



The determination of the linear alkylbenzene sulfonate isomers in water samples by gas-chromatography/mass spectrometry

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ABSTRACT

A number of 20 compounds of linear alkylbenzene sulfonates (LASs) family were identified by electron impact mass spectrometry (EI-MS) in water samples collected from wastewater treatment plants (WWTP). This paper presents the mass spectra of 20 compounds, the proposed mechanism of formation of the diagnostic ions obtained by EI-MS and the distribution of individual isomers in water samples collected from compartments of WWTP. The individual isomers from four homolog series C₁₀-, C₁₁-, C₁₂- and C₁₃-LAS were analyzed as methyl derivatives.

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1. Introduction

The linear alkylbenzene sulfonates (LASs) molecules contain an aromatic ring sulfonated at the para position, which is attached to a linear alkyl chain at any position except the terminal carbons. The LASs are the most used anionic surfactants in various industrial, household and commercial applications [1–5].

Alkyl sulfates (AS), alkyl ethoxysulfates (AES) and LAS are all high production volume (HPV) and are chemicals widely used in detergent and personal care product formulation. Today, LAS account for 45% of the anionic surfactants [6].

The global consumption of LAS was estimated to be about 2.2×10^9 kg in 2000 [7] and 2.5×10^9 kg in 2002 [6]. The European consumption of LAS was about of 4.3×10^8 kg in the year 2005 [8,9]. In Europe the average consumption of LAS per inhabitant per day is 5 g [10]. As a consequence, with or without prior treatment in sewage plants, these amounts generally reach the natural environment.

The concentration range of LAS in WWTP influent was reported as being in the range of 2.4–6.7 mg/l [11] and for effluent were 19,000–71,000 ng/l [11,12]. The conventional (WWTP) cannot entirely stop their discharge [13]. The concentrations of LAS in ground water account for about 0.6% of waste water average concentrations [6]. In the rivers sediment,

the average concentrations of LAS reported were of 780 ng/g [14].

The continuous inputs into the environment (e.g., via WWTP) of such compounds that although biodegrade rapidly, may result in chronic low exposures. Given this situation, numerous studies have been focused on the degradation of LASs in WWTP, since degradation is the main process able to eliminate them. The early reported papers present details of degradation of LAS [13,15–21] the main way of removal of LAS being biodegradation and sorption processes [7,22–25].

The homologous and isomeric analysis of LASs is important in environmental samples, because the biological degradation and aquatic toxicity depend on the alkyl chain length and the position of the phenyl ring. Biodegradation is faster for the higher alkyl chain LASs and external (2- and 3-phenyl) isomers [7]. Hydrophobicity is also the driving force for bio-concentration and therefore LASs with longer chains and the 2-phenyl isomers are the most toxic [7,25,26]. Some papers are concerned with the study of the effect of the molecular structure of surfactant on the reduction of interfacial tension [27]. These studies conclude that the degree of biodegradation and sorption depend on individual structure of LAS. Therefore, detailed studies of biodegradation and sorption by analytical methods, for determination of individual compounds from LASs family are crucial.

Although the analytical methods based on HPLC/MS [6,13,28–32] or capillary zone electrophoresis [33] were extensively used in early studies on LASs removal from environment, the complete separation of homologues and isomers were obtained

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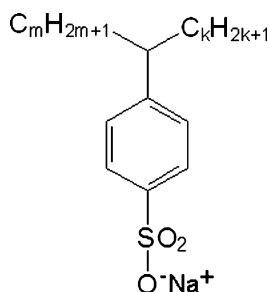


Fig. 1. Structure of investigated compounds; $n = 10\text{--}13$, $k = 1\text{--}5$; $m = 6\text{--}10$ (details in Table 1).

only by GC/MS methods [7,9,34–39]. The GC/MS is more common method used for isomer separation [40,41] and is a standard method applicable to determination of many classes of pollutants, according to European Water Framework Directive [42]. So far, a limited mass spectrometric data on LASs isomer have been published [1,7,35].

The present work discusses the mass spectra, structural correlation and distribution of 20 identified LASs compounds in samples collected in compartments of WWTP containing different amounts of zeolites. The compounds were analyzed as methyl esters derivatives. The basic structure of studied compounds is shown in Fig. 1 and structural details (chain length, position of aromatic ring, elution time and used symbols) are presented in Table 1.

The relative intensity of the ions produced by simple fission and rearrangement mechanism of the molecular ion are strongly depending of structural details [43,44], and are used for compound identification.

