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Determination of non-ionic and anionic surfactants in environmental water matrices

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ABSTRACT

Solid-phase extraction (SPE) combined with liquid chromatography electrospray mass spectrometry (LC–(ESI)MS) was used to determine 16 non-ionic and anionic surfactants in different environmental water samples at ng L^{-1} levels. The proposed method is sensitive and simple and has good linear range and detection limits (less than 50 ng L^{-1}) for most compound classes.

The effect of ion suppression was studied in aqueous matrices from several treatment plants—including urban and industrial wastewater treatment plants (WWTPs), drinking-water treatment plants (DWTPs) and seawater desalination plants (SWDPs)—and it was considered when quantifying our samples. In addition, conventional treatments and tertiary treatments that use advanced membrane technologies, such as ultrafiltration (UF) and reverse osmosis (RO) were evaluated in order to determine their efficiency in eliminating these compounds.

The concentrations of non-ionic surfactants in the raw waters studied ranged from 0.2 to 100 μg L^{-1}. In effluents, the concentrations ranged from 0.1 to 5 μg L^{-1}, which reflects consistent elimination. Anionic surfactants were present in all waters studied at higher levels. Levels up to 3900 μg L^{-1} of linear alkylbenzene sulfonates (LASs) and 32,000 μg L^{-1} of alkyl ethoxysulfates (AESs) were detected in urban WWTP influents, while levels up to 25 μg L^{-1} of LASs and 114 μg L^{-1} of AESs were found in drinking-water and desalination treatment plants.

The results indicate that conventional processes alone are not sufficient to completely remove the studied surfactants from waste streams. Tertiary treatments that use advanced membrane technologies such as UF and RO can further reduce the amount of target compounds in the effluent water.

1. Introduction

Synthetic surfactants are used mainly as surface-active ingredients in detergents, shampoos and other cleaning compounds. They are also used in the processing of textiles, pulp and paper, recycled paper, paint and plastics. Surfactants can be classified by the presence of polar head groups in their heads.

The annual worldwide consumption of surfactants has been steadily increasing. The total amount of surfactants (without soaps) consumed in Western Europe in 2008 was 2.98 Mt, 1.413 Mt of which were non-ionic, 1.222 Mt were anionic, 0.254 Mt were cationic and 0.093 Mt were amphoteric, according to statistics published by the European Committee of Surfactants and their Organic Intermediates (CESIO) [1].

The most abundant anionic surfactants, especially in household detergents and surface cleaners, are linear alkylbenzene sulfonates (LASs). These compounds have alkyl chains from C10 to C14. The second most abundant surfactants in this group are alkyl ethoxy sulfates (AESs). These compounds have an alkyl chain length of between 12 and 16 carbon units and a chain of 3 or 4 ethylene oxide (EO) units, on average [2]. The most abundant non-ionic surfactants in use are alcohol ethoxylates (AEOs) and alkylphenol ethoxylates (APEOs). The alkyl chain of AEOs usually has between 12 and 16 carbon units and between 1 and 23 EO units. In APEOs, the number of EO units is the same, while the alkyl chain can be either 8 or 9 units in length and are known as octylphenol ethoxylates (OPEOs) or nonylphenol ethoxylates (NPEOs) [3].

Surfactants and their metabolites are introduced into the environment due to the extensive use of the surfactants. However, these compounds are not effectively removed from the wastewater treatment plants [4–7]. González et al. [8] compared the removal of NP, LASs and NPEOs in a conventional activated sludge (CAS) system and membrane bioreactor (MBR) system and obtained higher removal rates for LASs and NPEOs in the MBR system than in the CAS system and the same removal rates for NP in both systems. However, of the few studies that have examined the behaviour of surfactants during MBR treatment [9,10], most report no significant differences between the MBR and CAS systems. To our knowledge,

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there are no publications focused on advanced membrane treatments, such as RO, and surfactants determination.

The biodegradation of surfactants in wastewater treatment plants has been studied in numerous papers [8,10–12]. The degradation products of LASs are long-chain sulfophenyl carboxylate compounds (SPCs) which have more than five carbon atoms in the linear chain apart from the benzene ring. APEOs decompose by the progressive loss of ethoxylate groups to form short-chain APEOs (1–2 EO units) and alkylphenols (APs). NPEOs with more than eight EO units are readily degraded, usually with >92% efficiency [13]. These substances are also recognized as endocrine disrupters and have more endocrine activity than their parent products [4]. Octylphenol (OP) is an important chemical intermediate that is mainly used for the production of phenolic resins and lacquers [5].

Once present in effluent sewage water, these substances enter the river, sea or ground waters, putting the drinking-water supply system at the risk. Numerous studies have discussed the various methods of sample preparation, chromatographic separation and detection systems used to determine non-ionic and anionic surfactants in environmental samples [2,14–16]. However, few of the methods developed are capable of determining both families simultaneously [6,7,17].

