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Determination of alcohol sulfates in wastewater treatment plant influents and effluents by gas chromatography-mass spectrometry

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ABSTRACT

In the present paper, we developed an accurate method for the analysis of alcohol sulfates (AS) in wastewater samples from wastewater treatment plant (WWTP) influents and effluents. Although many methodologies have been published in the literature concerning the study of anionic surfactants in environmental samples, at present, the number of analytical methodologies that focus in the determination of AS by gas chromatography in the different environmental compartments is limited. The reason for this is that gas chromatography–mass spectrometry (GC–MS) technique requires a previous hydrolysis reaction followed by derivatization reactions. In the present work, we proposed a new procedure in which the hydrolysis and derivatization reactions take place in one single step and AS are directly converted to trimethylsilyl derivatives. The main factors affecting solid-phase extraction (SPE), hydrolysis/derivatization and GC–MS procedures were accurately optimised. Quantification of the target compounds was performed by using GC–MS in selected ion monitoring (SIM) mode. The limits of detection (LOD) obtained ranged from 0.2 to 0.3 $\mu g\,L^{-1}$, and limits of quantification (LOQ) from 0.5 to 1.0 $\mu g\,L^{-1}$, while inter- and intra-day variability was under 5%. A recovery assay was also carried out. Recovery rates for homologues in spiked samples ranged from 96 to 103%. The proposed method was successfully applied for the determination of anionic surfactants in wastewater samples from one WWTP located in Granada (Spain). Concentration levels for the homologues up to 39.4 $\mu g\,L^{-1}$ in influent and up to 8.1 $\mu g\,L^{-1}$ in effluent wastewater samples.

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1. Introduction

In recent years, the contamination of environment by organic compounds (e.g., pharmaceuticals, surfactants, endocrine disruptors, polymers) has prompted the development of regulatory policies that reflects an increase in public concern about their potential, but still unknown, adverse effects on wildlife [1]. Water is the mainstay of any environment and water degradation may have serious environmental consequences. Protecting the water thus means protecting the surrounding ecosystems of which water is an integral part. Water is at great risk of contamination, which compromises the long-term availability of water, so measures need to be taken in this respect to limit futher degradation of water and reverse negative trends towards quality improvement, protecting water and restoring the quality of water that is in poor condition. The implementation of European Directives 91/271/ECC [2] and 98/15/EEC [3] concerning urban wastewater treatment has increased the number of WWTPs operating in the European Union. Raw municipal wastewater usually undergoes mechanical treatment (primary sewage effluents, effluents from the pre-settling tank), and biological treatment (second sewage effluents, effluents from the settling tank after activated sludge treatment). Membrane bioreactor (MBR) is a promising technology for wastewater treatment, but there is not much information as to how organic pollutants behave in wastewater when these treatments are applied [4–6].

Surfactants are produced and consumed in large quantities, a result of their multiple applications (household and industrial cleaning products, personal care products, detergent formulations, emulsifiers, pesticides, adjuvants and wetting agents). More than 15 millions mt of surfactants are produced annually worlwide [7]. Approximately 65% of this production corresponds to anionic surfactants, being alcohol sulfates (AS) one of the main groups of anionic sufactants, with an estimated annual production of 102,000 mt in Europe [8]. The main use of AS is household cleaning products and personal care products. The use of surfactants is therefore strongly associated with human and industrial activity and relatively large amounts of these compounds are being continously released into the environment.

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AS, among others surfactants, commonly enter the environment via wastewater discharge, either directly (without treatment) or after degradation in WWTPs. After being used, these chemicals are usually discharged into municipal WWTPs where they are completely or partially removed from the wastewater by a combination of sorption and biodegradation processes [9–11]. After wastewater treatment, non-degraded surfactants together with their biodegradation products (metabolites) are discharged by WWTP effluents into surface waters [12–14].

In spite of their widespread use, there has been little attention to these compounds and few data about the presence of residual AS in environmental samples are available. Consequently, it is essential to have the analytical methodologies for the determination of AS in the different environmental compartments in order to understand their distribution, behaviour and final fate once they reach aquatic environments.

