Available online at www.sciencedirect.com

SCIENCE DIRECT®

Talanta 64 (2004) 69–79

Talanta

www.elsevier.com/locate/talanta

Determination of photodegradation and ozonation by products of linear alkylbenzene sulfonates by liquid chromatography and ion chromatography under controlled laboratory experiments

J. Fernández [a], J. Riu [b], E. García-Calvo [c], A. Rodríguez [c],
A.R. Fernández-Alba [d], D. Barceló [b,*]

[a] *University of Caldas, Manizales A.A. 275, Colombia*
[b] *Department of Environmental Chemistry, IIQAB-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain*
[c] *Department of Chemical Engineering and Analytical Chemistry, Universidad de Alcalá de Henares, Alcalá de Henares, Spain*
[d] *Pestic. Resid. Research Group, Universidad de Almería, 04071 Almería, Spain*

Received 12 August 2003; received in revised form 12 January 2004; accepted 15 January 2004

Abstract

A Suntest solar simulator with arc xenon lamp was used to irradiate pure linear alkylbenzene sulfonates (LAS) standard and some commercial LAS solutions. The ozonation treatment was carried out in a pilot plant air-lift type reactor. Kinetic degradation curves were obtained showing an apparent first order reaction in both cases. Extraction and preconcentration of samples was carried out by off-line SPE using polymeric an RP-18 cartridges with recoveries varying from 77 to 93% for the LAS compounds. For LC chromatographic elution of LAS and degradation products an ion pair based on 5 mM triethylamine and 5 nM acetic acid had to the acetonitrile–water or methanol–water mobile phases. Fluorescence detection was achieved at 225 and 295 nm as excitation and emission radiation wavelength, respectively. Degradation by products were identified by liquid chromatography electrospray mass spectrometry detection (LC–ESI-MS). Ion chromatography (IC) was used to analyze refractory species such as oxalate, formate and acetate ions which were present in the treated solution even after 3 h of ozone treatment. The LAS mixture was almost totally degraded in less than 20 min using O_3/H_2O_2, the reaction being faster than in the case of catalyzed photodecomposition. TOC removal reached 84% after 3 h of ozonation process.

Keywords: Photodegradation; Ozonation; Linear alkylbenzene sulfonates; Liquid chromatography

1. Introduction

Linear alkylbenzene sulfonates (LAS) are currently discharged after use into waste waters and can reach surface waters and coastal sea waters [1]. According to recent statistical data LAS comprises about 50% of all used anionic surfactants. In 1995, the world production of LAS was ca. 2.8×10^6 tonnes but now more than 4×10^6 tonnes are consumed globally every year. LAS remains as the lowest-cost surfactant and its use is still dramatically increasing in developing countries such as China [3]. Commercial LAS mixtures were introduced in the mid 1960s consisting basically of five homologues from C_{10}LAS to C_{14}LAS, each one containing several phenyl positional isomers (26 in total: internal and external) Besides it, 3–8% DATs (dialkyl tetralin sulfonates, see Fig. 1c) and 3–6% iso-LAS (isomers with a methyl group branched to the linear aliphatic chain) may also be present in such a mix.

These linear compounds, unlike to branched ones, are usually classified as biodegradable, although several studies showed that biodegradation of C_{12}LAS, or DBS (dodecyl benzene sulfonate) is rather slow and inefficient [4,5]. Swisher and Schöbel [6,7] and lately, Di Corcia [2] have examined the biodegradation of the mixture of LAS and also DATs and iso-LAS and reported the formation of sulfophenyl carboxylic acids (SPCs) as a result of the primary biodegradation consisting in an oxidation of the external methyl groups followed by stepwise shortening of the alkyl chain via oxidative cleavage of C_2 units (β-oxidation). The

---

* Corresponding author. Tel.: +34-3-205-0063; fax: +34-3-204-5904

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.01.029

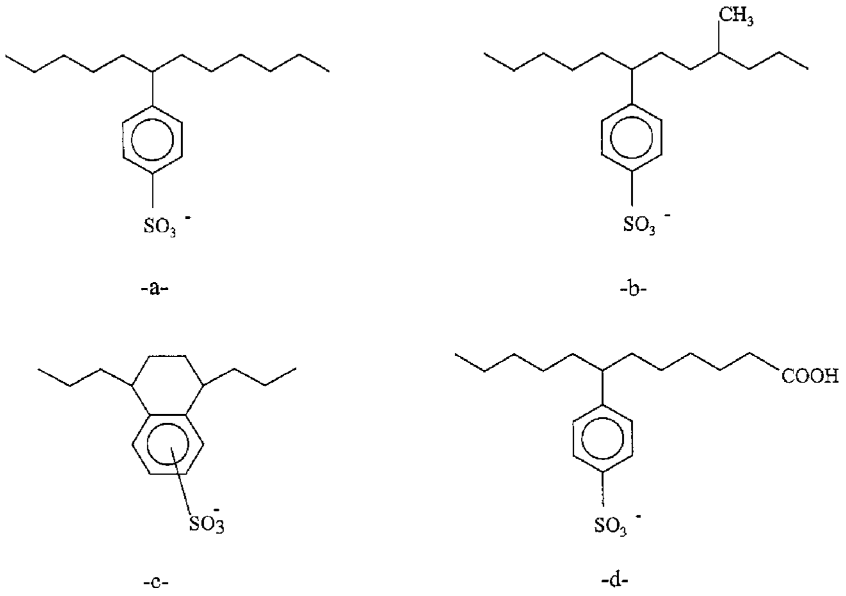

Fig. 1. Molecular structure of (a) an isomeric LAS homologue; (b) a typical type-I iso-LAS; (c) a DATS species; (d) a molecule of one SPC derivative.

second cycle involves opening the aromatic ring and/or desulfonation of SPC leading finally to CO_2, H_2O, inorganic salts and biomass. Kölbener et al. [8,9] followed the degradation of commercial LAS mixtures in laboratory, flowthrough system using immobilized activate sludge and found that Recalcitrant Organic Carbon (ROC) would be attributed to carboxylated metabolites of DATs and alkyl-branched LAS impurities (iso-LAS).

Nielsen et al. [10] have confirmed that the microbial population of domestic and industrial activated sludges, was very effective in the primary biodegradation of DATs and iso-LAS but was not capable of mineralizing most of the related metabolites. Some degree of persistency of the parent compounds in aquatic media has been also evidenced. Delvall et al. [11] using multivariate analysis while studying toxicity of LAS and some other contaminants in Cadiz Gulf (Spain) found that concentration of LAS remaining in sediment was around 2.6 mg kg^{-1} dry sediment.