The limited volatility of some surfactants restricts the use of gas chromatography–mass spectrometry (GC–MS) to analysis, and derivatization is incorporated into the protocol. Liquid chromatography–mass spectrometry (LC–MS) is currently the most suitable technique [18]. A wide variety of extraction techniques have been used and, of these, solid-phase extraction (SPE) with various sorbents such as graphitized carbon black [19], polymeric resins [20] and alkyl-bonded silica [21] is the most popular sample preparation technique [7,14]. Due to the characteristics of surfactants, SPE/LC–MS [6,11,22] and SPE/LC–MS/MS [12,19,23] are the techniques that have been used most frequently for their determination and show good results in terms of recovery and detection limits. A comparison of the detection limits for various analytes (APs, APEOs) clearly indicates that, in the case of LC–MS, electrospray (ESI) interface offers better sensitivity and specificity for a wider range of oligomeric mixtures of polyethoxylate surfactants than does atmospheric–pressure chemical ionization (APCI) interface [24].

The objective of this study was to develop an analytical method that is sensitive enough (ng L^{-1}) for the simultaneous determination of octylphenol, nonylphenol, alkylphenol ethoxylates, alcohol ethoxylates, linear alkylbenzene sulfonates and alkyl ethoxysulfates in several streams of wastewater (urban and industrial), drinking water and seawater desalination plants by using SPE/LC–(ESI)MS. The effect of ion suppression was studied and the efficiency of conventional and advanced membrane treatments such as UF and RO was evaluated.

2. Experimental

2.1. Materials and standards

All solvents, methanol, hexane, acetone, dichloromethane, ethyl acetate, water and acetic acid were of chromatography quality and were obtained from SDS (Peypin, France). Triethylamine was obtained from Sigma–Aldrich (Steinheim, Germany).

The standards used in this study were of the highest purity available. High-purity (98%) 4-*tert*-OP (CAS 140-66-9) and 4-NP (CAS 104-40-5) were obtained from Sigma–Aldrich. Alkyl chain isomers OP_1EO (CAS 2315-67-5), OP_2EO (CAS 2315-61-9), NP_1EO and NP_2EO were obtained from Dr. Ehrenstorfer through Cymit Química (Barcelona, Spain). Additionally, a technical mixture of OPEOs (CAS 9036-19-5) and NPEOs (CAS 68412-54-4) containing chain isomers and oligomers with an average of five ethoxy units, Igepal CA-520 and Igepal CO-520, respectively, were obtained from Sigma–Aldrich. Commercial LASs (CAS 85536-14-7) with a low dialkyltetralinsulfonate content (<0.5%) were supplied by Petroquímica Española (San Roque, Spain) in a single standard mixture with the proportional composition of the four homologs of: C_{10} (12.8%), C_{11} (32.2%), C_{12} (29.8%), C_{13} (24.1%). Commercial AEOs (CAS 68439-50-9) (Findet 1214N/23) and AESs (CAS 68585-34-2) (Emal 227E) mixtures were supplied by KAO Corporation (Barcelona, Spain) with the following homolog distribution: C_{12} (72.5%) and C_{14} (27.5%). The ethoxylated chains had an average of 8 units for the AEOs and 2.5 for the AESs. Fig. 1 shows the structures of the target compounds.

Stock solutions of individual standards and standard mixtures were prepared by dissolving precise amounts of pure standards in methanol at a concentration of 1000 mg L^{-1} and storing them at 4 °C. Working standard solutions were prepared daily and were obtained by further diluting the stock solutions with water or methanol.

The nitrogen used in solid-phase extraction to evaporate the solvents was of 99.9% purity and was purchased from Carburos Metálicos (Tarragona, Spain).

Isolute C18 500 mg solid-phase extraction cartridges were supplied by Biotage (Uppsala, Sweden). They were connected to a manifold (Teknokroma, Barcelona, Spain) and a pump that served as a vacuum source.

2.2. Solid-phase extraction

Isolute C18 SPE cartridges were selected for preconcentration. The sorbent was sequentially conditioned with 7 mL of methanol and 3 mL of water. Since ion suppression was evaluated, WWTP influents were diluted with ultrapure water 1:4 (v:v) and WWTP effluents were diluted 1:2 (v:v) before the SPE procedure. The extracted sample volume was 100 mL for wastewater influents and 250 mL for wastewater effluents. Drinking-water and seawater treatment samples were analysed without dilution and extracted volume was 250 mL.

The samples passed through the cartridge at a flow rate of 10–15 mL min^{-1}. Elution of the analytes was done with 4 mL of methanol and this step was repeated twice. After elution, the extracts were evaporated to dryness under a gentle stream of nitrogen and the residue was reconstituted in 1 mL of methanol. After being filtered through 0.45 μm syringe filters (Scharlab, Barcelona, Spain), 15 μL of this solution was injected into the chromatographic system.

2.3. Liquid chromatography–mass spectrometry

The chromatographic instrument was an HP 1100 series LC (Agilent Technologies, Waldbronn, Germany) equipped with an automatic injector, a degasser, a quaternary pump and a column oven. The detector was a mass spectrometer detector, MSD G1946B, with an electrospray ionization interface. LC separation was achieved on a 5 μm, 250 mm × 4.6 mm i.d., C18 reversed-phase column (Kromasil 100 C18, Teknokroma), preceded by a guard column (5 μm, 10 mm × 2 mm i.d.) of the same packing material, also from Teknokroma. The column temperature was kept at 35 °C and the flow rate was 1 mL min^{-1}.