Only a limited number of articles discuss the determination of AS in environmental matrices. The methods described are mainly based on the use of gas chromatography (GC) [15] or liquid chromatography (LC) coupled to mass spectrometry [16–22]. Solid phase extraction (SPE) [15], ultrasonic-assisted extraction [16,17], Soxhlet [20,21], and more recently pressurised liquid extraction [19,22] have been used as extraction techniques. The main limitation with these methodologies is that the extraction process becomes tedious because of the complexity of the matrix. Moreover, when a preconcentration step is also carried out in order to obtain better limits of detection, the difficulty increases because the matrix is also concentrated [15,19,21,22]. Additionally, the lack of UV absorbance by AS represents one of the main problems when trying to detect them by liquid chromatography with UV-fluorescence detection (LC–UV–FLD). On the other hand, to our knowledge, no method has been described in the literature for the determination of AS by GC–MS in which hydrolysis and derivatization take place in one step allowing fast and accurate identification and quantification of AS.

In the present work, an accurate and sensitive analytical method was proposed for the determination of AS in wastewater samples based on a SPE procedure and an improved hydrolysis/derivatization reaction which takes place in one step prior to GC–MS. We focussed on the optimization of the hydrolysis/derivatization reaction to convert sulfates to trimethylsilyl derivatives using *N*,*O*-bis-trimethylsilyl trifluoroacetamide (BSTFA)/1% trimethylchlorosilane (TMCS) and pyridine. Trimethylsilyl derivatives are very volatile and can be easily analysed by GC–MS. After validation, the method was succesfully applied in the analysis of samples obtained from one WWTP located in Granada, Spain.

2. Materials and methods

2.1. Chemicals and reagents

All reagents were of analytical grade unless otherwise specified. Individual standard of fatty alcohol (FA) and alcohol sulfates (AS): sodium dodecyl sulfate (AS–C_{12}), 1-dodecanol (FA–C_{12}) and 1-tetradecanol (FA–C_{14}) (purity 98.5–99.0%) were supplied by Fluka (Madrid, Spain). Individual stock standard solutions (100 mg L^{-1}) of FA and AS were prepared in methanol and stored at 4 °C in the dark, remaining stable for at least six months. Working standard solutions were prepared immediately before use by appropriate dilution in methanol. Sodium 1-tetradecyl sulfate (AS–C_{14}), sodium *n*-hexadecyl sulfate (AS–C_{16}) and sodium *n*-octadecyl sulfate (AS–C_{18}) (purity 95–99%) were supplied by Alfa Aesar (Barcelona, Spain). 1-hexadecanol (FA–C_{16}) (purity 99.0%), 1-octadecanol (FA–C_{18}) (purity 99.0%), acenaphtene (purity $\geq$99.0%) used as internal standards, and *N*,*O*-bis-trimethylsilyl-trifluoroacetamide/1% trimethylchlorosilane used as derivatization reagent, were supplied by Sigma–Aldrich (Madrid, Spain). Pyridine (PAI grade) and hydrochloric acid 37% were supplied by Panreac (Barcelona, Spain). Methanol (HPLC gradient-grade) was purchased from Merck (Darmstadt, Germany). Milli-Q plus system (Millipore, Bedford, MA, USA) was used to purify water (18.2 MΩ cm^{-1}). Isolute SAX (500 mg/3 mL) and Isolute C_{18} (500 mg/3 mL) SPE adsorbent cartridges were purchased from Isolute Sorbent Technologies (Mid Glamorgan, UK).

2.2. Instrumentation and software

GC–MS analyses were performed on an Agilent 6890 series gas chromatograph (Agilent Technologies, Wilmington, USA) equipped with a 7683 series injector and a quadrupole mass filter 5976 network mass selective detector (MSD). ChemStation E02.00493 software was used for data acquisition and integration of chromatographic peaks. SPE was performed on a Supelco 12-port vacuum manifold (Supelco, Sydney, Australia) connected to a vacuum tank which is fitted to a pump. The system uses SPE cartridges (3 mL) attached to 150 mL reservoirs. Statgraphics 5.0 software package [23] was used for statistical and regression analysis.

