S. Afr. J. Chem., 2014, **67**, 143–150,
<http://journals.sabinet.co.za/sajchem/>.

Determination of Triclosan and Ketoprofen in River Water and Wastewater by Solid Phase Extraction and High Performance Liquid Chromatography

Lawrence M. Madikizela,[a,b,*] Sindisiwe F. Muthwa[a] and Luke Chimuka[b]

[a]*Department of Chemistry, Durban University of Technology, P.O. Box 1334, Durban, 4000, South Africa.*

[b]*School of Chemistry, University of Witwatersrand, Private Bag X3, Johannesburg, 2050, South Africa.*

Received 7 November 2013, revised 17 September 2014, accepted 17 September 2014.

ABSTRACT

This paper describes a simple, sensitive and rapid method for the determination of triclosan and ketoprofen in wastewater influent, effluent and river water. The method involves solid phase extraction (SPE) of target compounds using Oasis HLB sorbent. Several extraction parameters such as sample pH, sample volume, SPE cartridge and SPE elution solvent were optimized. The pH of the collected samples was adjusted to 5.5, and then 100 mL of the sample was loaded into an Oasis HLB cartridge. Methanol was used to elute the retained compounds. The eluted compounds were analyzed using reversed-phase high performance liquid chromatography with photo diode array detection (HPLC-PDA). The method was validated by spiking ultra-pure water and wastewater with different concentrations of both compounds ranging from 5 μg L^{-1} to 1000 μg L^{-1}. Recoveries were in the range of 73 % to 104 %, and % RSD ranged from 8 % to 15 %. The method gave good detection limits of 0.01 and 0.08 μg L^{-1} for triclosan and ketoprofen, respectively. Traces of both compounds were detected in all wastewater (influent and effluent) samples at a range of 1.2 to 9.0 μg L^{-1} and in some river water samples.

KEYWORDS

Solid phase extraction, high performance liquid chromatography, wastewater treatment plants, triclosan, ketoprofen.

1. Introduction

The development of suitable quantitative methods for the assessment of environmental pollutants is ongoing. Increasing focus is directed to the analysis of water pollutants. Water pollutants such as triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol) and ketoprofen (2,3-benzoyl phenyl-propionic acid) (structures shown in Fig. 1) are among the environmental pollutants that are often detected in water.[1–4] Triclosan is a lipophilic compound that is used as an antibacterial agent in a number of household products such as toothpaste, liquid soap, sponge, plastic cutting boards, etc.[5] Ketoprofen is one of the most widely used acidic pharmaceutical compounds that belongs to the class of non-steroidal anti-inflammatory drugs. It is used as an analgesic in humans and animals.[6]

Both triclosan and ketoprofen have been detected in river water,[7] wastewater influent[7–9] and effluent.[7–9] Triclosan was even detected in human milk.[5] Triclosan inhibits the enoyl-acyl carrier protein reductase enzyme that is responsible for bacterial lipid biosynthesis. Triclosan is known to be toxic to aquatic organisms such as fish, *Daphnia magna* and algae at μg L^{-1} levels.[5] The toxicity of triclosan to humans is low, but it is known as a precursor for the formation of toxic dioxins. Various chlorinated dioxins are formed due to the exposure of triclosan to sunlight and ultraviolet-visible light.[10]

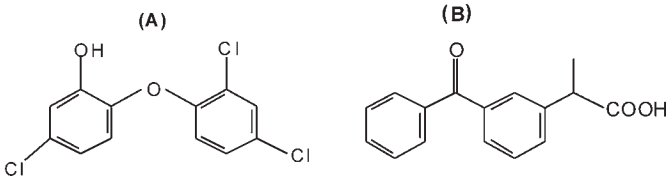

Figure 1 Structure of triclosan (**A**) and ketoprofen (**B**).

* To whom correspondence should be addressed. E-mail: lawrencem2@dut.ac.za

There are no reports found on the toxicity of ketoprofen to aquatic organisms. Presence of these compounds in the aquatic environment can be due to direct disposal to aquatic systems, water run-off from landfill sites and incomplete removal during wastewater treatment.

Chromatographic methods of analysis have been developed for the determination of these compounds in the aquatic systems. Both gas and high performance liquid chromatographic procedures have been reported in the literature.[5–11] When using gas chromatography (GC) for the analysis, derivatization is required to convert the compounds into more volatile forms. Derivatization can lead to the formation of unwanted products and can be time-consuming. High performance liquid chromatography (HPLC) is therefore a preferred technique for non-volatile compounds.

Sample preparation is one of the most important steps when addressing the issue of organic pollutants in the environment. Therefore considerable amount of time has been spent by several researchers in finding a suitable sample preparation technique for the extraction of organics from water samples. Different studies on the analysis of triclosan and ketoprofen[7–9] using solid phase extraction have been reported in foreign countries. However no published reports have been found for the simultaneous determination of these two well-known pollutants using SPE-HPLC-PDA in South African wastewater systems. The aim of this work was to determine a suitable analysis method that is simple, sensitive, accurate, rapid and affordable for the simultaneous quantification of both lipophilic (triclosan) and hydrophilic (ketoprofen) compounds in water. The proposed method involves

sample pre-treatment using a solid phase extraction technique and quantitation by HPLC with photo diode array detection. The proposed method was applied for the trace determination of both triclosan and ketoprofen in river water and water from a wastewater treatment plant (WWTP).