2. Experimental

2.1. Sampling and sample preparation

The samples were taken from a WWTP with three different lines (P1, P2 and P3) containing different amounts of zeolites: basin 1 (0 g/m^3 , reference site); basin 2 (9 g/m^3); basin 3 (15 g/m^3).

The samples were acidified with 2 N HCl to pH 2 and filtrated on a glass fiber filter of $0.45\text{ }\mu\text{m}$ (Whatman, Maidstone, England). The

Table 1
Structure of investigated compounds: $\text{C}_k\text{H}_{k+1}\text{--CH}(\text{C}_m\text{H}_{m+1})\text{--C}_6\text{H}_4\text{--SO}_2\text{--OCH}_3$.

No.	n	k	m	M_w	Elution time (min)	Symbol
1	10	1	8	312	23.29	10(1,8)
2		2	7		22.35	10(2,7)
3		3	6		21.81	10(3,6)
4		4	5		21.57	10(4,5)
5	11	1	9	326	25.37	11(1,9)
6		2	8		24.41	11(2,8)
7		3	7		23.84	11(3,7)
8		4	6		23.55	11(4,6)
9		5	5		23.49	11(5,5)
10	12	1	10	340	27.41	12(1,10)
11		2	9		26.43	12(2,9)
12		3	8		25.86	12(3,8)
13		4	7		25.52	12(4,7)
14		5	6		25.41	12(5,6)
15	13	1	11	340	29.38	13(1,11)
16		2	10		28.43	13(2,10)
17		3	9		27.81	13(3,9)
18		4	8		27.50	13(4,8)
19		5	7		27.34	13(5,7)
20		6	6		27.32	13(6,6)

n : number of carbon atoms in alkyl chain; k , m : the number of carbon atoms of every alkyl branch: ($n = k + m + 1$).

cartridge (OASIS 60 mg) was conditioned with 6 ml methanol and 6 ml HPLC water. The samples (500 ml) were percolated through the cartridge at a flow of 3 ml/min. The cartridge was rinsed with 1 ml HPLC water and dried under vacuum for 50 min. The elution was carried out with 2.5 ml of methanol. The average extraction recovery was of 82% determined by comparison of peak areas with the area of IS (diphenylamine) in two different experiments: first one with Internal Standard added before of SPE process and the second one with IS added after SPE extraction. The recovery of IS was determined in a separate experiment.

The derivatization of LASs to methyl ester was directly obtained in GC injection port by introduction of samples in methanol extract.

The quantification method was based on comparison of compound peak area with IS peak area.

2.2. GC/MS analysis

The GC/MS analyses were performed using a Thermo Electron Polaris Q mass spectrometer operating in EI mode at 70 eV. The source temperature was $230\text{ }^\circ\text{C}$ and emission current $300\text{ }\mu\text{A}$. The gas chromatograph was equipped with a capillary column HP-5MS ($30\text{ mm} \times 0.25\text{ mm}$) with $0.25\text{ }\mu\text{m}$ film thickness. The temperature was programmed from $90\text{ }^\circ\text{C}$ (1 min) to $120\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$ and than to $200\text{ }^\circ\text{C}$ at $3.5\text{ }^\circ\text{C}/\text{min}$ and than to $315\text{ }^\circ\text{C}$ at $5\text{ }^\circ\text{C}/\text{min}$ (keeping this temperature for 11 min). The injector temperature was of $250\text{ }^\circ\text{C}$ and $2\text{ }\mu\text{l}$ of sample was injected by splitless technique, with split flow $50\text{ ml}/\text{min}$ and splitless time 1 min.

3. Results and discussions

3.1. Mass spectra of LASs

The mass spectra of the detected compounds of four LAS homologue series are shown in the Tables 2 and 3. The proposed mechanism of production of the diagnostic ions (simple fission and rearrangement of the molecular ion with transfer of H [43]) is shown in Fig. 2.

The molecular distribution of the isomers in a sample collected from WWTP is described by the characteristic ion profiles (m/z 199, 312, 326, 340 and 354) after methylating, and is shown in Fig. 3. The ion at m/z 199 is a main peak in all mass spectra, and the ions at m/z 312, 326, 340 and 354 are the molecular ions of homologues series $\text{C}_{10}\text{-LAS}$, $\text{C}_{11}\text{-LAS}$, $\text{C}_{12}\text{-LAS}$ and $\text{C}_{13}\text{-LAS}$, respectively. All isomers are completely separated except the compound **11**(5,5) relative at **11**(4,6) and **13**(5,7) relative at **13**(6,6).