2.3. Sample collection

Wastewater samples were collected from a MBR pilot plant located in Granada (South-East Spain). A total of 16 wastewater samples were collected on different days over one month, and kept in amber glass bottles. Samples 1a, 2a, 3a, 4a, 5a, 6a, 7a, 8a were collected from the primary clarifier of the WWTP and samples 1b, 2b, 3b, 4b, 5b, 6b, 7b, 8b were collected from the effluent of the bioreactor (Fig. 1). Samples were preserved immediately with 1% (v/v) formaldehyde to inhibit the biological activity of the analytes of interest until the chemical analyses were performed. Once in the laboratory, the samples were centrifuged at 5000 rpm (4050 × *g*) for 15 min to separate solid material, and they were stored refrigerated in the dark at 4 °C until analysis.

Spiked wastewater samples were prepared in a 100 mL volumetric flask by adding different volumes of standard solutions of analytes in methanol to 50 mL wastewater samples and filling up to the mark with methanol.

2.4. Extraction and derivatization procedure

Aliquots of 75 mL of wastewater samples were centrifuged at 5000 rpm (4050 × *g*) for 15 min. The residue was removed and 50 mL of wastewater sample were transferred to a 100 mL volumetric flask and methanol was added up to the mark. SPE

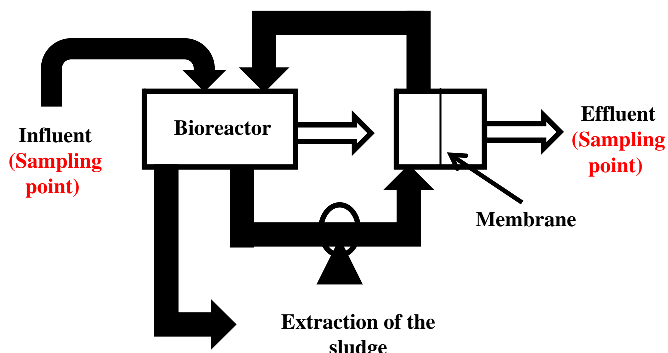

Fig. 1. Configuration of the the membrane bioreactor (MBR).

was used for purification and preconcentration of these water-methanolic extracts using 150 mL reservoirs and SAX cartridges loaded with 500 mg of solid-phase and preconditioned with 10 mL of methanol. A volume of 100 mL of water/MeOH (1:1, v/v) sample or reference standard solution was passed through the column. Then, 5 mL of methanol was used to rinse the cartridge. The cartridges were dried under vacuum for 5 min. The retained material was eluted with 10% HCl in methanol (5 mL), evaporated to dryness under a nitrogen stream and heated to 80 °C. For the hydrolysis/derivatization procedure, once the eluate was evaporated to dryness, 50 μL of pyridine were added. The mixture was shaken for 1 min at room-temperature to redissolve the residue, and then 50 μL of BSTFA/1% TMCS were added and shaken for 5 s in order to mix together. Finally, the solution was heated at 60 °C for 1 h and shaken before injection on the GC system.

2.5. Gas chromatography analysis

Analytes were separated on a ZB-5 MS Zebron capillary column (30 m × 0.25 mm i.d.; 0.25 μm film thickness) from Phenomenex (Torrance, CA, USA). The injection port of the GC was set at 180 °C. Samples were automatically injected using the split-less-injection mode. The injection volume was 1 μL. The transfer line of the GC to the MS was set at 290 °C and the electron impact (EI) ion source of the MS at 250 °C. The ionization energy was 70 eV. The oven temperature setting was as follow: initial temperature 120 °C for 5 min and then increased to 270 °C at 10 °C min^{-1} maintained for 3 min. The helium carrier gas (99.999% purity) flow was maintained at 1 mL min^{-1}. A solvent delay time of 3.5 min was used to prevent saturation of the ion multiplier of the MS instrument. In SIM mode two qualifier ions were used for the internal standard and AS–C_{12}, AS–C_{14}, AS–C_{16} and AS–C_{18} (Table 1). The dwell time per ion was 100 ms in all cases.