2. Experimental

2.1. Chemicals, Reagents and Equipment

Ketoprofen (98 %), Triclosan (97 %), HPLC-grade methanol (≥99.9 %) and HPLC-grade ethyl acetate (≥99.7 %) were purchased from Sigma-Aldrich (Steinheim, Germany). HPLC-grade acetonitrile (≥99.9 %) and glacial acetic acid (100 %) were purchased from Merck (Darmstadt, Germany). Sodium hydroxide (≥98 %) and formic acid (approx. 98 %) were purchased from Fluka (Steinheim, Germany). Hydrochloric acid (37 %) was purchased from Merck (Johannesburg, South Africa). Sodium chloride (≥99.5 %) was purchased from Associated Chemical Enterprises (Johannesburg, South Africa). Hexane (60–66 %) was purchased from Honeywell (Muskegon, United States of America).

The mobile phase used consisted of a mixture of acetonitrile: 0.2 % formic acid (60:40, v:v) at a flow rate of 1 mL min^{-1}.

A mixture of 100 mg L^{-1} of ketoprofen and triclosan was prepared in acetonitrile. Working standards were prepared from this solution.

Chromatographic separation using a linear solvent system was performed on a high performance liquid chromatography (HPLC) system that consisted of a Waters 600E pump (Waters, Milford, USA), and a photo diode array detector (Shimadzu, Kyoto, Japan). Samples and standards were injected using a Rheodyne 7010 injector equipped with a 20 μL sample loop (California, USA). A Gemini C_{18} HPLC column 150 ×4.60 mm × 5 μm was obtained from Phenomenex (California, USA). Shimadzu LC Solutions software was used for recording of chromatograms. Ketoprofen and triclosan were measured at 255 nm and 200 nm, respectively.

A pH meter (model 691) was obtained from Metrohm (Herizau, Switzerland) and was used for pH reading of all the samples.

The following solid-phase extraction cartridges were investigated; Oasis HLB 6cc 200 mg, Oasis MAX 6cc 150 mg, both obtained from Microsep (Johannesburg, South Africa), and Isolute 500 mg C_{18} was obtained from Separations (Johannesburg, South Africa).

2.2. Sampling Sites and Sample Collection

Pre-cleaned brown glass bottles were used to collect influent and effluent water samples from a wastewater treatment plant (WWTP) located along the Mbokodweni River south of Durban, South Africa. The grab samples were kept in a refrigerator at 4 °C until SPE-HPLC-PDA analysis. Three sampling points were identified in the Mbokodweni River and grab samples were collected on the upper surface of the river (Fig. 2). Sampling point A was located at approximately 1 km downstream from WWTP, and this point is about 1 km away from the ocean. Sampling points B and C are about 1 km and 3 km, respectively upstream of the WWTP. Monthly collection of samples was done over a three-month period from August to October 2013.

For sample preparation, samples were filtered through 0.45 μm filter paper to remove the suspended solids, and thereafter the pH was adjusted.

2.3. The Optimization of Sample pH, Sorbent Type, Elution Solvent, Sample Volume and Ionic Strength

The optimization of sample pH, sorbent type, elution solvent, ionic strength of the sample and sample volume were carried out on spiked ultra-pure water (1000 μg $L^{-1}$of each compound) by varying one parameter while keeping others constant. Each optimization procedure was repeated three times (n = 3).

Sample pH was optimized by varying the pH of ultra-pure water spiked with 1000 μg $L^{-1}$of each compound. The pH was adjusted to 2, 4, or 5.5 with HCl (1 mol L^{-1}) and NaOH (0.6 mol L^{-1}). Target compounds were extracted using Oasis HLB

Figure 2 A map showing the sampling sites and areas surrounding the Mbokodweni river.

prior to HPLC-PDA analysis. The following parameters were kept constant while varying the pH of the spiked sample, each cartridge was conditioned with 5 mL methanol and 5 mL of ultra-pure water at a flow rate of 1 mL min^{-1}. A 100 mL volume of the sample was loaded onto the cartridge at a flow rate of 5 mL min^{-1} and sent to waste. The cartridge was vacuum-dried for 30 min and the adsorbed compounds were eluted with 10 ml of methanol at a flow rate of 1 mL min^{-1}.

Flow rates usually vary from 1 to 10 mL min^{-1}, and they are controlled by the use of a vacuum pump.[2,3,4,7] When flow rates are too high, the retention of target compounds might be compromised. For the sample loading step, the flow rate was increased slightly to avoid long sample preparation time.

In order to vary the type of sorbent, three different SPE cartridges were investigated; Oasis HLB (200 mg), Oasis MAX (150 mg) and Isolute C_{18} (500 mg).

Three solvent combinations were tested in order to get the best elution solvent for the Oasis HLB cartridge. These were (1) methanol, (2) methanol and acetic acid, 9:1 (v/v), and (3) 0.2 % formic acid and acetonitrile, 4:6 (v/v). The other experimental parameters were kept constant while varying the elution solvent.

The effect of sample volume was investigated by passing different volumes of ultra-pure water (pH 5.5) spiked with 1000 μg L^{-1} of each compound through the Oasis HLB SPE cartridge. The volumes of spiked ultra-pure water were in the range of 10 to 300 mL. The compounds retained by SPE cartridge were eluted with methanol. The other experimental parameters were kept constant while varying the sample volume.

The effect of ionic strength of the sample was studied by spiking ultra-pure water with different concentrations of sodium chloride in the range of 0.5–6.0 % (w/v).

2.4. Quality Assurance

Stock solution (100 mg L^{-1}) was diluted with acetonitrile to the desired concentrations until the limit of detection was reached. Four point calibration curves were constructed for both compounds and used for method validation. Recovery, accuracy and precision of the analytical method were determined by spiking ultra-pure water at concentration levels ranging from 5 to 1000 μg L^{-1} and effluent with a concentration of 50 μg L^{-1}. Target compounds were extracted from each spiked sample using the optimized SPE conditions. The analysis was done in triplicate. The extracted compounds were analyzed using HPLC-PDA.

