0.6	2.3 ± 0.4	12.3 ± 0.9	2.7 ± 0.1
Mefenamic acid	8.4 ± 0.5	2.3 ± 0.5	2.0 ± 0.3	6.3 ± 0.2	1.2 ± 0.1
Diclofenac	1.5 ± 0.1	2.8 ± 0.7	1.3 ± 0.4	1.3 ± 0.1	1.1 ± 0.2

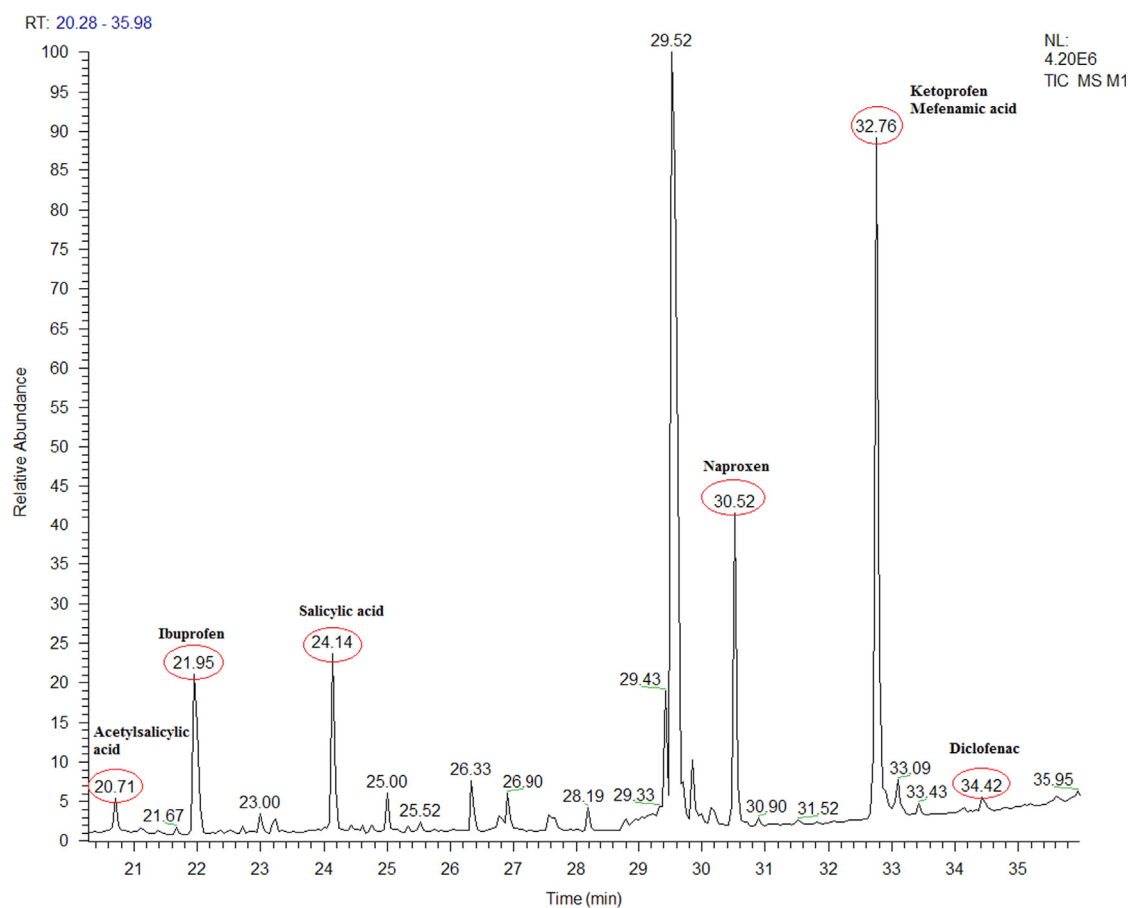[a] Determined as the sum of acetylsalicylic acid and salicylic acid.

Fig. 6. GC–MS signal (TIC) in SIM mode of a real water sample from the influent of WWTP1.

extraction of analytes was performed in samples (WWTP1-I and WWTP1-E), and the obtained results are shown in Table 3. When comparing the results obtained by RDSE and SPE, no significant differences ($p < 0.05$) were observed in most of the cases (two samples t-test, equal variances). A comparison between RDSE and its SPE counterpart indicates that RDSE is a simpler technique that does not require the use of vacuum pumps nor successive clean-up steps (with methanol and n-hexane). In addition, in the disk configuration, the sorbent can be used at least five times. However, the main disadvantage of RDSE is that the time involved in the extraction is longer than that of SPE (90–100 min vs 45 min approx.).

Comparison with other modern extraction methods such as SBSE [35] and MMM [36] is not proper because these extraction techniques use other sorbent for this analytes different to Oasis™ HLB. Despite that, the LOD in the present method was lower than those observed for SBSE and MMM, and the time involved in sample preparation, in this case, is similar to the expended in MMM, considering conditioning of the extraction device, however is significantly lower than in SBSE (4–6 h).

4. Conclusion

The determination of NSAIDs in water samples using RDSE containing Oasis™ HLB as a sorbent phase was feasible because the method presented extraction efficiencies between 71 and 104% as recovery, with RSD less than 8%.

Similar concentrations were found when the proposed method and that based on SPE using Oasis™ HLB were applied to real samples, indicating that RDSE is a reliable alternative as sample preparation method. RDSE is a simple technique and in the disk configuration the sorbent can be used five times, assuring a good level of recovery and precision. The primary disadvantage of the present method is the relatively long extraction processing time compared to the SPE methodologies. However, when RDSE is compared with SBSE [35], the extraction time was considerably shorter, recoveries were higher and the LODs were lower.

The six NSAIDs were determined in both the influent and effluent of WWTPs in Santiago, Chile, suggesting that these pollutants are reaching natural waters in similar concentrations to those observed in other countries.

Acknowledgments

Appendix A. Supporting material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.06.003.

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