ESI interface was used with two ionization modes, positive ionization (PI) and negative ionization (NI). Extracts were analysed using an ESI interface in PI for the non-ionic surfactants (OPEOs, NPEOs and AEOs); the $[M+Na]^+$ adduct ions, which produced no fragmentation, were monitored. Extracts were analysed using an ESI interface in NI for the anionic surfactants (OP, NP, LASs and AESs); the deprotonated molecules $[M-H]^-$ were monitored. In both ionization modes, selected ion monitoring

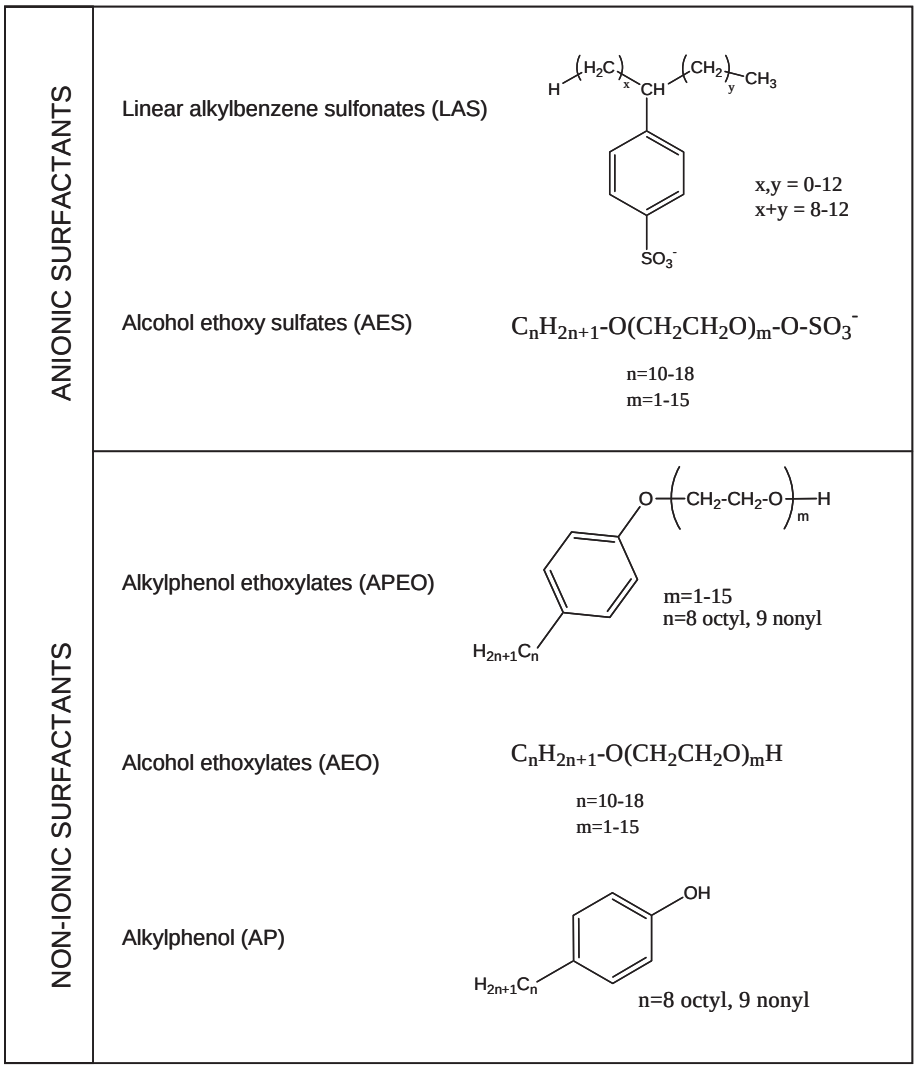

Fig. 1. Chemical structures of the surfactants determined.

(SIM) mode was used for the quantitative and qualitative analysis.

For determination in PI mode, the following mobile phase was used: water (A) and methanol (B). The following solvent programming was used: initial conditions 60% methanol (B), linearly increased to 100% in 20 min and further maintained at these conditions for 8 min.

In NI mode, the following mobile phase was used: water containing 5 mM acetic acid and 5 mM triethylamine (A) and methanol (B). The elution gradient started with 40% methanol (B) and was linearly increased to 100% in 7 min and further maintained at these conditions for 10 min.

The operating parameters of ESI were 12 L min^{-1} (NI mode) and 13 L min^{-1} (PI mode) for drying gas flow, 350 °C for drying gas temperature, 40 psi for nebulizer pressure and 4500 V for capillary voltage (the last three for both ionization modes).

The fragmentation voltage was optimized for each compound, ranging from 70 V for OP_1EO, OP_2EO, NP_1EO and NP_2EO to 120 V for the OPEO(n_{EO} = 3–15), NPEO(n_{EO} = 3–15) and AEOs in PI mode and from 120 V for OP and NP to 220 V for LASs and AESs in NI mode. Table 1 shows the ions monitored in SIM mode and the fragmentor voltages.