Very few reports were found on other ways of LAS degradation such as the physicochemical ones, among which the advanced oxidation processes (AOP) have been lately considered as a group of emerging strong oxidation procedures for degradation of organic contaminants. Hidaka et al. [12] have examined photocatalytic degradation of linear dodecylbenzene sulfonate (DBS), which is the same C_2LAS homologue, by solar exposure in aqueous suspensions of TiO_2, using vertical and horizontal reactors. Semiconductor TiO_2 used as photocatalyst favored a more rapid degradation in contrast to dark and/or no-catalyzed experiments. The authors reported the detection of aldehydes and peroxides as intermediates species. Zhao et al. [13] compared the photo-oxidation of aromatic moieties in sodium dedecylbenzene sulphonate (DBS) and in sodium phenyldodecyl sulphonate (PDS) and could in fact show that the aromatic ring was photodegraded more easily than the aliphatic chain because the former is the primary target of UV radiation. Besides, the aromatic moiety in DBS was photo-oxidized more easily than in PDS because of the different position of the aromatic ring in the two isomeric structures being better positioned in DBS (nearer to the semiconductor surface) than in PDS.

No reports were found in the literature concerning the degradation of LAS by ozonation using O_3/H_2O_2, and to our knowledge this work is the first study about that topic. Masten and Davies [15] reviewed the use of ozonation to degrade organic contaminants in wastewater of pulp and paper production, dye and textile manufacturing, and several others. No reference to degradation of LAS has been mentioned in their review.

The use of integrated ozonation-biotreatment indicated that biotreatment is less expensive than ozonation, and sequential combining both procedures may reduce overall costs [16]. Kopf [17] reported the use of TiO_2 and O_3 in photocatalytic oxidation of different organic compound such as oxalic acid, pyrrol-2-carboxylic acid and found that the rate and yields of the combined TiO_2/O_3 process were higher than when either the TiO_2 or the O_3 was used. However O_3/H_2O_2 was not considered in that work. A pre-treatment by ozonation prior to photocatalytic treatment using TiO_2 facilitates the degradation of some stable agricultural chemicals as it was shown by Tanaka et al. [18]. For a long time DBS analysis was carried out by traditional UV spectroscopy (absorbance of benzene group, 224 nm) or by the dye-extraction procedure [19] following the mineralization degree through CO_2 evolution by GC or by analyzing other ionic species such as $SO_4{}^{2-}$ as well. Fendinger [20] and Field [21] respectively, also analyzed LAS and AE (alcohol polyethoxylated surfactants) by SFE/GC and GC–MSD involving derivatization. In our group an analytical method for LAS and SPC determination in waste water using an off line extraction procedure and LC–ESI–MS identification and quantification was developed [1]. Determination of LAS was also carried out by Riu et al. [22] using Capillary Electrophoresis with electrospray-MS detection (EC–ESP-MS) after 200-fold off-line extraction and simultaneous preconcentration.

Most of the reports about degradation are related to the C_{12}LAS homologue but no reports were found concerning the degradation of the four-LAS typical mixture commonly present in detergent products discharged into wastewaters. So, the purpose of this work is to explore ozonation and photocatalytic processes as well as of degrading the most common mixture of LAS frequently in municipal and industrial wastewater.

2. Experimental section

2.1. Materials and methods

2.1.1. Solvents and standards

The LAS standard mix was supplied by Petroquímica Española S.A. (Spain) with the following composition: 3.9, 37.4, 35.4, 23.1%, for C_{10}-, C_{11}-, C_{12}-, and C_{13}LAS, respectively. No individual LAS standards were available.

For the ozonation process a 43.6% LAS containing semisolid raw material with the same mentioned proportional composition, dissolved in distilled water was used.

All of the compounds and solvents used were analytical and chromatographic grade, respectively.

2.1.2. Irradiation

Photodegradation was carried out with natural solar light and by using a CPS Suntest device from Heraus–Hanau (Germany) equipped with a 550 W arc xenon lamp. Solar irradiation was carried out during the summer season in order to assure a comparable number of hours of solar exposure. Typically 500 ml of 0.2 ppm LAS solution in deionized and tap water were irradiated in a quartz receptacle. Samples of 50–150 ml were taken each half an hour in the case of non catalyzed experiments, and each 10 min in the case of catalyzed ones. Samples were put in amber bottles which immediately were covered with aluminum foils and put in the freezer until the extraction process could be carried out. After that, an off-line solid phase extraction (SPE) procedure followed by liquid chromatographic analysis was carried out to determine the concentration of the samples. In some cases TOC measurements were done. Oxygen was provided when the quartz receptacle was opened every time for sampling. For the photosensitized process, the TiO_2 suspensions and the Fe^{3+}/H_2O_2 solutions were prepared and used as in previous experiences in our group [23].

2.1.3. Ozone treatment

The ozonation process was carried out in a laboratory made, pilot-plant scale, Airlift reactor. Its main characteristics were already described in a previous paper [24]. In the reactor 50 l of 10 ppm LAS solution in distilled water underwent a uniform 252 l h^{-1} flow of 10% O_3 in O_2 gaseous mix from an ozone generator. When the process has started an unique injection of H_2O_2 is required to have an initial concentration of 22.1 μm in the reactor. The pH value was monitored and regulated by adding NaOH when it was necessary. Different experimental condition and dynamics of reactants addition were assayed in order to find the optimal kinetic behavior and yield in the reacting system.

2.1.4. Analytical measurements

An ozone analyzer was set on line to the airlift reactor in order to measure the concentration of O_3 in both input and output. The remaining O_3 was eliminated by catalyzed decomposition, to avoid its releasing in the laboratory atmosphere. Samples of LAS solution were taken (at 0.5, 10, 15, 20, 30, 45, 60, 90, 120, 150 and 180 min) for measuring current concentrations of LAS, O_3, H_2O_2 and TOC, present in the reaction system. Concentration of O_3 and H_2O_2 were determined by spectrophotometric procedures using Indigo colorimetric method 4500-O_3 B, and by peroxydase-catalyzed oxidation in the *N*,*N*-diethyl-*p*-phenylendiamine (DPD) method, respectively [25].

For LC–MS analysis a VG Platform from Micromass (Manchester UK) equipped with a quadrupole mass spectrometer and Megaflow ESI-MS interface was used. MS detection conditions were similar to those discusses elsewhere [1,22]. A voltage f 3.7 kV was applied to the needle tip. The extraction cone voltage was set at −20V and selected ion monitoring (SIM) modality was used in order to get maximum sensitivity. Then 50 mM ammonium acetate was added to the mobile phase to maintain a constant pH value during the analysis.

A Perkin-Elmer LC 250 with LC 240 fluorescence detector was used also for LAS determination. For the LC fluorimetric detection, excitation and emission wavelength were 225 and 295 nm, respectively. A LiChroCart RP-18 (75 mm length × 4 mm internal diameter) column from Merck (Darmstadt, Germany) was used with a flow rate of 0.8 ml min^{-1} and a solvent gradient previously used in our group: eluent conditions varied from 95% of solvent A (H_2O) and 5% of solvent B (AcN/H_2O: 80/20) to 100% of solvent B in 20 min. Isocratic conditions were then maintained until complete elution of all compounds. 5 mM trethylamine and 5 mM acetic acid had been previously added to both A and B.