Table 1
Qualifier ions selected for SIM mode GC–MS analysis.

Compounds	Retention time (min)	Fragment (*m/z*)
Acenaphtene	7.07	153, 154
AS–C_{12}	8.44	243, 244
AS–C_{14}	11.22	271, 272
AS–C_{16}	13.46	299, 300
AS–C_{18}	15.44	327, 328

3. Results and discussion

3.1. Optimization of the GC–MS method

In order to avoid the hydrolysis reaction, derivatised fatty alcohols instead of alcohol sulfates were used to optimize the chromatographic and spectrometric conditions. Acenaphtene was used as internal standard. The GC method was optimised by injecting a mixture of the analytes in full scan mode. The influence of temperature in the injection port of the gas chromatograph on the analytical signal was analysed. Different temperatures, ranging 180–280 °C, were tested and 180 °C was considered optimal. Additionally, different oven temperature settings were tested in order to obtain the best compromise between resolution and analysis time. Other parameters such as initial column temperature (50 to 180 °C), ramps (3.5 to 10 °C min^{-1}) and final column temperature (215 to 290 °C) were also optimised. The optimal results were obtained using 120 °C for 5 min as initial column temperature and increasing at 10 °C min^{-1} up to a final column temperature of 270 °C. A flow of 1.0 mL min^{-1} was selected because this is the optimal flow recommended for the mass spectrometer turbo-pump.

The MS detection method was optimised first injecting each individual derivatised fatty alcohol in full scan mode in order to select the most intense ions with the highest *m/z* ratio for SIM mode. The chromatogram obtained in SIM mode using the above described conditions is shown in Fig. 2.

The chromatogram exhibits five peaks with retention times of 7.07, 8.44, 11.22, 13.46 and 15.44 min for the internal standard and the derivatised compounds, respectively. Moreover, the mass spectra show the base peaks at 153, 243, 271, 299 and 327 *m/z* corresponding to the molecular ion (target ion) for internal standard, and for the four homologues. The peaks at 154, 244, 272, 300 and 328 *m/z* corresponding to $[M+1]^+$ were used as qualifier ions.

3.2. Hydrolysis/derivatization procedure

AS must undergo an hydrolysis reaction to obtain the fatty alcohols, which can be easily derivatised allowing analysis

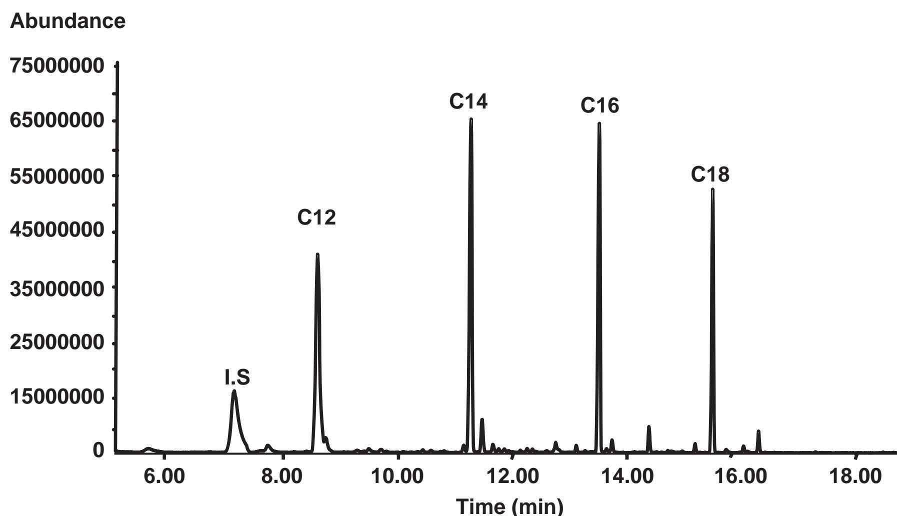

Fig. 2. SIM mode chromatogram of a standard mixture of internal standard (2.5 ppm) and trimethylsilyl alcohol derivatives of fatty alcohols (5 ppm).