In both modes, two SIM MSD signal windows were selected in order to increase sensitivity. Four LASs homologs (C_{10}–C_{13}), OP and NP were detected in one MSD signal window and C_{12} and C_{14} AESs were detected in another MSD signal window in NI mode. OPEOs (n = 1–13) and C_{12}EOs were detected in one signal window while NPEOs (n = 1–13) and C_{14}EOs were detected in another window in PI mode.

Table 1
Performance of LC–MS method: ions monitored and fragmentor voltage.

Compound	m/z	Fragmentor voltage (V)
OP_1EO	273 $[M+Na]^+$	70
OP_2EO	317$[M+Na]^+$	70
OPEOs (n_{EO} = 3–15)	361 + Δ44$[M+Na]^+$	120
NP_1EO	287 $[M+Na]^+$	70
NP_2EO	331 $[M+Na]^+$	70
NPEOs (n_{EO} = 3–15)	375 + Δ44 $[M+Na]^+$	120
AEOs		
C_{12}AEOs	297 + Δ44 $[M+Na]^+$	120
C_{14}AEOs	325 + Δ44 $[M+Na]^+$	120
OP	205 $[M-H]^-$	120
NP	219 $[M-H]^-$	120
LASs		
C_{10}LAS	297 $[M-H]^-$	220
C_{11}LAS	311 $[M-H]^-$	220
C_{12}LAS	325 $[M-H]^-$	220
C_{13}LAS	339 $[M-H]^-$	220
AESs		
C_{12}AES	309 + Δ44 $[M-H]^-$	220
C_{14}AES	337 + Δ44 $[M-H]^-$	220

Table 2
Description of analysed samples.

Samples	Type of water	Sampling points
WWTP A	Urban wastewater	Influent, effluent CAS and effluent RO
WWTP B	Urban wastewater	Influent and effluent CAS
WWTP C	Industrial wastewater	Influent and effluent MBR(UF)
WWTP D	Industrial wastewater	Influent and effluent CAS
DWTP	River water	Influent and effluent carbon filters
SWDP	Seawater	Influent, effluent of UF and effluent of RO

CAS, conventional activated sludge.
MBR(UF), membrane bioreactor with ultrafiltration membranes.
RO, reverse osmosis.

2.4. Study area and sample collection

Table 2 summarizes the sampling points. These waters had different origins and matrix complexities and underwent different treatment processes. Several streams of wastewater (urban and industrial), drinking-water and seawater treatment plants were analysed.

At WWTPs A, B and D, the treatment consisted of a primary treatment and a conventional secondary treatment with activated sludge (CAS). At WWTP C, the treatment consisted of an MBR that uses UF membranes to treat wastewater. WWTP A also had an RO treatment (FILMTEC™ BW30XFR), and its effluents, concentrate and permeate, were also analysed.

The study also included several sampling points at a DWTP with conventional treatment and a SWDP with integrated UF and RO membrane treatment (Dow™ SFP 2660, FILMTEC™ SW30HRLE).

For each type, 500 mL samples were taken in amber glass bottles, filtered through a 0.45 μm nylon filter (Whatman, Maidstone, UK), stored at 4 °C and analysed within two or three days.

3. Results and discussion

3.1. LC–MS optimization

The most suitable ionization mode was NI for LASs, AESs and APs and PI for APEOs and AEOs, as already reported in the literature [7,17]. As a result, it was necessary to perform two injections for each sample to quantify all target compounds: one in NI mode and the other in PI mode. The MS parameters optimized and the ranges tested were as follows: drying gas flow (10–13 L min^{-1}), drying gas temperature (300–350 °C), nebulizer pressure (30–60 psi) and capillary voltage (3000–4500 V). Once previous parameters were optimised, the fragmentor voltage was studied individually from 70 to 220 V in 20 V steps for each group of surfactants. The operating parameters that showed the highest responses are presented in Section 2.

The extensive use of surfactants in a wide range of consumer products implies a high potential risk of samples being contaminated. The determination of surfactants could therefore be made more reliable by using special precautions such as cleanings throughout the analytical procedure.

Calibration curves were obtained for each homolog of the target compounds, assuming the same response for every ethoxymer in the case of AESs, AEOs, OPEOs and NPEO. Quantitative analysis was performed in SIM mode using external calibration. The linear range was from 10 μg L^{-1} to 10 mg L^{-1} for all of the compounds except for the short alkyl OPEOs, for which it was from 50 μg L^{-1} to 10 mg L^{-1}.

3.2. SPE optimization

According to the literature, C18 cartridges are preferred for enriching the target compounds in environmental water samples [7,14,17,25]. However, there is no agreement as to the amounts and type of solvent mixtures used for elution when a wide range of compounds is selected [17], as in our case.