The total organic carbon variation was followed in a TOC-5000 Shimatzu system following the differential mode TC-TIC = TOC, where TC is total carbon, TIC is total inorganic carbon and TOC is total organic carbon.

2.1.5. Extraction and preconcentration

The off-line extraction procedure was carried out in an ASPEC XL Gilson apparatus with C-18 and polymeric

Isolute ENV+ cartridges previously conditioned with 7 ml of MeOH 3 ml of H_2O acidified to pH 3. Elution was done with 10 ml of MeOH.

The used method combining SPE with polymeric ENV+ cartridges and LC–MS permitted the identification and quantification of C_{10}- to C_{13}LAS and some SPC by monitoring the diagnostic ion at *m/z* 183 and the base peak at $[M - H]^-$. The detection limits were in the low range ppt range when 150 ml were preconcentrated. Recoveries of the different analytes were reported in a previous work [29] and varied from 77 to 93% and from 60 to 97% for LAS and SPC, respectively.

Calibration data in LC–FLD analysis were similar to those of LC–MS although in most of cases sensitivity of the former was not higher than in LC–MS.

3. Results and discussion

The different trials carried out on simple (no catalyzed) photodecomposition of the LAS mixture show that a slow process with natural solar light and also with Xe lamp irradiation takes place. So, when an aqueous solution of standard LAS mixture of 0.2 mg l^{-1} dissolved in milli-Q water was affected by natural and simulated sun radiation, only after 3 h the concentration of the LAS mixture components started slightly to decrease.

Concentration reduction curves of LAS homologues obtained from several simple (non catalyzed) photolytic treatments of this sulfonate mix solution exposed to Xe lamp irradiation for time periods of at least 7 h showed that in these conditions there was no significant decreasing of LAS concentration.

When the experiment was repeated with natural solar light exposition the removal percentages of the same components was even lower; the distribution of removal percentages between major and minor components was however similar to that in the former experiment with lamp irradiation. Similar results in terms of rate and removal percentage were obtained when tap water was used instead of pure one. The maximum LAS degradation yields reached in 7 h of both natural an simulated irradiation ranged from 8.0 to 13.2%.

Semiconductor TiO_2 (Degussa P-25) and Fenton reagent in the form of Fe^{3+}/H_2O_2 were then used in this study to catalyze the photodegradation of LAS. The concentration of TiO_2 suspension in the irradiate LAS solution was 10 mg l^{-1}. The concentration of $Fe^{3+}$and H_2O_2 solution were 15 mg l^{-1} and 0.05% (v/v) respectively, according to previous experiments carried out in our group with other contaminants. Extraction and preconcentration were carried out in the same way as explained above. Some results obtained in both kinds of experiments with these two catalysts are summarized in Tables 1 and 2. In both cases an increase in the degradation reaction rate of all four homologues was observed in comparison to the non-catalyzed procedure.

When using TiO_2 as photosensitizer in the already mentioned conditions, removal percentages reached in 1 h of treatment had varied between 71.3 and 85.2% as shown in Table 1. This shows a considerable increase in degradation yields as compared to the former 7 h of simple photolytic treatments.

The TiO_2 photocatalyzed degradation, at least for the major components of the LAS mixture (that is C_{11}- and C_{12}LAS) was clearly a first order kinetics reaction.

Consequently rate constants and the half life times were evaluated from the known first order kinetic equation

$$C = C_o \exp(-kt) \qquad (1)$$

where C is current concentration; C_o initial concentration; k the rate constant and t is current time. Assuming the same first order for all degrading components of the LAS mixture the values of half life times and the rate constants are calculated and summarized Table 3. In this same table one may notice that the reaction rate for C_{12}LAS (taken as an example) is slightly higher at pH 3.4 than at pH 8.7. And both values are slightly lower than those using Fenton reagent as catalyst. Similar tendency is observed for the rest of the LAS homologues.

In biological degradation of LAS it is known that the carbon chain length is relevant because of the distance principle [6]. However, in photodecomposition, it is not totally clear

Table 1
Concentration evolution of the four LAS homologues photodegraded in the solar simulator in presence of TiO_2 suspension at two different initial pH values: 3.4 and 7.8

Time (min)	C_{10}LAS, *m/z* 297 ($\mu g\,l^{-1}$)		C_{11}LAS, *m/z* 311 ($\mu g\,l^{-1}$)		C_{12}LAS, *m/z* 325 ($\mu g\,l^{-1}$)		C_{13}LAS, *m/z* 339 ($\mu g\,l^{-1}$)	
	pH 3.4	pH 8.7	pH 3.4	pH 8.7	pH 3.4	pH 8.7	pH 3.4	pH 8.7
0	7.8	7.7	74.8	75.1	70.8	70.9	46.2	45.5
10	7.0	7.0	57.0	57.5	55.0	62.3	37.0	38.0
20	6.4	6.1	43.4	44.0	43.0	49.9	32.3	31.8
30	5.8	5.7	33.0	33.7	33.3	38.8	27.1	26.7
40	5.2	5.0	25.2	36.6	25.8	30.6	22.6	22.3
50	4.7	4.8	19.2	19.8	19.9	24.1	18.9	18.7
60	4.3	4.3	14.6	15.1	15.4	19.0	15.8	15.6
70	3.8	3.9	11.1	11.6	12.1	13.4	13.2	12.0

Initial LAS concentration: 0.2 mg l^{-1}. Ions used for LAS monitoring: *m/z* 297, 311, 325, 339.

Table 2
Degradation of a 0.2 ppm LAS standard mix solution photosensitised with Fenton reagent in the Suntest solar simulator

Irradiation time (min)	C_{10}LAS *m/z* 297 ($\mu g\,l^{-1}$)	C_{11}LAS *m/z* 311 ($\mu g\,l^{-1}$)	C_{12}LAS *m/z* 325 ($\mu g\,l^{-1}$)	C_{13}LAS *m/z* 339 ($\mu g\,l^{-1}$)
0	7.2	72.1	68.3	4.4
10	5.3	50.5	47.0	3.07
20	3.7	35.4	33.8	2.14
30	2.6	24.8	23.1	1.49
40	1.8	17.3	15.8	1.04
50	1.3	12.2	11.8	0.72
60	nq	8.6	7.9	0.51
70	nq	3.7	nq	nq

nq: non quantified.

which role the difference in the aliphatic chain length of LAS plays on the degradation kinetics. It should be expected not to have a decisive influence, because the aromatic ring is the primary target of the photo-oxidative process. A possible explanation for the predominant photodecomposition of C_{11}- and C_{12}LAS should be explored from the mechanism of the process. But according to the most photo-oxidation reaction mechanism [19] a previous adsorption of the anionic surfactant molecules of LAS to the positively charged photoactivated centers on the TiO_2 semiconductor surface should take place. Molecules of LAS compete for the active centers in the surface of TiO_2 where the adsorption may take place. Then the photooxidation attack of OH (and/or OOH) radicals upon the LAS takes place in the same surface of TiO_2 particles or, at least no far from there: within a few mono-layers around the same surface of TiO_2 particles (or, at least no far from there: within a few mono-layers around the photocatalyst surface). These radicals might have been generated on the irradiated TiO_2 surface.