The simple fission of an ion is produced by a reaction of decomposition involving a bond cleavage (a_{0s}), which is initiated at favourite site by unpaired electron and the positive charge. Such a site is viewed as the driving force for specific types of reactions, which are characteristic for the chemical nature of the site [43].

A reaction initiated by a phenyl π -system yields in the first stage to a benzyl ion of type a_{0s} (with the preferential elimination of the longer branch) as can be seen in Fig. 2. The same type of fragmentation was reported for production of the base peak at aromatic amines [45]. In each mass spectrum can also be seen ions produced from a_{0s} by elimination of an olefin with 3–8 carbons leading to ions from series 185, 199, 213, etc.

The experimental results show that the elimination of the shorter branch in the first stage can also occur, leading to the ion b_{0s} .

Rearrangement reaction involving the transfer of an H atom to an unsaturated group with β -cleavage is based on the observation that an unpaired electron can be donated to an adjacent atom to form a new bond. The second electron of this pair (which forms new bond) is obtained by transfer from another bond to

Table 2
EI mass spectra of compounds 1–10.

m/z compound	1	2	3	4	5	6	7	8	9	10
77	12.90	10.80	18.39	25.48	11.29	10.32	14.68	19.35	13.22	10.96
91	9.03	33.55	56.13	70.00	12.90	31.29	50.00	49.35	47.09	13.22
103	40.48	8.38	17.42	30.97	30.00	9.03	15.32	19.03	4.67	32.90
104	63.55	1.93	8.06	16.61	52.58	4.84	6.13	5.16	–	50.96
105	56.13	5.16	10.97	23.87	48.39	7.09	11.29	14.51	–	54.03
117	7.10	36.61	40.64	72.90	8.39	32.25	35.48	53.54	74.19	7.42
119	12.58	20.64	9.68	14.84	15.16	21.93	7.74	11.93	9.99	13.22
121	7.42	50.32	61.93	74.52	9.35	40.00	54.84	56.45	50.96	9.03
131	3.87	26.13	100.00	30.81	5.16	20.64	100.00	53.54	24.83	3.87
135	10.32	2.58	4.19	15.97	11.29	4.19	5.16	8.38	4.19	11.61
145	2.58	9.68	4.52	100.00	3.22	16.77	12.58	100.00	3.55	5.48
151	–	3.22	10.81	20.97	0.80	3.06	11.93	16.13	11.93	0.96
159	2.90	1.13	1.29	62.58	3.54	5.81	1.61	0.96	100.00	1.45
167	24.19	12.26	23.22	40.00	19.35	12.26	21.29	42.58	30.64	21.29
173	1.93	–	27.09	3.87	0.96	1.93	1.77	35.16	0.80	–
185	9.68	100.00	57.26	60.64	14.51	100.00	58.71	62.90	53.54	14.84
187	–	16.77	3.22	5.81	2.25	6.13	17.74	3.87	6.77	2.26
195	–	15.48	50.97	1.77	0.80	13.55	69.35	12.90	–	1.29
199	*100.00	41.29	63.06	95.48	*100.00	42.58	62.58	98.38	60.32	*100.00
200	**45.16	3.55	7.58	10.64	**50.64	4.84	7.74	7.42	–	**45.16
209	–	3.55	–	45.16	1.61	11.61	5.00	42.58	–	4.19
213	2.58	*50.64	25.64	17.74	8.38	*49.67	29.68	38.38	20.96	5.16
214	0	**25.16	3.22	3.22	0.96	**29.35	3.87	4.51	2.58	0.96
217	3.87	5.16	6.13	11.61	–	0.32	–	–	–	1.29
223	0.98	0.32	–	23.87	0.80	2.58	0.32	0.96	51.29	2.42
227	–	24.35	*38.71	1.92	1.93	24.52	*67.09	11.77	–	3.22
228	–	3.22	**25.64	0.32	–	3.55	**36.77	2.26	0.32	–
231	0.32	0.16	0.48	0.16	2.58	3.87	6.29	7.09	9.35	–
237	–	–	10.64	–	0.32	–	–	16.13	0.16	–
241	1.77	5.16	0.64	*38.06	1.61	25.16	8.39	*39.99	0.16	4.67
242	0.32	0	0	**25.48	0.81	4.19	1.29	**31.93	0.32	0.80
245	–	0.16	0.16	0.64	1.13	0.16	0.16	0.32	–	0.48
251	–	5.81	–	–	–	0.16	6.45	0.32	–	0.16
255	1.93	0.64	0	*38.06	3.55	7.58	0.97	1.29	*x70.96	1.61
256	0.64	0.97	0	xx16.77	1.45	1.29	0.64	0.80	**xx49.67	1.29
259	–	0.16	0.32	0.16	–	0.16	–	–	1.13	1.29
269	1.29	–	x24.52	–	2.25	0.16	–	x27.42	–	0.32
270	0.48	–	xx8.39	–	1.61	0.80	–	xx16.77	–	–
281	–	0.64	–	2.58	0.32	–	–	0.32	0.32	–
283	–	x18.71	–	0.64	0.32	0.16	x20.32	–	–	2.26
284	–	xx3.87	–	–	0.16	–	xx9.35	0.32	–	0.80
297	–	–	–	–	0.16	x11.93	0.32	0.16	–	0.16
298	–	–	–	–	0.16	xx2.58	–	0.16	–	1.61
311	–	–	–	0.32	x0.32	–	–	–	0.32	–
312 (M)	M16.77	M10.32	M9.52	M10.00	xx–	–	–	–	–	–
325	–	–	–	–	–	–	–	–	–	x–
326 (M)	–	–	–	–	M14.35	M12.26	M11.61	M13.54	M8.55	xx–
339	–	–	–	–	–	–	–	–	–	–
340 (M)	–	–	–	–	–	–	–	–	–	M15.48
354 (M)	–	–	–	–	–	–	–	–	–	–