To determine the best solvent for elution, the isolute C18 sorbent was sequentially conditioned with 7 mL methanol and 3 mL water, and then 250 mL of a standard solution (0.5 mg L^{-1} of each group of compounds) in ultrapure water was passed through the sorbent. Following the literature, we tested three different elution mixtures. The mixtures were: (a) 5 + 5 mL of methanol, (b) 5 mL of methanol:acetone 1:1 and 5 mL dichloromethane:ethyl acetate 1:1, and (c) 5 mL of methanol and 5 mL of dichloromethane. After elution, the extracts were evaporated to dryness under a gentle stream of nitrogen and the residue was re-dissolved in 1 mL of methanol. The higher recoveries were obtained when using 5 + 5 mL of methanol (≥80%). We then tried to minimize the volume of the elution solvent and observed that 4 + 4 mL of methanol gave similar recoveries. Recoveries of SPE using Isolute C18 cartridges with 4 + 4 mL of methanol as the elution solvent ranged from 82 to 109% for all target compounds.

3.3. Method validation

Due to the complexity of the samples, SPE was applied to 250 mL in all cases (samples of wastewater effluents and influents and effluents of drinking water and seawater desalination plants) except for the samples of wastewater influents where sample volume was 100 mL.

Previous to the method validation, the effect of ion suppression was evaluated for the studied environmental matrices. When the comparison of the signal intensity obtained in a direct injection of a standard solution (methanol) and that obtained after spiking an SPE extract shows signal differences higher than 20%, the SPE extracts can be diluted with methanol and reanalysed or the water samples can be diluted with ultrapure water prior to SPE procedure in order to minimize the ion suppression [7,26,27]. In our study, ion suppression was observed in influents and effluents of wastewater treatment plants (signal differences higher than 30%), while less-complicated matrices (samples from DWTP or SWDP including effluents from RO treatment) showed negligible loss of sensitivity. Consequently, influents were diluted 1:4 (v:v) and effluents were diluted 1:2 (v:v) before the SPE procedure (signal differences below 15%).

In the next step, SPE conditions were checked with the above dilutions. Recoveries ranged from 77% to 110% for influent samples and from 75% to 116% for effluent samples. Table 3 shows the results.

The limits of detection (LODs) of the compounds that did not appear in the samples were defined as the concentrations giving a response corresponding to a signal-to-noise ratio of 3:1. The LODs of the compounds that did appear in the samples were defined as the concentrations giving a signal average of plus three times the standard deviation. The LODs ranged from 40 to 200 ng L^{-1} for DWTP and SWDP samples, from 90 to 440 ng L^{-1} for WWTP effluents, and from 0.4 to 2 μg L^{-1} for WWTP influents.

The precision of the method was evaluated by preparing an effluent sample from WWTP A fortified with the analytes at levels of 200 ng L^{-1}. The repeatability ($n = 3$) and reproducibility between days ($n = 3$) gave results that were lower than 9% and 15% (% RSD), respectively, as shown in Table 3.

3.4. Presence of studied compounds in treatment plants

The developed SPE/LC–(ESI)MS method was applied to determine the presence of non-ionic and anionic surfactants in four kinds of water matrices (urban and industrial wastewater, drinking-water and seawater from different treatment plants). As expected, the levels found in drinking-water and seawater desalination sam-

Table 3
Validation method parameters.

Compound	SPE recovery (%) (n = 3, 500 μg/L) RSD ≤ 10%			RSD (%)[a]	RSD (%)[b]
	Standard solution	WWTP influent	WWTP effluent	n = 3 (200 ng/L)	
OP_1EO	92	92	77	1.4	15
OP_2EO	90	89	78	2	10
OPEOs (n_{EO} = 3–15)	95	97	75	4.7	8
NP_1EO	91	80	88	2.3	13
NP_2EO	90	82	92	1.7	9
NPEOs (n_{EO} = 3–15)	92	77	89	3.5	9
AEOs					
C_{12}AEOs	83	102	83	5.4	8
C_{14}AEOs	84	110	85	5.5	9
OP	102	77	102	9	10
NP	93	98	79	3	7
LASs					
C_{10}LAS	89	77	116	3	8
C_{11}LAS	86	78	114	2	7
C_{12}LAS	95	82	99	2	9
C_{13}LAS	109	80	83	4	8
AESs					
C_{12}AES	82	86	114	4	13
C_{14}AES	89	98	111	3.8	11

[a] Repeatability.
[b] Reproducibility between days.