From the molecular structure of LAS (Fig. 1a), it may be assumed that it is the aromatic ring, the moiety that will be first attacked. This process must be favored by the nearer position of the ring to the adsorbed $SO_3{}^-$ moiety and consequently to the TiO_2 surface as previously discussed [13]. It should be concluded that the carbon chain length probably does not play a determining role in the rate of degrading photoreaction of LAS, heterogeneously catalyzed by TiO_2. Observed predominance in the decomposition rate of C_{11}- and C_{12}LAS would rather be associated with the rate of adsorption to the TiO_2 phase, which must be favored for C_{11}- and C_{12}LAS are the homologues of higher initial concentration.

3.1. LAS degradation with photo-Fenton

Using photo-assisted Fenton reagent in the above described experimental conditions results in an even more rapid degradation reaction of the LAS mix components than using TiO_2.

The process was carried out in an acidic media (pH around 3) in order to prevent ferric ion precipitation as hydroxide; diluted H_2SO_4 was added for this purpose till the desired initial pH value. Other authors [26] have also found that the optimum pH for using Fenton mixture in oxidative procedures (with or without light) of different contaminants should be 2.8 to 3.0. Results in Table 2 show the evolution of the LAS homologue concentrations in a standard mix solution irradiated with Xe lamp in presence of Fenton reagent. As it is observed removal percentages reached in 1 h are higher than in the TiO_2 experiments. In Table 3 the rate constants estimated on the base of first order model are compared.

Second order rate constant for OH radical reactions with typical C–H and unsaturated C–C organic bonds were recently reported while studying photodegradation of pesticides [26]. However the observed rate constants reported in the same work for the photo-Fenton degradation of the respective active ingredients and estimated from the initial rate procedure were in all cases first order constants. It was also found that reaction rate of LAS degradation was increased with the concentration of Fe^{3+}. This is consistent

Table 3
Comparative rate constants K_c, half life times $T_{1/2}$ and removal percentages for C_{12}LAS taken as an example

Experimental conditions	Rate constants, K_c (seg^{-1})	Half life times, $T_{1/2}$ (seg)	Removal percentage (%)	Treatment time
Direct photolysis			8–13.2	7 h
Irradiation-*n*-TiO_2 pH 3.4	0.0252	27.5	78.2	60 min
Irradiation-*n*-TiO_2 pH 8.7	0.028	29.2	73.2	60 min
Irradiation with				
Fenton	0–0.339	19.3	88.4	60 min
Ozonation	0.152	4.57	100	20 min

with previous findings which showed that the oxidation rate of different organic substrates in presence of Fenton reagent depends both on the peroxide and (even more) the Fe^{3+} or Fe^{2+} concentrations [26]. But in such cases the LC chromatographic signals (peaks and base line) were worse, making more difficult the interpretation, probably due to incomplete clean up implicated in the SPE procedure when Fe^{3+} concentration has increased.

It is well known in both cases (TiO_2 and Fenton) that OH radicals are the species which exert the oxidative action over the organic contaminant. But while in presence of TiO_2 this reaction between the OH radicals and the organic substrate molecules takes place in the TiO_2–water interface, in presence of Fenton reagent it should occur in the bulk of the solution, where the four LAS homologues should be homogeneously dispersed (no micelles formation should take place at the present concentration). This will also explain a more effective degradation using Fenton reagent as photocatalyst.

The use of photo-assisted Fenton reagent is a good alternative for LAS decontamination because it is fast, effective and low-cost way degradation technology. But there is a serious limitation for its broad implementation in waste water treatment system related to the management of the required acidic pH values in the treatment facilities.

3.2. Ozonation

The following advanced oxidation process (AOP) tested in this study to check the oxidative decomposition of LAS was ozonation with the use of O_3/H_2O_2, and thus exploring possibilities of application for elimination of surfactants and their transformation products TPs.

In the ozonation process carried out in pilot plant Airlift reactor the degradation of LAS has shown a higher reaction rate than in photochemical experiments. So when a 10 ppm LAS solution in water was treated with the ozonation mixture O_3/H_2O_2, LAS concentration in all the cases was reduced to less than 1 mg l^{-1} in the first 3 min.

In Fig. 2a, LAS concentration versus time profile in an ozonation experiment at pH 9.3 is shown. This alkaline pH, as said below, was found as the optimum for degradation of LAS by ozonation. In this case total degradation of all four homologues was completed in 15 min, when LC-analytical signal decreased under LOD levels. Again, the degradation of the major components of LAS mix clearly behave as an approximate first order reaction. Rate constant and half life times were evaluated in the same way as in the former photochemical degradations. For C_{11}LAS, as an example, the rate constant K_c and half life time $T_{1/2}$ were 152 min^{-1} and 4.57 min, respectively. Compared to the respective values in Table 3 it is noticed that ozonation was faster and more efficient than photocatalyzed degradation. Several alkaline pH were tested (e.g. 11.5 and 9.3) as it is shown in Fig. 2a and b. In the same way, several forms of addition the H_2O_2 solution were assayed: (a) step y step injecting little solution volumes in the bottom region of the reactor every 5 min during all the time of the process, (b) adding a unique amount at the beginning of the process, (c) no adding H_2O_2 at all, etc. this was done in order to get optimal operation conditions. In relation to this assessment some authors have found that the performance of some AOP may be influenced even by the dynamics of oxidant addition [27]. However, results of the experiments at the different assayed conditions reflect a high decomposition rate and subsequently a considerable high percentage of parent compounds degrade in a relatively short period of time. In all samples treated during 45 to180 min LAS were only detected, if so, at no quantifiable levels.

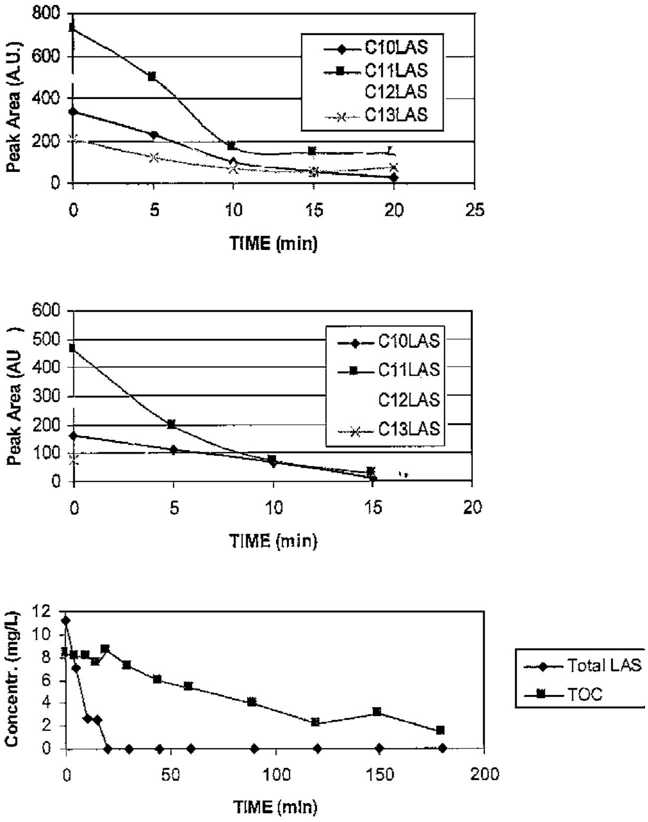

Fig. 2. (a and b) concentration variation of the LAS mix components in an ozonation process at two different conditions of pH and H_2O_2 addition. (c) Decaying of summary concentration of all four LAS homologues compared with TOC variation.