3. Results and Discussion

3.1. Optimization Results

3.1.1. *Sample pH*

The best recoveries for these two compounds were obtained at pH 5.5 (Fig. 3). As a result of these experiments, the optimum pH for selected compounds was chosen as pH 5.5. Low pH is required for the analysis of acidic pharmaceuticals to prevent the dissociation of acidic compounds. However, the pH must not be too low because if the samples are too acidic wastewater interfering substances can also be extracted.[8] Patrolecco *et al.*[7] obtained similar recoveries when extracting ketoprofen and related compounds at pH 3.6 (acidic). Santos *et al.*[8] obtained a mean recovery of 80 % for ketoprofen at neutral pH. In this study this recovery was improved when lowering the pH.

3.1.2. *Sorbent Type*

Three SPE packing materials were investigated in this work. Oasis HLB and Isolute C_{18} cartridges yielded acceptable recoveries (Fig. 4). Oasis HLB exhibits both hydrophilic and lipophilic retention characteristics; therefore it is capable of extracting both polar and non polar compounds.[12] C_{18} cartridges are capable of extracting a wide range of organic compounds from aqueous solutions. Both these cartridges gave acceptable recoveries but extra care needs to be taken when using C_{18} cartridges to ensure that the sorbent stays wet before loading the sample and this is not the case when using Oasis HLB. Therefore Oasis HLB was found to be the best sorbent for this work. Azzouz *et al.*[13] obtained acceptable sorption results when comparing Oasis HLB and C_{18} sorbents. When using Oasis MAX, good recoveries were obtained for triclosan but ketoprofen could not be retained. It is not clear why this is the case; further research needs to be conducted on this.

3.1.3. *Elution Solvent*

Different solvent combinations were tested for the elution of analytes from the SPE cartridge. Due to the polarity of the target compounds, only polar solvents were investigated.

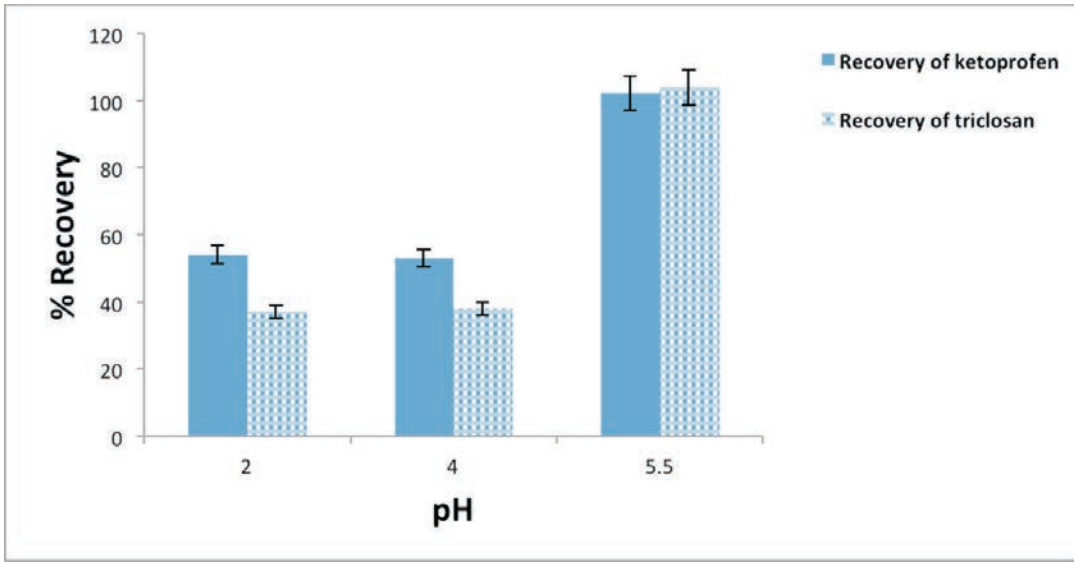

Figure 3 Effect of pH on the recovery of triclosan and ketoprofen. Ultra-pure water was spiked with the target compounds, adjusted to the indicated pHs and 100 mL passed through Oasis HLB. $n = 3$.