Symbol significance: (*) ion a_{0s} produced by simple fission of k branch; (**) ion a_{0r} produced by rearrangement of k branch; (x) ion b_{0s} produced by simple fission of m branch; (xx) ion b_{0r} produced by rearrangement of m branch; (M) molecular ion. Bold values indicate diagnostic ions.

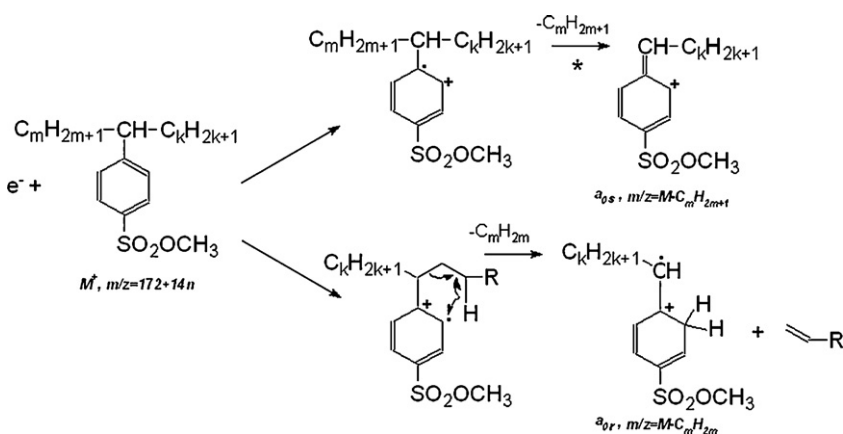


Fig. 2. The mechanism of production of the diagnostic ions: (a) simple fission of the molecular ion and (b) fragmentation by rearrangement of the molecular ion (transfer of H).

Table 3
EI mass spectra of compounds 11–20.