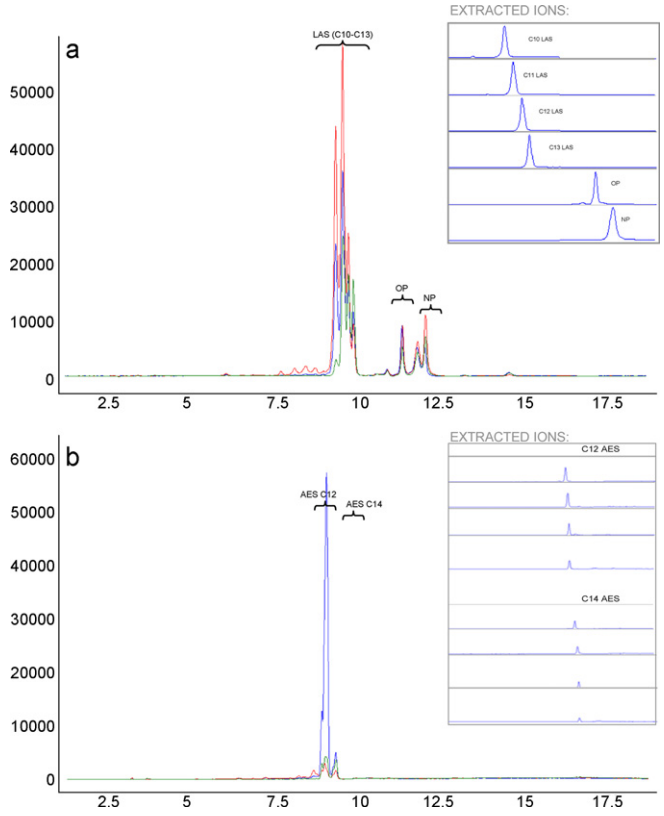

Fig. 2. Chromatograms for WWTP A streams in NI mode: (a) LASs and APs, and (b) AESs. Blue corresponds to influent, red to concentrate effluent and green to RO permeate effluent. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

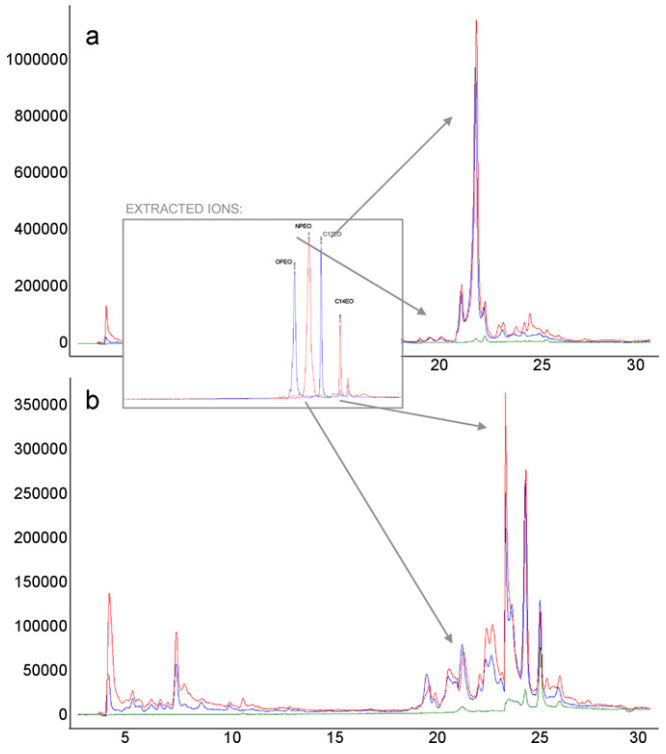

Fig. 3. Chromatograms for WWTP A streams in PI mode: (a) OPEO and C_{12}EO, and (b) NPEO and C_{14}EO. Blue corresponds to influent, red to concentrate effluent and green to RO permeate effluent. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ples were considerably lower than those found in wastewater [28].

Table 4 shows the concentration of the target compounds in all studied samples, influents and effluents of the plants that use secondary treatment (CAS or MBR) and influents and effluents of the plants that use a tertiary treatment with advanced membrane treatments such as UF or RO. As an example, Figs. 2 and 3 show the SIM chromatograms for compounds detected under NI and PI conditions, respectively, for WWTP A streams. Because of required sample dilution, the chromatograms do not show a visual rejection of the target compounds. However, this effect can be seen in Table 4.

In most cases, except for membrane treatments, for samples of the same origin, the effluent did not correspond exactly to the treated influent because of differences in hydraulic retention time. We were unable to perform a strict comparison between influent and effluent concentrations, but due to the homogeneity of the samples, we made a comparison in general terms.

Table 4
Concentration (μg/L) of target compounds in studied samples.