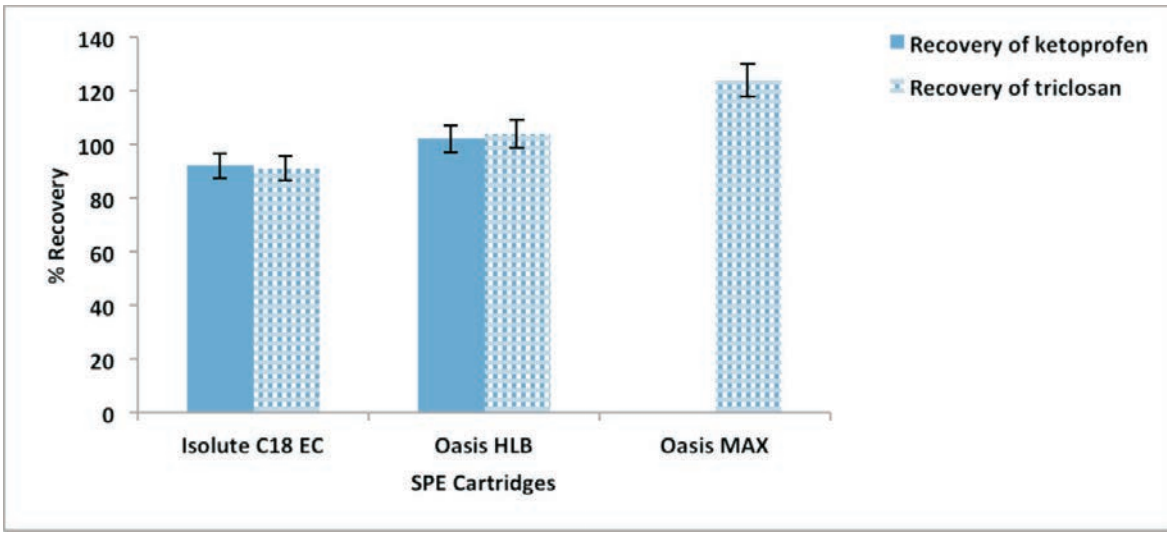

Figure 4 Recovery of triclosan and ketoprofen from different SPE cartridges. Ultra-pure water was spiked with the target compounds, adjusted to pH 5.5 and 100 mL passed through the cartridge. $n = 3$.

Methanol (MeOH) gave the best extraction recoveries compared to other solvents tested. This is in agreement with the results reported in literature.[14,19] Boleda *et al.*[14] obtained recoveries of 86 % and 79 % for triclosan and ketoprofen, respectively, when surface water was spiked with pharmaceutical compounds followed by Oasis HLB extraction and methanol elution of target compounds. Recoveries obtained by Ying *et al.*[19] for effluent samples spiked with 50 ng L^{-1} of each compound were more than 70 % when the target compounds were eluted with methanol from Oasis HLB cartridges. Figure 5 shows the recoveries obtained when using different solvents for SPE elution. To the best of our knowledge, a mixture of formic acid and acetonitrile has not been used as elution solvent for compounds retained on Oasis HLB. It was considered and tried in this study since it is used as a mobile phase, but recoveries were poor. Hexane (non-polar solvent) was tested by Santos *et al.*,[8] and it was discovered that it has a potential of removing lipophilic components although it can remove the hydrophobic interferences as well.

3.1.4. *Effect of Sample Volume*

It was noted that the recoveries of both compounds were affected by the volume of the sample loaded into the SPE cartridge (Fig. 6). This trend was also observed in other study.[15] This is due to capacity of the sorbent being exceeded and has to do with breakthrough volume of the sorbent. A sample volume of 100 mL gave the best recoveries and it was selected for this study. Optimization of sample volume is important when performing the solid phase extraction as higher volumes tend to overload the SPE cartridge and target compounds end up competing for the adsorbing material with matrix interferences. Reduction of ketoprofen recovery to 72.8 % when sample volume was increased to 1000 mL using a molecularly imprinted polymer as SPE sorbent was reported elsewhere[16]. High sample volume can also lead to the saturation of the SPE sorbent and results in poor recoveries.

3.1.5. *Effect of Ionic Strength*

Effect of ionic strength was investigated by spiking ultra-pure water with different concentrations of sodium chloride in the range of 0.5–6.0 % (w/v). It was noted that the presence of sodium chloride affected the retention of target compounds in HLB sorbent (Fig. 7). The recovery of compounds decreased as the amount of sodium chloride increased in the water solution.

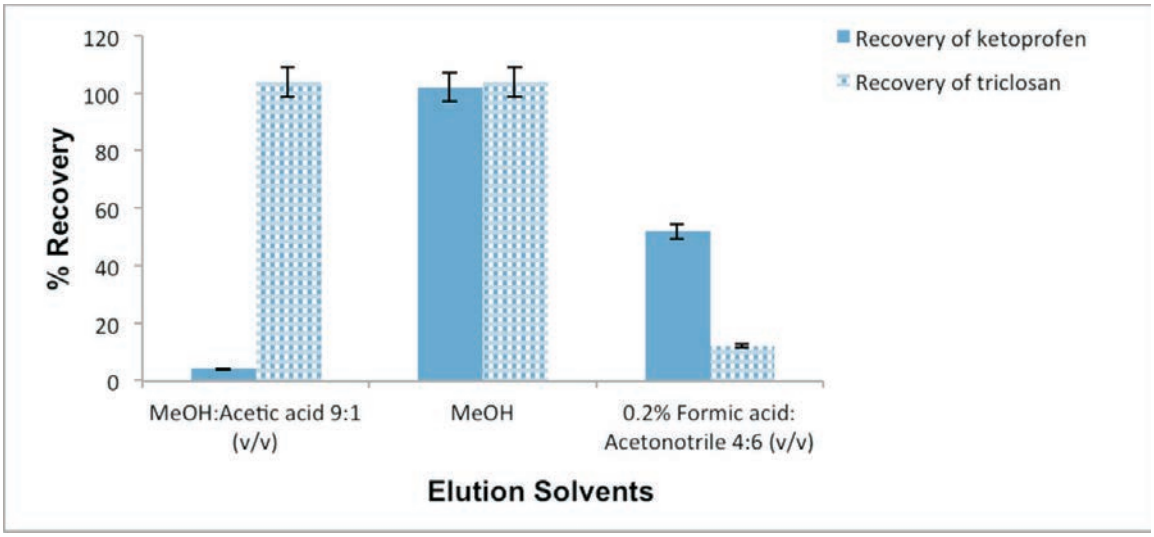

Figure 5 Effect of elution solvent on the recovery of triclosan and ketoprofen. Ultra-pure water was spiked with the target compounds, adjusted to pH 5.5 and 100 mL passed through Oasis HLB. $n = 3$.