The pH conditions selected for ozonation process ere alkaline in all cases. It had been already found that the O_3/H_2O_2 oxidant mixture operates better than O_3 alone; and even better at high pH conditions (where the rate of hydroxyl radical formation is higher) than al low pH values [15]. Under acidic conditions where the rate of formation of OH is slow several organic pollutants are essentially unreactive. From the results obtained in several trials it was concluded that among the optimal conditions for the degradation of 10 ppm solution of LAS in pure water were pH moderately alkaline (around 9.3) and the addition of hydrogen peroxide solution in a single initial injection when the process has just started.

3.3. TOC removal

Despite of the rapid disappearance of parent LAS compounds, Total organic carbon (TOC) did not decrease as fast as the LAS concentration. In fact, although in most of cases after 30 min ozonation there were no detected signals of any of LAS homologues in the samples, TOC decreasing only reached 13.6% at the same time.

Fig. 2c shows the simultaneous behavior of the total LAS concentration and TOC evolution along the 180 min treatment. The relatively high TOC values decreased slowly and after 180 min, when ozonation process was over, only a

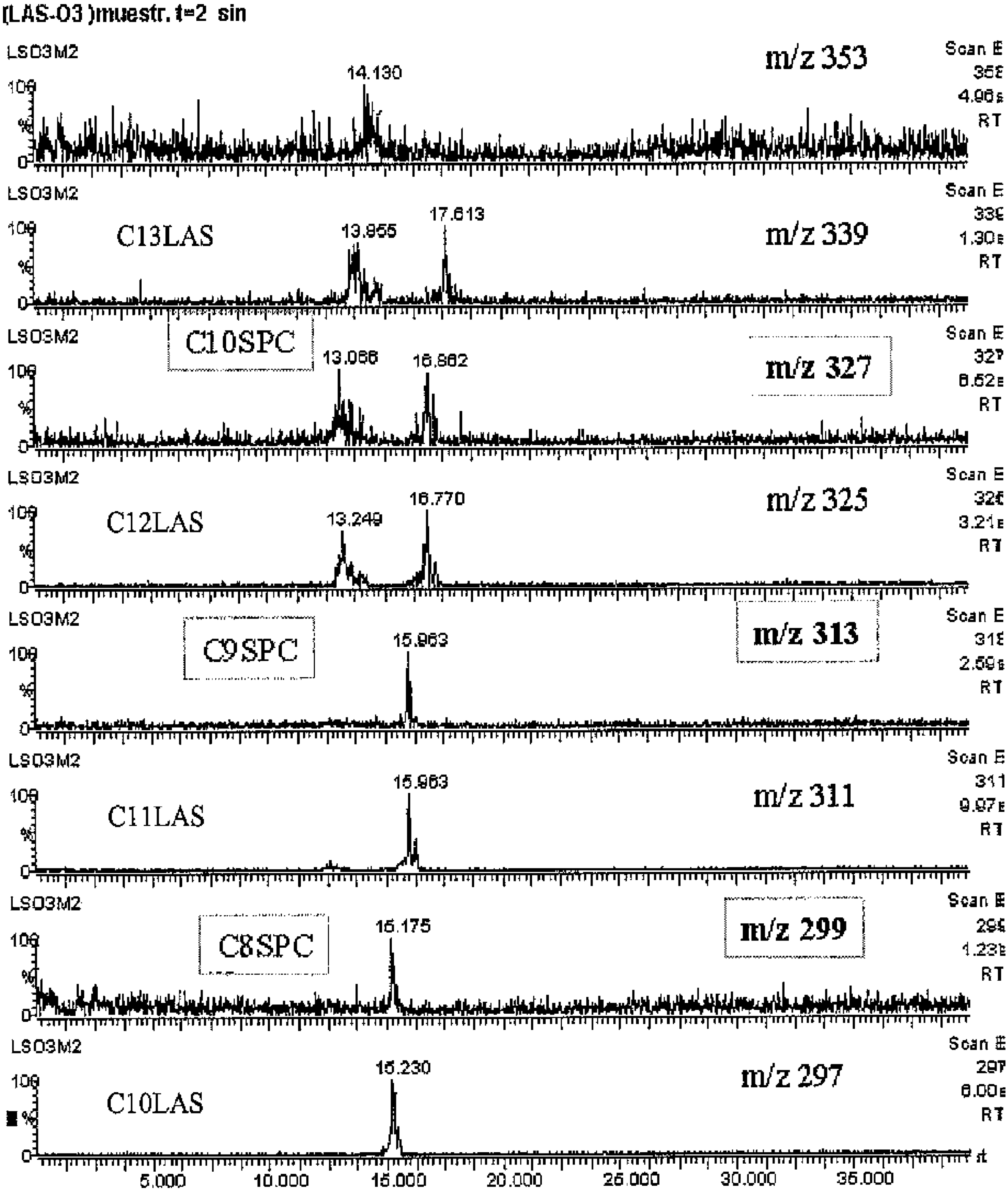

Fig. 3. Some cone-extracted *m*/*z* peaks corresponding to the LAS and SPC derivatives, from total ion chromatogram of a degrading by ozonation sample.

refractory 16.2% of the initial TOC was still remaining in the system.

3.4. Identification of transformation products (TPs)

The persistency of some remaining TOC while the LAS mix components were almost totally degraded, means that some other organic compounds (probably having its origin from the LAS decomposition) remain in the solution. For this reason, the identification and quantification of some of these eventual transformation products, responsible of the refractory TOC, were carried out. SIM and Full scan LC–ESI-MS in positive and negative modes along with the use of ion chromatography (IC) were the tools for this approach.

While analysis of parent compounds was carried out with fluorescence detection (a well recognized sensitive technique in LC for LAS determination [28]), LC–ESI-MS was used for the same purpose and also for detection and identification of TPs. The selected ion monitoring (SIM) mode of detection with a low cone voltage (−20 V), was used for quantification purposes, as it provides higher sensitivity. In full scan mode several cone voltages (from –20 till −80) were used. Rising in this way the ion fragmentation the identification of several TPs was possible, as it gives structural information for the detected compounds.

As it is shown in Figs. 3 and 4, besides the four LAS signals, additional chromatographic peaks corresponding to *m*/*z* signals such as 299, 313 and 327 were found and were the LAS metabolites, C_8SPC, C_9SPC and C_{10}SPC, previously found by our group while monitoring real samples [22,29].