	WWTP A			WWTP B		WWTP C		WWTP D		DWTP		SWDP		
	Influent	Effluent	RO permeate	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	UF influent	UF effluent	RO permeate
LASs														
C_{10}LAS	629	236	0.3	1058	27	3	1	47	1	0.8	0.7	3	1.1	0.4
C_{11}LAS	857	379	2	2115	163	31	10	156	9	15	6	14	9	5
C_{12}LAS	311	93	2.0	570	79	12	5	71	6	6	3	10	8	7
C_{13}LAS	114	16	1.3	104	31	7	3	37	4	4	2	8	8	7
Σ LAS	1912	725	6	3847	300	53	19	312	20	25	12	36	26	20
OP	55	11	n.d.	340	114	40	12	15	8	49	10	5	4	n.d.
NP	8	9	n.d.	12	1	0.4	5	141	0	0.6	0.1	0.5	0.5	0.4
AESs														
$C_{12}EO_1S$	6222	18	5	2815	159	86	25	103	25	33	20	38	21	8
$C_{12}EO_2S$	8211	28	3	6654	223	91	56	156	28	37	15	22	13	5
$C_{12}EO_3S$	8692	71	3	7472	183	45	12	181	14	17	9	16	10	4
$C_{12}EO_4S$	8573	38	3	6986	178	37	9	218	11	16	8	12	7	3
$C_{12}EO_5S$	8810	28	3	8140	218	31	7	343	11	11	8	10	6	2
Σ C_{12}EOS	40,508	183	17	32,067	962	289	109	1001	90	114	61	98	58	21
$C_{14}EO_1S$	354	19	1.7	48	35	18	7	20	8	10	7	11	11	8
$C_{14}EO_2S$	335	20	1.5	81	58	13	6	37	8	7	5	7	7	5
$C_{14}EO_3S$	403	22	1.3	66	72	12	4	24	6	6	4	6	6	4
$C_{14}EO_4S$	430	22	1.4	119	85	11	4	34	7	6	4	5	4	2
Σ C_{14}EOS	1521	84	6	315	249	54	22	115	29	29	20	28	28	19
APEOs														
OP_1EO	n.d..	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.8	n.d.	n.d.	0.3	n.d.	n.d.	n.d.
OP_2EO	1.5	0.3	n.d.	1.5	0.3	1.5	0.6	1.6	0.3	n.d.	n.d.	n.d.	n.d.	n.d.
OPEOs (n_{EO} = 3–15)	1.9	0.6	0.05	1.0	0.3	0.8	0.2	7	0.1	0.7	0.2	n.d.	n.d.	n.d.
NP_1EO	n.d.	0.2	n.d.	n.d.	0.3	2	n.d.	n.d.	3	n.d.	n.d.	n.d.	n.d.	n.d.
NP_2EO	0.3	0.2	0.09	1.2	0.4	1.0	n.d.	n.d.	5	1.0	0.2	0.1	0.1	n.d.
NPEO (n_{EO} = 3–15)	1.9	2.0	0.09	6	1.0	3	0.5	102	3	1.7	0.6	0.3	0.2	0.2
AEOs														
$C_{12}EO$	11	2	0.2	8	4	0.7	0.4	4	0.2	2	0.8	1.5	1.0	1.5
$C_{14}EO$	3	3	0.1	1.0	2	0.3	0.3	30	0.5	0.9	0.4	0.4	0.3	0.8

n.d., Not detected.
RSD ≤ 15% (n = 3).

In all cases, non-ionic surfactants were either not detected or found at very low levels compared to the anionic surfactants. AESs and LASs were the main target compounds present in the WWTP A and B influents because these WWTPs mainly treat urban wastewater and those compounds are used for domestic purposes. The non-ionic compounds (APEOs and AEOs), which are mainly used for industrial cleaning, were found at low concentrations. However, its degradation products, OP and NP, were present at higher levels. This behaviour has also been reported by other authors [7,9,11]. In all cases, the effluents showed reduced concentrations of surfactants than influents.

In the industrial WWTPs (C and D), the same trend was observed. In influent WWTP D, the concentrations of anionic surfactants were found to be up to 100 times lower than in influent urban wastewater. In the effluent, the concentration of long-chain NPEOs decreased by nearly a factor of 40 (97% removed) while the short-chain species, NP_1EO and NP_2EO, appeared due to the degradation of the longer oligomers. The WWTP D water streams presented low values for all of the target compounds. The main compounds found were AESs and LASs. In the effluents, the levels of all of the target compounds were reduced. The estimated removals of the target compounds in the WWTP with CAS treatment (D) and in the WWTP with MBR (C) were quite similar, which is in agreement with the findings of other authors [9,10].

In the DWTP samples, the influent was river water, which is in accordance with the low levels found. The LASs and AESs values were 150 and 230 times lower than in wastewater, and non-ionic surfactants were found at similar levels. However, the main compounds found were the same as in wastewater, i.e., AESs, LASs, OP and NP. Similar results can be found in the literature [7,17]. In this case, due to the low influent levels, the effluent values were on the same order of magnitude as those of the influents.

From the results, we can conclude that the compounds are partially removed by the conventional treatment of the WWTP or DWTP. Anionic surfactants (LASs and AESs) are mostly removed, while the NPEOs and the AEOs are somewhat removed. This observation could be related to the low values of these compounds, which might affect the precision of the results.

These results indicate that conventional processes alone are not sufficient to remove the studied surfactants from waste streams (40–90%). Therefore, tertiary treatments with advanced membrane technologies such as RO in wastewater treatment plant or integrated UF–RO in seawater desalination plant were evaluated. Table 4 shows the results.

In the SWDP samples, the surfactant concentrations were lower than in the rest of the applications, comparable with the levels obtained for samples of the drinking water treatment plant; this result has been reported previously in the literature [7,17]. As it has been shown in Table 4, UF decreases up to 3 times most surfactant concentrations in seawater, while some compounds such as NP, NP_2EO and some AESs do not change their concentration. However, a post-treatment with RO membranes allows up to 3 times concentrations to be reduced. Thus, the combination of both membranes means a good alternative to conventional treatments to remove surfactants from seawater. In the case of urban wastewater from WWTPA, RO membranes are more effective in the removal of surfactants, especially LASs whose concentration is reduced up to 787 times. For the other surfactants, concentration reductions are from 3 to 13 times. In both wastewater and seawater treatment plants, the UF and RO membranes can further reduce the amount of the target compounds in the effluent water to obtain removals higher than 90%.