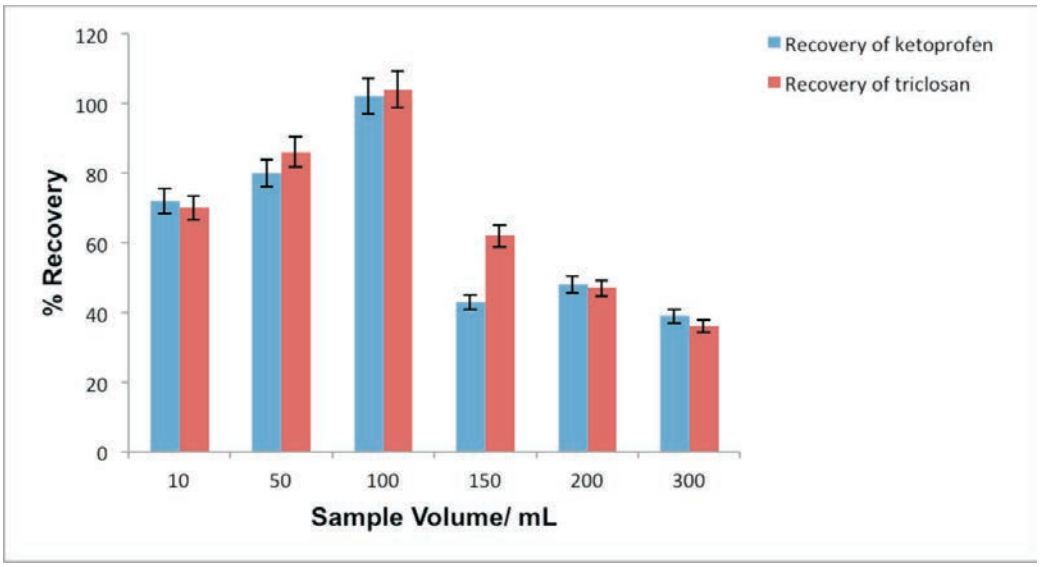

Figure 6 % Recoveries obtained when loading different volumes of spiked ultrapure water onto Oasis HLB cartridge. $n = 3$.

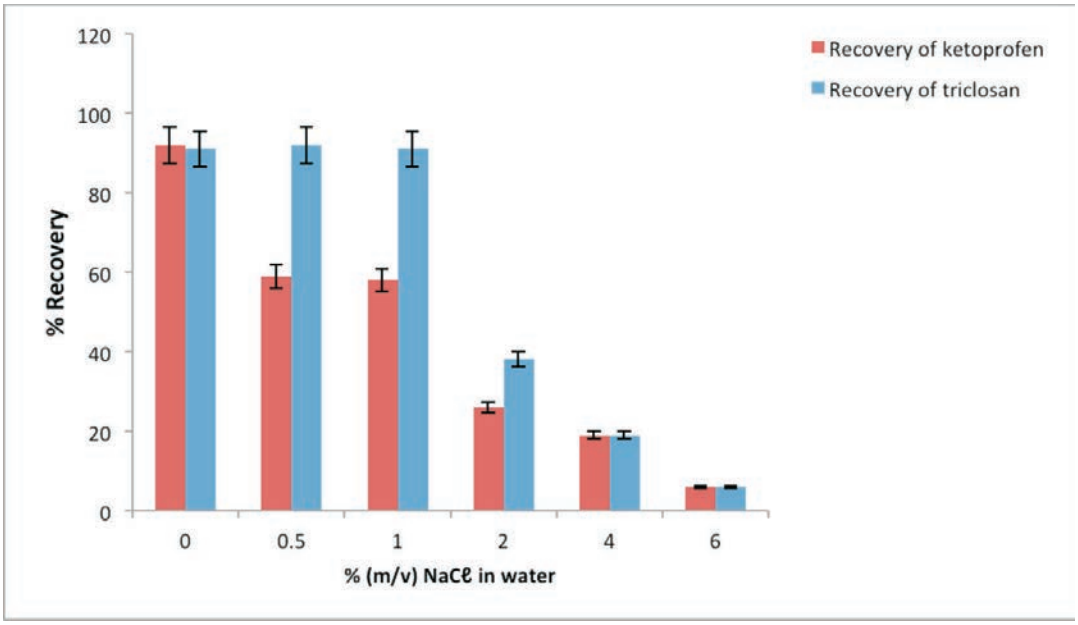

Figure 7 Effect of ionic strength on SPE extraction recoveries.

According to Azzouz *et al.*,[13] the ionic strength of water samples had no effect on adsorption of target compounds onto Oasis HLB on the signals up to 2 mol L^{-1}. Effect of ionic strength was also investigated in another study[17] for the adsorption of pharmaceuticals onto porous silica in the range of 0 to 50 mmol L^{-1} (0 to 0.29 % (w/v)). No significant effect was observed in this range for ketoprofen however triclosan was not included in the study. This was confirmed in the current investigation, and the results were even better when HLB sorbent was used instead of porous silica. From our results, the developed method cannot be applied in the analysis of the same compounds in sea water, because of high levels of salt content in sea water.

3.2. Quality Assurance

To determine the accuracy of the proposed method, validation was carried out by spiking wastewater effluent and ultra-pure water with different concentrations of each compound ranging from 5 μg L^{-1} to 1000 μg L^{-1}. Percentage recoveries obtained after SPE and HPLC-PDA determination are given in Table 1. Calibration curves were found to be linear ($R^2 > 0.99$) for both com-

Table 1 LODs, LOQs, accuracy (% recovery) and repeatability (% RSD, shown as ± values) in ultrapure water spiked at concentration levels ranging from 5 to 1000 μg L^{-1} ($n = 3$) and effluent spiked at 50 μg L^{-1} using optimized SPE conditions.