by GC–MS. Derivatization reactions usually improve the chromatographic characteristics of the derivatives, providing them with higher volatility, polarity and thermal stability. Several derivatization reagents and procedures for the determination of AS by GC–MS have been described in the reviewed literature [15,24,25]. This work presents an improved procedure in which the hydrolysis and derivatization reactions are carried out in one step, which reduces the number of intermediate stages, thus resulting in a reduction of analyte loss. The main parameters affecting the hydrolysis/derivatization reaction (reaction time, temperature and amount of reagents) were optimised. Additionally, we analysed the application of heat at different temperatures to evaporate the SPE eluate under a nitrogen stream.

Reaction times between 45 and 120 min at 60 °C were studied, remaining the reaction efficiency constant and maximum for all compounds with reaction times >60 min, thus selected as optimum. The temperature was studied in a range of 50 to 100 °C. Although the maximum signals were obtained at 70 °C, an intermediate temperature of 60 °C, near the optimum for all compounds, was selected because of the lack of reproducibility observed at 70 °C. As for BSTFA/1% TMCS ratio–pyridine, ratios between 50 and 100% were tested, keeping constant the values for time and temperature previously optimised. 50% of BSTFA/1% TMCS was selected as optimum percentages to carry out the hydrolysis/derivatization reaction. Finally, regarding the effect of heat on the evaporation of the SPE eluate under a nitrogen stream, temperatures between 40 and 100 °C were analysed, and 80 °C was selected as optimum.

In order to evaluate the yield of the reaction for each AS homologue, the analyte/internal standard peak area ratios of fatty alcohol that underwent the hydrolysis/derivatization procedure were compared to the peak area ratios of pure AS, assuming that the reaction that takes place with the fatty alcohol provides 100% yield. The conversion percentages obtained were between 97.8 and 101.5%. These values show that the compounds can be quantitatively hydrolysed and derivatised by using our method.

3.3. Solid-phase extraction

Because of the complex nature of wastewater samples, SPE was the technique chosen for clean up and pre-concentration of the extracts. SPE procedure was optimised by adjusting those parameters that affect adsorption and desorption of analytes, i.e., nature of stationary phase and eluent. Two types of commercially available SPE sorbent cartridges (Isolute C_{18} and Isolute SAX) were tested. Since we found that fatty alcohols were retained on Isolute C_{18} cartridges, although the recoveries obtained with these cartridges were better, we finally selected SAX cartridges. The conditions proposed by Fendinger et al. [15] were set up prior to the optimization of the SPE procedure. The aqueous samples (100 mL) were passed through the SAX cartridges, previously activated with 10 mL of methanol, at a flow rate of 2.3 mL min^{-1}. The cartridges were dried under vacuum for 5 min and eluted with 5 mL of 10% HCl in methanol. Under these conditions the recoveries were approximately 72%. Different conditioning parameters were tested. First, the role of load composition was studied by testing samples (100 mL) containing from 0 to 100% of methanol in water. Table 2 shows the influence of methanol-to-water ratio on recovery of AS from SPE. For loads greater than 50% MeOH, recoveries decrease, probably due to the elution of analytes during loading. The optimal recoveries were obtained with 50% MeOH. Clean-up step was tested by using different volumes of methanol (from 1 to 10 mL). We selected 5 mL because this allows removal of fatty alcohols. Drying time was also analysed (ranging from 0 to 15 min) and the best recoveries were obtained when the cartridges were dried for 5 min under vacuum. Regarding eluent composition (from 5 to 30% v/v of HCl – 37%, w/v – in methanol) a significant increase in the recoveries was observed with 10% HCl in methanol. Table 3 shows the influence of eluent composition on SPE. Finally, different elution volumes (from 2 to 5 mL) were also tested and a 5 mL volume selected. These optimised conditions provided recoveries of approximately 89%.