Other compounds corresponding to *m*/*z* values such as 157 and 141 were also found. On base to their respective spectral signals, these peaks were assigned to the ionic species such as $C_6H_5–SO_3^-$ and $C_6H_5–SO_2^-$. Consequently the presence of those intermediate ions in the degradation process is suggested (although no standards were available to confirm such hypothesis). Similarly, the observed *m*/*z* 173 and 191 correspond to molecular masses of the $C_7H_9SO_3^-$ and $C_7H_{10}–(OH)–SO_3^-$ compounds resulting from the ring opening of methyl benzene sulfonate and its hydroxyl derivative, respectively. Both are presented in Fig. 5a and b. The *m*/*z* values of 137 and 179 were also found. The former is

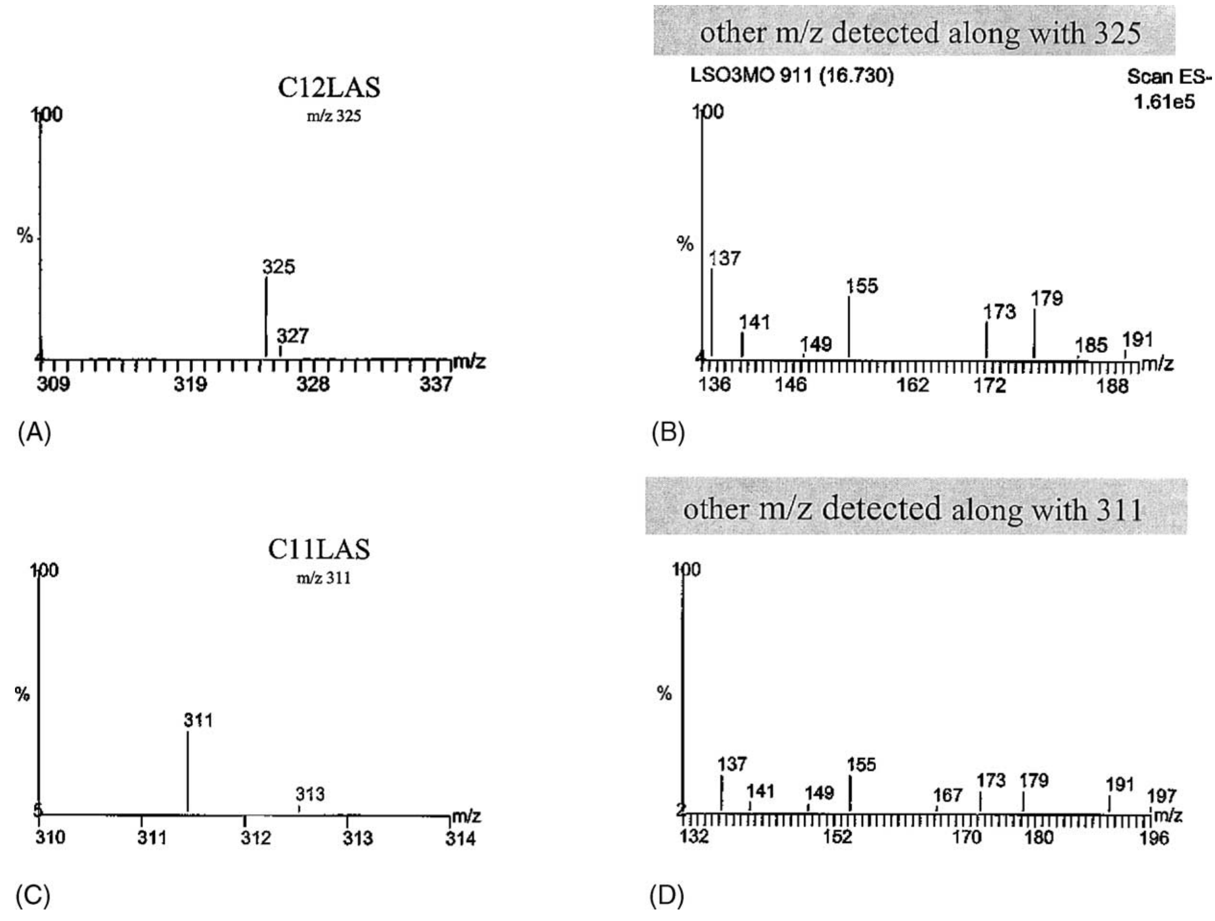

Fig. 4. Spectral signals of (A) chromatographic peak of C_{11}LAS, (B) the additional peak formed during its degradation (see also Fig. 3), (C) peak of C_{12}LAS and (D) the respective additional peak formed during its degradation (see Fig. 3 also).

pretty abundant and both should correspond to the aliphatic adducts such as CH_3–$(CH_2)_m$–SO_3^-, where m is 3 and 6, respectively (Fig. 5f).

The confirmation of the presence of this intermediate species will allow to clarify the different steps of mechanism of LAS degradation involving not only the known β- and w-oxidation [6] but dealkylation, ring opening and adduct formation as well.

3.5. Ion chromatography

Ion chromatography was also carried out in almost all of the ozonation samples. It enabled the detection of low molecular short anionic species such as deprotonated formic acid, acetate, oxalate and sulfate ions, which were no detected by LC–MS. Fig. 6 shows a typical chromatogram of the analyses of these ionic compounds. The evolution of the concentration of these compounds during the time in which the degradation process took place are presented in Table 4. In this table, the evolution of oxalate concentration, which increases as the LAS degradation process goes on, is remarkable. This strong increasing tendency during LAS degradation suggest that this compound should be one of the major species responsible for the remaining TOC in the system when the treatment was over after 180 min of ozonation.

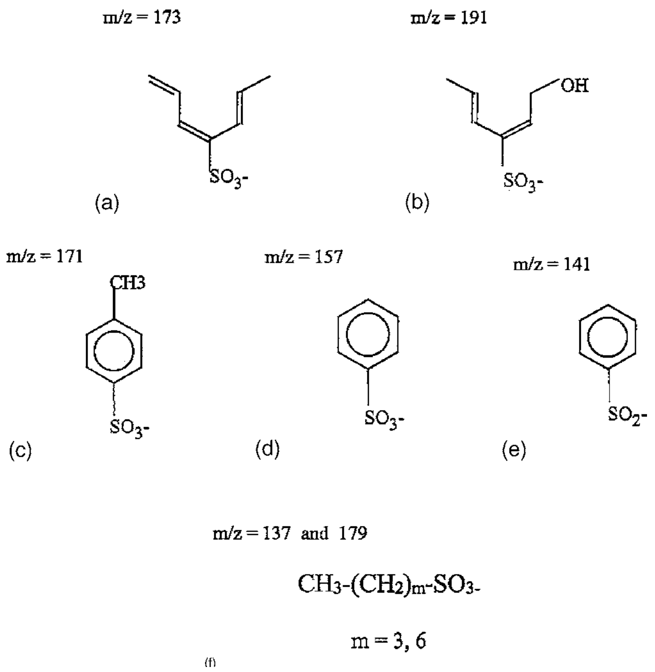

Fig. 5. Some structures proposed for the m/z spectral species detected by LC–MS in the degradation of LAS.