Compound	LOD/μg L^{-1}	LOQ/μg L^{-1}	% Recovery for ultra-pure water				Effluent
			1000 μg L^{-1}	100 μg L^{-1}	50 μg L^{-1}	5 μg L^{-1}	50 μg L^{-1}
Ketoprofen	0.08	0.26	102 ± 9	83 ± 10	84 ± 8	85 ± 11	96 ± 14
Triclosan	0.01	0.34	104 ± 8	80 ± 15	73 ± 10	78 ± 9	75 ± 10

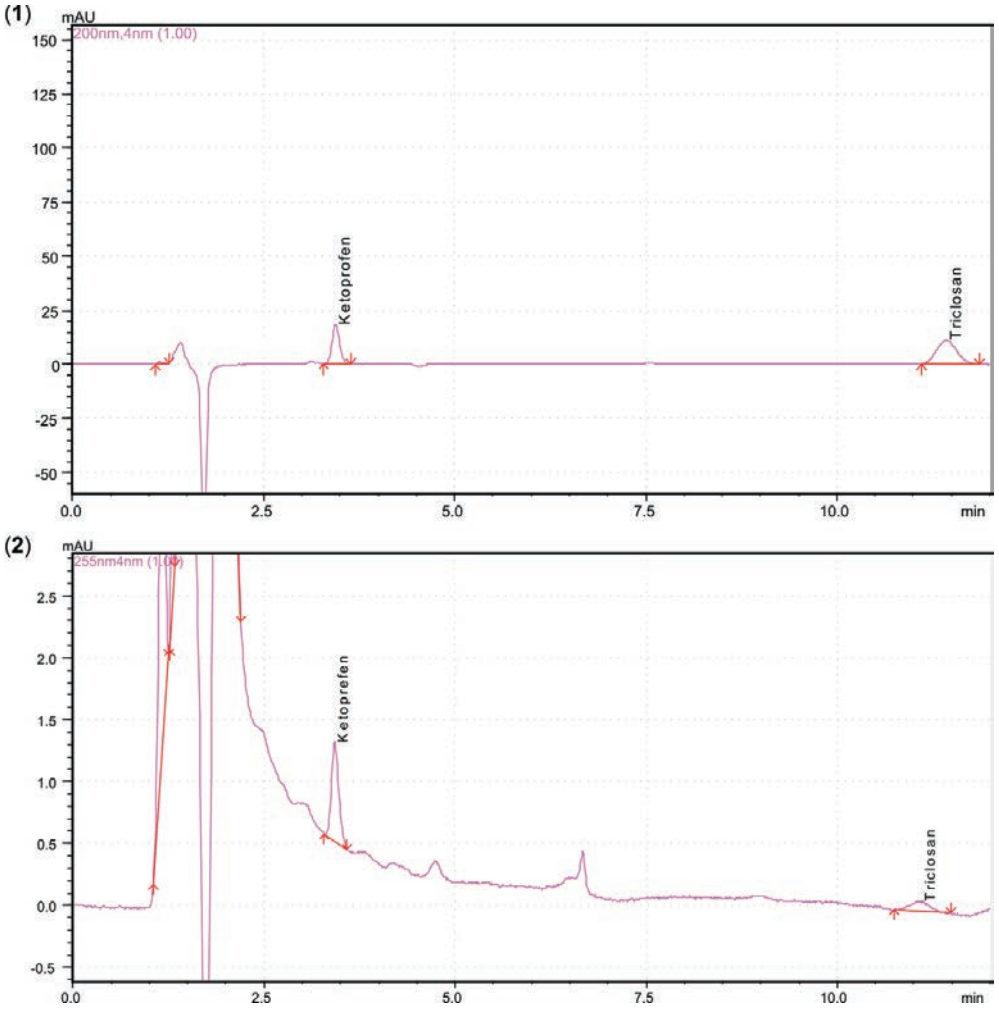

Figure 8 **(1)** Chromatogram for 1000 μg L^{-1} mixture of both compounds, and **(2)** chromatogram of the effluent sample after SPE.

pounds over a wide concentration range. All methods were conducted in triplicate with % RSD reported as ± values in Table 1. Limit of detection (LOD) and limit of quantification (LOQ) were calculated by a signal to noise ratio of 3 and 10, respectively. From the data obtained (data in Table 1), it can be seen that the proposed method can be applied for the environmental monitoring of these two compounds at sub-μg L^{-1} levels.

3.3. Application of the Method to Environmental Samples

The described method was applied for the qualitative and quantitative determination of triclosan and ketoprofen in wastewater influent, effluent and river water. Identification of compounds present in real samples was based on retention times, and compounds were also confirmed using PDA spectra. Figure 8 shows the chromatograms for the mixture of two compounds and effluent sample and Fig. 9 shows the PDA spectra of both compounds. Both compounds have been detected in all the influent and effluent samples. The WWTP receives approximately 23 000 m^3 d^{-1} of water from two industrial areas (Prospecton and South Gate), and semi-urban areas (Amanzimtoti, Athlone Park, Ispingo, Kwa Makhuta and Folweni). It is well known that WWTPs around the world are not capable of entirely removing the pharmaceutical compounds during the wastewater treatment process.[16,18–,20] The WWTP studied here is not an exception. It has been reported that there is a seasonal variation for the levels of pharmaceuticals in wastewater, where higher concentrations are expected in winter than in summer.[21,22] The explanation for this is that the human consumption of pharmaceuticals is higher during the winter season and compounds degrade faster during summer when temperatures are high.[21,22]

The compounds have been detected in some river samples (Table 2). Mbokodweni River is a long river that cuts in-between Umlazi Township and Kwa Makhuta. One side of the river is

Table 2 Concentrations (μg L^{-1}) of target compounds (n = 3) in river water and wastewater treatment plant.