3.4. Analytical performance and validation of the method

Calibration graphs were obtained in SIM mode for samples treated using the analytical procedure described above. Acenaphtene was used as internal standard. First, the method was applied to blank wastewater samples to confirm the absence of target compounds according within the LOD of the method. Absence of analyte contamination from the containers and materials used to handle the samples was accurately checked. Calibration curves were built using the analyte/internal standard peak area ratio versus analyte concentration for the GC analysis. Linearity of the calibration graphs was tested according to the Analytical Methods Committee guidelines [26]; the *lack-of-fit* test was applied to two replicates and two injections of each standard. The results for the intercept (a), slope (b), correlation coefficient (R^2) and probability level of the *lack-of-fit* test, P_{lof} (%), are summarised in Table 4. The behavior of all compounds was linear in the range between LOQ and 50 $\mu g \cdot L^{-1}$ with r values higher than 0.999 for each homologue.

Two fundamental aspects need to be examined in the validation of any analytical method: the limits of detection (LOD) and the limits of quantification limits (LOQ) in order to determine if an analyte is present in the sample. The LOQ is the minimum

Table 3
Influence of eluent composition in the SPE recoveries (% HCl, 37% w/v, in MeOH).

Eluent (%)	AS–C_{12}	AS–C_{14}	AS–C_{16}	AS–C_{18}
5	64.3	75.4	63.5	70.3
10	79.8	88.2	77.6	76.0
20	76.1	85.0	75.1	74.4
30	70.3	81.3	70.4	68.6

Table 2
Influence of MeOH/water ratio in the SPE recovery.

Compound	% Recovery					
	0% MeOH	5% MeOH	25% MeOH	50% MeOH	75% MeOH	100% MeOH
AS–C_{12}	63.5	68.8	70.4	79.3	71.5	69.9
AS–C_{14}	70.4	72.3	81.3	88.2	84.6	82.6
AS–C_{16}	67.5	69.8	71.4	77.3	72.0	71.3
AS–C_{18}	64.2	66.2	70.7	76.7	71.7	70.4

Table 4
Analytical parameters.

Parameter*	AS–C_{12}	AS–C_{14}	AS–C_{16}	AS–C_{18}
n	9	9	9	9
a	-4.0×10^{-4}	$-6.0\cdot10^{-4}$	-1.6×10^{-3}	-9.0×10^{-4}
s_a	2.0×10^{-5}	4.0×10^{-5}	5.0×10^{-5}	5.0×10^{-5}
b (L μg^{-1})	8.7×10^{-3}	8.6×10^{-3}	9.0×10^{-3}	9.4×10^{-3}
s_b (L μg^{-1})	9×10^{-6}	2×10^{-5}	2×10^{-5}	2×10^{-5}
r	1.000	0.999	0.999	0.999
$s_{y/x}$	1.1×10^{-4}	1.8×10^{-4}	2.3×10^{-4}	2.3×10^{-4}
P_{lof} (%)	7	25	28	18
LOD (μg L^{-1})	0.2	0.3	0.3	0.3
LOQ (μg L^{-1})	0.5	0.8	1.0	1.0
LDR (μg L^{-1})	0.5–50.0	0.9–50.0	1.0–50.0	1.0–50.0

* *n*, points of calibration; *a*, intercept; s_a, intercept standard deviation; *b*, slope; s_b, slope deviation; *r*, linear coefficient; $s_{y/x}$, regression standard deviation; P_{lof}, *P*-value for lack-of-fit test; LOD, limit of detection; LOQ, limit of quantification; LDR, linear dynamic range.

amount of analyte detectable in the sample, while the LOQ is the minimum amount that could be quantified. In this paper, these parameters were calculated by taking into consideration the standard deviation of residuals $S_{y/x}$, the slope *b* of the calibration curve and an estimate S_0 obtained by extrapolation of the standard deviation of the blank [27]. The LOD is $3\times S_0$ and the LOQ is $10\times S_0$. The LOD and LOQ ranged from 0.2 to 0.3 μg L^{-1} and from 0.5 to 1.0 μg L^{-1}, respectively, for AS–C_{12} to C_{18}.