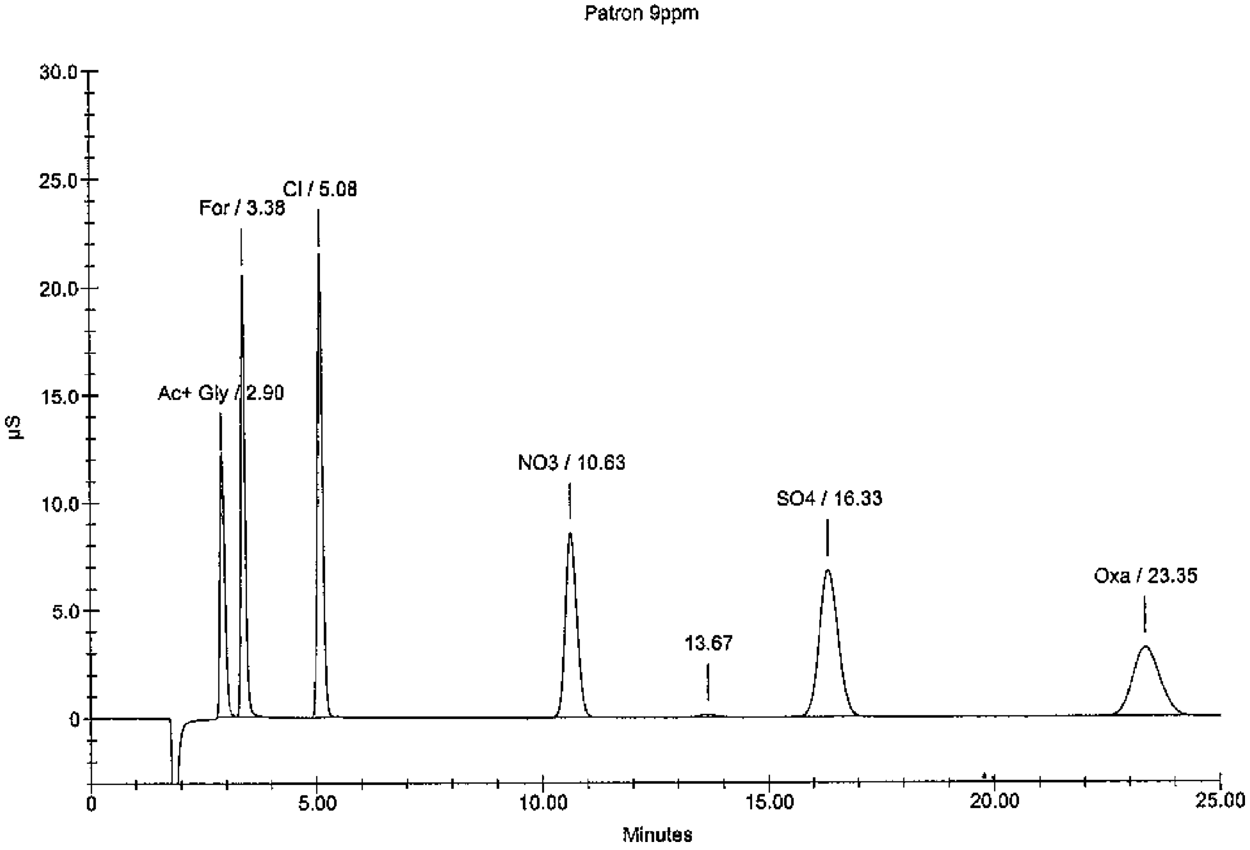

Fig. 6. Typical ion chromatogram (IC) of a standard mix of selected species commonly generated in LAS oxidative decomposition.

Table 4
Some ionic species detected and quantified by ionic chromatography in an ozonation process of LAS degradation and their evolution after 180 min treatment

Time (min)	Ac + Gly	Formate	Cl^-	NO_3^-	SO_4^{2-}	Oxalate
0	–	–	0.02	–	0.21	–
5	0.16	0.42	0.68	0.15	0.82	–
10	0.21	0.66	0.29	–	1.11	–
15	0.25	0.89	0.02	–	1.55	–
20	0.43	1.02	0.06	–	1.93	0.46
30	0.69	1.21	0.04	–	2.69	1.01
45	0.96	1.14	0.10	–	3.26	1.52
60	1.01	1.00	0.03	–	3.71	2.40
90	0.99	0.76	0.02	0.07	4.20	4.01
120	0.53	0.97	0.04	0.12	4.02	6.01
150	0.48	1.15	0.13	0.24	4.32	8.34
180	0.35	1.06	0.14	0.28	4.32	9.05

In the same way a notable increase in the concentration of sulfate ions was also noticed and reported in the same Table 4. The concentration variation of sulfate ions is also a method used sometimes to assess the mineralization degree or ultimate degradation of sulfonate organic compounds [14]. The rise of sulfate ion concentration from 0.21 to 4.32 ppm shown in Table 4 after 3 h of treatment means stoichiometricly a 41% mineralization since it must represent the conversion degree of sulfonate derivatives to sulfate ion. Clearly this result is not concordant with TOC removing in the same period of time (around 83.8%). But on the other hand this partial conversion of sulfonate to sulfate ion may suggest that some other sulfonate species may remain in the treated LAS solution, such as those found by LC–MS.

3.6. LAS ozonation in a commercial product

Degradation of LAS contained in commercial detergent product was also carried out under similar conditions. Detergent concentration was 50 ppm, in order to have a total LAS concentration of 3.5–7.5 ppm in solution or suspension. HPLC results showed that LAS degradation rate was similar to those found in the experiments with standard solutions. However, Toc decrease whose initial value in this case was considerably higher, turned out less satisfactory in rate and efficiency percentage. After 180 min of treatment with ozone, there was approximately 60% of TOC still remaining in the commercial detergent solution.

It should be pointed that at high concentrations, the commercial product did not become completely soluble because of commercial detergent additives. In such cases, a sonication step had to be introduced in order to improve its dissolution. After a sedimentation period a solid phase and an upper solution resulted. The last one was decanted, and the ozonation process was carried out with the resulting homogeneous water solution.

As it is already documented [15], different kind of organic and inorganic species acting as scavengers can react with OH radicals thereby terminating both the radical chain reaction that result in radical hydroxyl formation and the oxidative reaction of decomposition of LAS. This fact is consistent with the less efficient removal of LAS in the commercial detergent which contained several additives than in the standard mix solution.

4. Conclusions

The use of ozonation proved to be the most efficient approach for degrading the typical LAS mix present in municipal and industrial wastewaters where the typical pH values are slightly basic. Degradation of LAS is fast and almost complete. In 15 min LAS concentration was reduced to LOD levels when optimal conditions were used. In the different experiments a less than a half-an-hour treatment was enough for reducing LAS concentration below the 1 ppm levels starting from 10 ppm of total concentration.