Sample	Month	Triclosan	Ketoprofen
Influent	August	2.1 ± 0.45	1.7 ± 0.7
	September	9.0 ± 2.0	6.4 ± 2.2
	October	8.5 ± 3.0	4.8 ± 0.90
Effluent	August	1.3 ± 0.50	1.2 ± 0.35
	September	6.4 ± 1.0	3.2 ± 0.80
	October	4.1 ± 8.0	4.3 ± 1.00
MR – A	August	0.9 ± 0.22	<LOQ
	September	0.4 ± 0.10	1.1 ± 0.30
	October	<LOQ	2.0 ± 1.50
MR – B	August	n.d.	n.d.
	September	n.d.	n.d.
	October	n.d.	n.d.
MR – C	August	n.d.	n.d.
	September	n.d.	n.d.
	October	n.d.	n.d.

MR – A: Mbokodweni river-sampling point A; MR – B: Mbokodweni river-sampling point B; MR – C: Mbokodweni river- sampling point C; LOQ result means that the concentration was >LOD but below LOQ; nd means the compound was not detected. Sampling points are those explained in section 2.2.

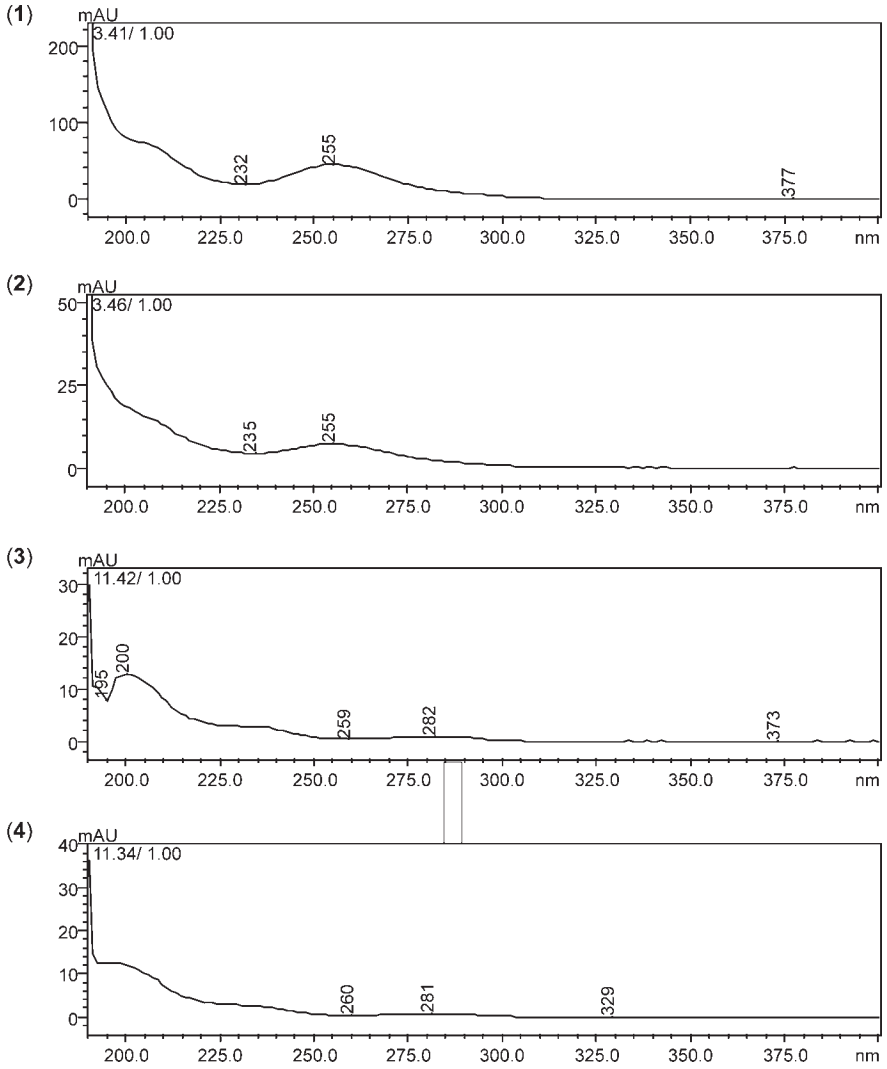

Figure 9 (1) PDA spectrum for ketoprofen standard, **(2)** PDA spectrum for ketoprofen in the effluent sample, **(3)** PDA spectrum for triclosan standard and **(4)** PDA spectrum for triclosan in the effluent sample.

occupied by scattered rural houses. The results obtained for river samples show that as the river flows towards the sea the level of pollutants increases. The samples from upstream of the river were cleaner than the samples downstream, and the target compounds were not detected in upstream samples.

The levels of the compounds obtained in wastewater samples are high compared to what is reported in literature by researchers of other countries (Table 3), therefore something should be done to reduce the levels of these pollutants in South Africa.

4. Conclusions

A simple, sensitive, accurate, rapid and affordable method was developed for the quantitative determination of triclosan and ketoprofen in the aquatic environment. The developed method involves the simultaneous extraction of both compounds using Oasis HLB sorbent. The extracted compounds were pre-concentrated prior to HPLC determination. The method is not suitable for samples that contain high salt content. The described method was applied for the qualitative and quantitative deter-

Table 3 Maximum concentration levels of triclosan and ketoprofen reported in foreign countries.