The accuracy of the method in terms of trueness and precision was also studied. Due to the absence of certified materials, a recovery assay was performed in order to validate the method in terms of trueness. Blank wastewater samples were analysed to ensure that they did not contain the analytes or they were below the LOD of the method. Trueness was evaluated by determining the recovery of known amounts of the tested compounds in wastewater at four concentration levels (3.0, 15.0, 30.0 and 45.0 μg L^{-1}). Samples were analysed using the proposed method and the concentration of each compound was determined by interpolation from the standard calibration curve within the linear dynamic range and compared with the amount of analytes previously added to the samples. The obtained recoveries are shown in Table 5. The recoveries were very close to 100% (96 to 103%). To evaluate the overall precision of the method, intra- and inter-day precision (as relative standard deviation, RSD) were assessed at the four concentration levels. The procedure was repeated three times on the same day to evaluate repeatability and was repeated for seven consecutive days to determine inter-day reproducibility. Repeatability and inter-day reproducibility values (RSD) are summarised in Table 5. Precision and recovery values demonstrate the accuracy of the proposed methodology.

Table 5
Recovery assay, precision and trueness.

Homologue	Spiked (μg L^{-1})	Observed* ± SD (μg L^{-1})	RSD (%)	Recovery (%)
AS–C_{12}	**3.0**	3.1 ± 0.1	3.2	103
	15.0	14.4 ± 0.5	3.5	96
	30.0	30.2 ± 0.7	2.3	101
	45.0	44.2 ± 0.9	2.0	98
AS–C_{14}	**3.0**	3.1 ± 0.1	3.2	103
	15.0	14.6 ± 0.6	4.1	97
	30.0	30.7 ± 0.8	2.6	102
	45.0	44.4 ± 0.9	2.0	99
AS–C_{16}	**3.0**	2.9 ± 0.1	3.4	97
	15.0	15.1 ± 0.4	2.6	101
	30.0	30.5 ± 0.9	3.0	102
	45.0	44.2 ± 0.8	1.8	98
AS–C_{18}	**3.0**	2.9 ± 0.1	3.4	97
	15.0	15.4 ± 0.5	3.2	103
	30.0	29.3 ± 1.3	4.4	98
	45.0	44.1 ± 1.1	2.5	98

* Mean value of 21 determinations; SD, standard deviation; RSD, relative standard deviation.

Table 6
AS concentration observed in analysed wastewater samples.

Sample	*C ± SD (μg L^{-1})			
	AS–C_{12}	AS–C_{14}	AS–C_{16}	AS–C_{18}
1a	0.65 ± 0.03	4.3 ± 0.2	14.7 ± 0.5	11.2 ± 0.4
1b	ND	2.4 ± 0.1	5.7 ± 0.2	7.7 ± 0.3
2a	10.7 ± 0.4	24.0 ± 0.7	39.4 ± 0.6	30.3 ± 0.9
2b	ND	1.9 ± 0.1	5.8 ± 0.2	8.1 ± 0.3
3a	ND	1.4 ± 0.1	7.0 ± 0.3	3.2 ± 0.1
3b	ND	ND	1.4 ± 0.1	1.6 ± 0.1
4a	ND	6.7 ± 0.3	17.5 ± 0.7	9.4 ± 0.4
4b	ND	D	4.0 ± 0.2	5.4 ± 0.2
5a	0.81 ± 0.03	4.3 ± 0.2	9.2 ± 0.4	5.7 ± 0.2
5b	ND	ND	2.3 ± 0.1	3.1 ± 0.1
6a	0.66 ± 0.02	7.1 ± 0.3	20.2 ± 0.8	14.1 ± 0.4
6b	ND	D	3.7 ± 0.1	3.6 ± 0.2
7a	ND	1.5 ± 0.1	9.1 ± 0.4	2.7 ± 0.1
7b	ND	ND	ND	1.1 ± 0.1
8a	15.5 ± 0.6	12.7 ± 0.5	24.6 ± 0.7	11.2 ± 0.5
8b	ND	ND	ND	1.4 ± 0.1

* Mean value of 6 determinations; ND, < LOD; D, between LOD and LOQ.