Although LAS were almost totally degraded in 30 min approximately, there was a higher percentage of TOC removal in 180 min was around 84% in the case of the LAS standard mix solution and 60% in the case of the commercial product suspension.

Photolytic degradation with arc xenon lamp, whose irradiation spectrum is closely similar to the natural light from the sum, also degraded LAS mix particularly in aqueous dispersion of the commercial product. The process, however, was slower and less efficient than ozonation. The photocatalytic process using TiO_2 or even Fenton reagent appears to have higher rates and efficiency than a non sensitized process. The ozone treatment removed TOC as well as parent compounds more efficiency than a non sensitized process.

LC–FLD which is recognized as a sensitive method allowed to follow the concentration evolution of the individual constituents of LAS mix and to characterize their degradation kinetics. LC–ESI-MS allowed also to follow the LAS concentration evolution with comparable (and in some cases higher) sensitivity. Besides, full scan MS permitted to identify some of the TPs that may cause the incomplete TOC removal, although final confirmation with authentic standards is needed.

Ion chromatography allowed the determination of some refractory low molecular anionic compounds partly responsible for the TOC remaining at the end of a 180 min ozonation treatment, such as oxalate, formate and acetate ions. Some inorganic ions such as sulfate were also identified. Evolution of sulfate ion concentration was compared with TOC evolution in assessing the mineralization degree.

Enhancement of the degradation process of LAS must be feasible and one of the recommended ways would be the combination of both procedures presented in this work. This combination consisting in successive ozonation and photocatalysis, has been tested for other pollutants [18,30,31]. In addition, improvement of waste water biological treatments by means of ozonation [32] and photocatalysis [33] has been proposed.

Acknowledgements

This work has been supported by the Project FEDER (IF-AMB98-08). J. Fernandez would also like to acknowledge the support from Universidad de Caldas in Colombia and to thank the Convenio Andres Bello for economic support.

References

[1] J. Riu, E. González-Mazo, A. Gómez Parra, D. Barceló, Chromatographia 50 (1999) 275–281.
[2] A. Di Corcia, F. Casassa, C. Crescenzi, A. Marcomini, R. Samperi, Environ. Sci. Technol. 33 (22) (1999) 4112–4118.
[3] Y. Zhu, M.J. Rosen, S.W. Morral, J. Tolls, J. Surf. Deter. 1 (2) (1998) 187–193.
[4] C.F. Tabor, L.B. Baber, Environ. Sci. Technol. 30 (819) (1996) 161–171.
[5] H. Hidaka, H. Kubota, M. Gratzel, N. Serpone, E. Pelizzeti, Nouv. J. De Chemie 9 (2) (1985) 67–69.
[6] R.D. Swisher, Surfactants Biodegradation, second ed., Marcel Dekker, New York, 1987.
[7] P. Schöberl, H.K. Klotz, R. Spilker, L. Nitschke, Tensid. Surf. Deter. 31 (4) (1994) 243–252.
[8] P. Kölbener, U. Baumamm, T. Leisinger, A.M. Cook, Environ. Toxicol. Chem. 14 (4) (1995) 571–577.
[9] P. Kölbener, U. Baumamm, T. Leisinger, A.M. Cook, Environ. Toxicol. Chem. 14 (4) (1995) 561–569.
[10] A.M. Nielsen, L.N. Briton, C.E. Beall, T.P. McCormick, G.L. Russell, Environ. Sci. Technol. 31 (1997) 3397–3404.
[11] T.A. Delvall, J.M. Forja, A. Gómez-Parra, Cienc. Mar. 24 (2) (1998) 127–154.
[12] H. Hidaka, J. Zhao, Colloids Surf. 67 (1992) 165–182.
[13] J. Zhao, H. Oota, H. Hidaka, E. Pelizzetti, N.J. Serpone, Phontochem. Photobiol. A Chem. 69 (1992) 251–256.
[14] H. Hidaka, K. Nohara, K. Ooishi, J. Zhao, N. Serpone, E. Pelizzetti, Chemosphere 29 (12) (1994) 2619–2624.
[15] S.J. Masten, S.H.R. Davies, Environ. Sci. Technol. 28 (4) (1994) 180A–185A.
[16] E. Heinzle, H. Stockinger, M. Stern, M. Fahmy, O.M. Kut, J. Chem. Technol. Biotechnol. 62 (1995) 241–252.
[17] P. Kopf, Wiss. Ber-Forschungzent, Doctorate thesis, Karlsruhe, FZKA 6318, 1999, p. 167.
[18] K. Tanaka, A. Kiji, C.Y. Sheng, T. Hisanaga, Environ. Sci. Technol. 26 (12) (1992) 2534–2536.
[19] H. Hidaka, S. Yamada, S. Suenaga, H. Kubota, N. Serpone, E. Pelizzetti, M. Gratzel, J. Photochem. Photobiol. A Chem. 47 (1989) 103–112.
[20] N.J. Fendinger, W.M. Begley, D.C. McAvoy, W.S. Echoff, Environ. Sci. Technol. 29 (4) (1995) 856–863.
[21] J.A. Field, D.J. Miller, T.M. Field, S.B. Hawthorne, W. Giger, Anal. Chem. 64 (1992) 3161–3167.
[22] J. Riu, P. Eichhorn, J.A. Guerrero, Th.P. Knepper, D. Barcelo, J. Cromatogr. A 889 (2000) 221–229.
[23] G. Peñuela, D. Barcelo, J. Chromatogr. A 754 (1996) 187–195.
[24] E. García-Calvo, A. Rodríguez, A. Prados, J. Klein, Chem. Eng. Sci. 54 (1999) 2359–2370.
[25] H. Bader, V. Struzenegger, J. Hoigné, Water Res. 22 (9) (1998) 1109–1115.
[26] P.L. Houston, J.J. Pignatello, Water Res. 33 (55) (1999) 1238–1246.
[27] J. Bandara, V. Nadtochenko, J. Kiwi, C. Pulgain, Water Sci. Technol. 35 (4) (1997) 87–93.
[28] C. Vogt, K. Heinig, J. Fressenius, Anal. Chem. 363 (1999) 612–618.
[29] J. Riu, A. Ginebreda, E. Martinez, L.L. Tirapu, D. Barcelo, J. Fresenius, Anal. Chem. 371 (2001) 448–455.
[30] T.S. Müller, Z. Sun, G. Kumar, K. Itoh, M. Murabayashi, Chemosphere 36 (9) (1998) 2043–2055.
[31] K. Abe, K. Tanaka, Chemosphere 38 (12) (1999) 2747–2752.
[32] C.D. Adams, P.A. Scalan, in: Proceedings of the 11th Ozone World Congress, Ozone in Water and Waste Water Treatment, vol. 1, San Francisco, CA, August/September 1993, pp. S-3-60–S-3-75.
[33] J. Kiwi, C. Pulgarin, P. Peringer, M. Graetzel, Appl. Catal. B Environ. 3 (1993) 295.