Compound	Influent/μg L^{-1}	Effluent/μg L^{-1}	Country	Reference
Triclosan	0.8	0.25	United States	23
	0.8	0.15	Korea	24
	0.057	Not reported	Spain	25
	2.42	0.51	Spain	26
	Not reported	0.324	Canada	27
	2.11	0.24	Greece	28
Ketoprofen	1.2	0.28	United States	23
	0.29	0.037	Korea	24
	0.80	0.54	Spain	26
	Not reported	0.210	Canada	27
	1.28	0.12	Greece	28
	0.37	Not reported	Tokyo	29

mination of both compounds in wastewater and river water. High levels of these compounds were detected in wastewater, whereas small residues were occasionally found in river water. The effect of these compounds on aquatic animals of the polluted river is not known. Further research needs therefore to be conducted on health effects of these compounds on aquatic organisms in the Mbokodweni river.

Acknowledgements

The authors would like to thank Mr. T. Msukwini of Durban University of Technology for organizing CHIETA funding and WWTP sampling permit; and Mrs Avy Naicker for her assistance in the HPLC laboratory.

References

1 S. Bayen, H. Zhang, M.M. Desai, S.K. Ooi and B.C. Kelly, *Environ. Pollut.*, 2013, **182**, 1–8.

2 T.E. Felix-Canedo, J.C. Duran-Alvarez and B. Jimenez-Cisneros, *Sci. Total Environ.*, 2013, **454–455**, 109–118.

3 N.H. Tran, J. Hu and S.L. Ong, *Talanta*, 2013, **113**, 82–92.

4 J. Zhao, G. Ying, L. Wang, J. Yang, X. Yang, L. Yang and X. Li, *Sci. Total Environ.*, 2009, **407**, 962–974.

5 M. Adolfsson-Erici, M. Pettersson, J. Parkkonen and J. Sturve, *Chemosphere*, 2002, **46**, 1485–1489.

6 E. Sagrista, E. Larsson, M. Ezoddin, M. Hildago, V. Salvado and J.A. Jonsson, *J. Chromatogr. A*, 2010, **1217**, 6153–6158.

7 L. Patrolecco, N. Ademollo, P. Grenni, A. Tolomei, A.B. Caracciolo and S. Capri, *Microchem. J*, 2013, **107**, 165–171.

8 J.L. Santos, I. Aparicio, E. Alonso and M. Callejon, *Anal. Chim. Acta*, 2005, **550**, 116–122.

9 Y. Yu and L. Wu, *J. Chromatogr. A*, 2011, **1218**, 2483–2489.

10 J.Y. Shen, M.S. Chang, S. Yang and G.J. Wu, *J. Liq. Chromatogr. Relat. Technol.*, 2012, **35**, 2280–2293.

11 C. Grove, W. Liebenberg, J.L. Du Preeze, W. Yang and M.M. De Villiers, *J. Cosmet. Sci.*, 2003, **54**, 537–550.

12 L.M. Madikizela, *Optimisation of HPLC-based methods for the separation and detection of herbicide glyphosate and its major metabolite in water*, M.Tech. thesis, Durban University of Technology, Durban, South Africa, 2010.

13 A. Azzouz, B. Souhail and E. Ballesteros, *J. Chromatogr. A*, 2010, **1217**, 2956–2963.

14 R. Boleda, T. Galceran and F. Ventura, *J. Chromatogr. A*, 2013, **1286**, 146–158.

15 J. Patsias and E. Papadopoulou-Mourkidou, *J. Chromatogr. A*, 2000, **904**, 171–188.

16 Y. Duan, C. Dai, Y. Zhang and L. Chen, *Anal. Chim. Acta*, 2013, **758**, 93–100.

17 T.X. Bui and H. Choi, *Chemosphere*, 2010, **80**, 681–686.

18 N. Lindqvist, T. Tuhkanen and L. Kronberg, *Water Res.*, 2005, **39**, 2219–2228.

19 M. Farre, I. Ferrer, A. Ginebreda, M. Figueras, L. Olivella, L. Tirapu, M. Vilanova and D. Barcelo, *J. Chromatogr. A*, 2001, **938**, 187–197.

20 G. Ying, R.S. Kookana and D.W. Kolpin, *J. Environ. Monit.*, 2009, **11**, 1498–1505.

21 Y. Yu, L. Wu and A.C. Chang, *Sci. Total Environ.*, 2013, **442**, 310–316.

22 A. Azzouz and E. Ballesteros, *Chemosphere*, 2013, **93**, 2046–2054.

23 J.T. Yu, E.J. Bouwer and M. Coelhan, *Agric. Water Manage.*, 2006, **86**, 72–80.

24 S.K. Behera, H.W. Kim, J. Oh and H. Park, *Sci. Total Environ.*, 2011, **409**, 4351–4360.

25 R. Rodil, J.B. Quintana, E. Concha-Grana, P. Lopez-Mahia, S. Muniategui-Lorenzo and D. Prada-Rodriguez, *Chemosphere*, 2012, **86**, 1040–1049.

26 R. Rosal, A. Rodriguez, J.A. Perdigon-Melon, A. Petre, E. Garcia-Calvo, M.J. Gomez, A. Aguera and A.R. Fernandez-Alba, *Water Res.*, 2010, **44**, 578–588.

27 L. Lishman, S.A. Smyth, K. Sarafin, S. Kleywegt, J. Toito, T. Peart, B. Lee, M. Servos, M. Beland and P. Seto, *Sci. Total Environ.*, 2006, **367**, 544–558.

28 V.G. Samaras, A.S. Stasinakis, D. Mamais, N.S. Thomaidis and T.D. Lekkas, *J. Hazard. Mater.*, 2013, **244-245**, 259-267.

29 N. Nakada, T. Tanishima, H. Shinohara, K. Kiri and H. Takada, *Water Res.*, 2006, **40**, 3297–3303.