4. Conclusions

Solid-phase extraction (SPE) combined with liquid chromatography–mass spectrometry with electrospray (LC–(ESI)MS) was used to determine 16 non-ionic and anionic surfactants, including the various homologs and oligomers of OPEOs, NPEOs, AEOs and their degradation products, OP and NP as non-ionic surfactants, and LASs and AESs as anionic surfactants. The developed method is sensitive and simple, shows good linear range, and has detection limits lower than 50 $ng\,L^{-1}$ for most of the compounds tested.

Several samples from different treatment plants—including wastewater, urban and industrial, drinking-water, and seawater treatment plants—were analysed in order to assess the applicability of the method. Due to the high complexity of the samples and the presence of ion suppression, some of the samples required dilution prior to SPE/LC–(ESI)MS.

Almost all of the target compounds were detected in all of the samples, due to the fact that these species are commonly used in domestic and industrial applications.

The results indicate that the conventional processes alone are not sufficient to completely remove the studied surfactants from waste streams. The use of advanced membrane technologies, such as UF and RO, can further reduce the amount of target compounds in effluent water.

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References

[1] European Committee of Surfactants and their Organic Intermediates (CESIO), Statistics. http://www.cefic.be/cesio, 2008.
[2] P.A. Lara-Martín, A. Gómez-Parra, E. González-Mazo, J. Chromatogr. A 1114 (2006) 205–210.
[3] M. Cantero, S. Rubio, D. Pérez-Benito, J. Chromatogr. A 1067 (2005) 161–170.
[4] D. Berryman, F. Houde, C. DeBlois, M. O'Shea, Chemosphere 56 (2004) 247–255.
[5] R. Céspedes, S. Lacorte, A. Ginebreda, D. Barceló, Environ. Pollut. 153 (2008) 384–392.
[6] M. Petrovic, A.R. Fernández-Alba, F. Borrull, R.M. Marcé, E. González-Mazo, D. Barceló, Environ. Toxicol. Chem. 21 (2002) 37–46.
[7] S. González, M. Petrovic, D. Barceló, J. Chromatogr. A 1052 (2004) 111–120.
[8] S. González, M. Petrovic, D. Barceló, Chemosphere 67 (2007) 335–343.
[9] H.Q. Li, F. Jiku, H.F. Schröder, J. Chromatogr. A 889 (2000) 155–176.
[10] M. Clara, B. Strenn, O. Gans, E. Martinez, N. Kreuzinger, H. Kroiss, Water Res. 39 (2005) 4797–4807.
[11] S. González, M. Petrovic, D. Barceló, J. Hidrol. 356 (2008) 46–55.
[12] S. González, M. Petrovic, M. Radetic, P. Jovancic, V. Ilic, D. Barceló, Rapid Commun. Mass Spectrom. 22 (2008) 1445–1454.
[13] M. Ahel, W. Giger, M. Koch, Water Res. 5 (1994) 1131–1142.
[14] M. Petrovic, A. Diaz, F. Ventura, D. Barceló, Anal. Chem. 73 (2001) 5886–5895.
[15] H. Sanderson, S.D. Dyer, B.B. Price, A.M. Nielsen, R. van Compernolle, M. Selby, K. Stanton, A. Evans, M. Ciarlo, R. Sedlak, Sci. Total Environ. 368 (2006) 695–712.
[16] T. Frömel, T.P. Knepper, Trends Anal. Chem. 27 (2008) 1091–1106.
[17] P.A. Lara-Martín, A. Gómez-Parra, E. González-Mazo, J. Chromatogr. A 1137 (2006) 188–197.
[18] S. González, M. Petrovic, D. Barceló, Trends Anal. Chem. 26 (2007) 116–124.
[19] F. Houde, C. DeBlois, D. Berryman, J. Chromatogr. A 961 (2002) 245–256.

[20] J.E. Loyo-Rosales, I. Schmitz-Afonso, C.P. Rice, A. Torrents, Anal. Chem. 75 (2003) 4811–4817.
[21] M. Clara, S. Scharf, C. Scheffknecht, O. Gans, Water Res. 41 (2007) 4339–4348.
[22] M. Castillo, E. Martínez, A. Ginebreda, Ll. Tirapub, D. Barceló, Analyst 125 (2000) 1733–1739.
[23] M. Petrovic, D. Barceló, A. Diaz, F. Ventura, J. Am. Soc. Mass Spectrom. 14 (2003) 516–527.
[24] M. Petrovic, D. Barceló, J. Mass Spectrom. 36 (2001) 1173–1185.
[25] S. Wangkarn, P. Soisungnoen, M. Rayanokorn, K. Grudpan, Talanta 67 (2005) 686–695.
[26] J.B. Quintana, T. Reemtsma, Rapid Commun. Mass Spectrom. 18 (2004) 765–774.
[27] A. Göbel, C.S.M. Ardell, M. Suter, W. Giger, Anal. Chem. 76 (2004) 4756–4764.
[28] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, Water Res. 42 (2008) 3498–3518.