3.5. *Application to wastewater samples*

The proposed method was applied to determine the amounts of AS in 16 wastewater samples collected from influents and effluents of one WWTP-MBR located in Granada (Spain). Samples 1a, 2a, 3a, 4a, 5a, 6a, 7a, 8a were collected from the primary clarifier influent, and samples 1b, 2b, 3b, 4b, 5b, 6b, 7b, 8b were collected from the effluent of a membrane bioreactor. Concentration values for six replicate samples are shown in Table 6. Concentration of each homologue was determined by interpolation in its standard calibration curve within its linear dynamic range. A representative chromatogram of a natural sample is depicted in Fig. 3.

The most abundant AS in wastewater are AS–C_{16} and AS–C_{18}, while AS–C_{12} is the least commonly found. The highest concentrations were detected in samples from influents, with higher concentrations for AS–C_{14} (24.0 μg L^{-1}), AS–C_{16} (39.4 μg L^{-1}) and AS–C_{18} (30.3 μg L^{-1}). The data shown in Table 6 suggest that the use of MBR plays an important role in AS elimination.

4. Conclusions

Determination and quantification of AS in wastewater samples by GC–MS was successfully performed. The method is based on preconcentration of the analytes by means of a SPE procedure and an improved hydrolysis/derivatization reaction performed in one step. Analytical performance of this method was validated and the method was successfully used for determination of AS in natural samples collected from a WWTP located in South-East Spain. In influent samples were found up to 39.5 μg L^{-1} of AS, while in effluent samples were found up to 8.1 μg L^{-1} of AS. The application of the method also suggests that the use of MBR as wastewater depuration system allows the degradation of AS in

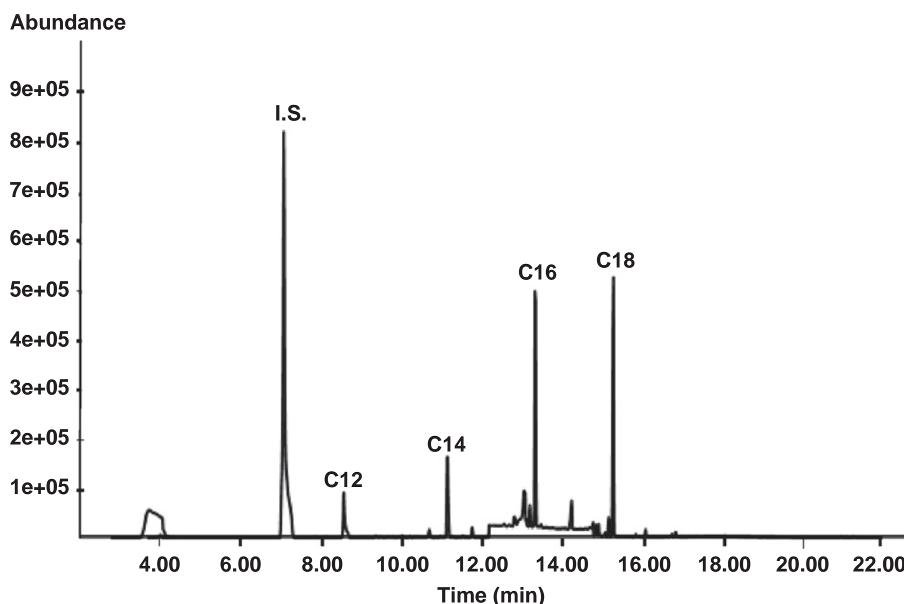

Fig. 3. SIM mode chromatogram of a natural sample (influent wastewater).

this environmental compartment and the production of effluents of high quality.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2012.06.065.

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