<i>m/z</i> compound	11	12	13	14	15	16	17	18	19	20
77	9.67	14.51	19.67	14.51	4.19	–	12.09	–	23.38	26.45
91	35.48	45.80	47.90	38.70	–	1.93	–	11.45	54.51	64.19
103	6.45	13.38	17.90	20.32	9.67	8.87	13.22	–	25.96	27.09
104	2.90	7.74	11.45	1.93	26.61	8.06	7.09	–	6.13	13.87
105	8.06	11.93	17.90	11.93	20.64	8.87	–	20.64	58.71	57.42
117	31.93	38.06	43.22	53.87	4.03	33.38	66.13	–	49.03	35.96
119	23.54	8.06	9.99	13.71	3.55	37.09	–	–	27.42	35.16
121	41.93	49.19	52.25	38.38	–	22.25	77.09	–	46.45	34.19
131	18.06	100.00	43.87	38.38	–	2.90	100.00	–	49.35	79.35
135	5.80	4.83	9.67	5.48	–	–	0.64	–	15.64	18.06
145	12.25	19.99	100.00	6.13	–	–	9.68	96.77	40.64	56.77
151	3.55	11.61	13.06	6.77	–	21.61	8.06	–	16.13	15.48
159	14.03	6.77	–	39.99	3.55	–	37.42	13.22	35.64	16.13
167	12.58	19.67	30.96	36.77	3.22	–	32.26	–	30.16	14.83
173	5.16	2.58	0.96	26.77	–	2.90	8.22	–	7.74	34.03
185	100.00	50.96	53.87	55.48	24.19	100.00	59.35	22.25	59.83	47.42
187	6.45	3.54	19.67	5.16	8.38	0.64	7.06	–	26.45	38.71
195	14.19	62.90	20.48	5.48	–	0.64	72.90	–	8.06	3.54
199	43.87	58.22	78.06	100.00	*100.00	29.67	62.56	100.00	100.00	100.00
200	4.51	6.13	8.71	7.42	**34.19	0.96	–	–	13.71	27.09
209	11.93	14.19	47.09	0.32	1.29	2.09	0.32	37.42	9.35	7.42
213	*49.35	25.80	34.03	42.58	6.45	*46.29	46.45	16.13	49.35	55.80
214	**29.99	3.87	3.87	5.48	–	**23.87	–	9.35	6.13	15.64
217	0.96	0.32	–	–	–	3.06	–	10.32	–	14.19
223	5.48	3.55	–	19.35	11.93	3.87	3.87	9.99	13.22	3.71
227	16.77	*63.87	32.58	12.58	10.64	23.87	*58.39	9.67	23.38	13.22
228	3.22	**37.74	5.64	0.64	–	–	**32.26	1.29	3.54	1.61
231	–	1.13	0.16	–	–	–	–	1.13	6.45	6.45
237	1.13	0.80	–	11.77	0	1.29	8.22	–	–	11.93
241	20.64	26.13	*49.35	1.93	6.77	10.96	23.55	*44.83	4.83	–
242	2.42	4.19	**42.90	0.16	1.29	1.29	2.90	**29.67	–	–
245	3.71	5.64	9.52	7.09	2.58	0.81	–	0.97	0.32	3.06
251	0.96	–	9.16	–	–	0.64	–	3.22	1.45	0.32
255	26.77	7.42	–	*29.67	–	21.61	30.32	–	*29.35	3.87
256	4.51	0.80	–	**23.22	6.13	3.87	8.71	0.80	**17.42	1.93
259	0.48	0.16	0.16	0.32	–	1.29	10.32	7.09	10.64	8.06
269	7.09	0.32	–	*22.58	1.93	19.35	–	1.29	8.38	*26.77
270	2.25	1.93	–	**21.93	–	5.16	2.56	–	6.45	**xx37.90
281	0.16	0.32	0.96	0.64	12.58	12.26	–	–	–	1.29
283	0.64	0.32	*27.74	0.32	1.93	–	10.00	7.90	*18.22	1.61
284	–	–	**18.38	–	0.32	5.16	–	8.06	**14.67	5.80
297	0.32	*12.58	0.32	–	5.48	0	5.64	*13.87	1.45	0.64
298	2.90	**5.80	–	–	–	12.74	–	**13.22	–	2.25
311	*5.48	0.16	–	0.16	4.51	3.22	*6.77	–	–	–
312	**1.29	0.32	0.32	–	3.06	3.22	**8.22	–	–	0.32
325	–	0.64	–	–	5.48	^x –	–	–	4.51	–
326	–	0.32	0.16	–	–	^{xx} –	–	–	0.96	1.61
339	0.16	–	0.32	0.16	*0.48	–	1.25	–	0.80	1.93
340	M11.29	M12.25	M14.51	M8.06	**4.99	–	–	0.32	–	–
354	0.32	0.16	0.16	–	M3.87	M11.61	M17.90	M3.22	M6.45	M5.48

Symbol significance: (*) ion a_{0s} produced by simple fission of k branch; (**) ion a_{0r} produced by rearrangement of k branch; (x) ion b_{0s} produced by simple fission of m branch; (xx) ion b_{0r} produced by rearrangement of m branch; (M) molecular ion. Bold values indicate diagnostic ions.

this adjacent atom, resulting in its cleavage. The H is probably transferred by a six-member transition state mechanism [43]. This type of reaction leads to the formation of characteristic ion for a wide variety of compounds containing unsaturated functional groups, such as aldehydes, ketones, esters, acids, amides, alkenes and alkylbenzenes [43,46]. Details of the rearrangement mechanism for LAS compounds are shown in Fig. 2. The rearrangement process involves elimination of neutral olefin (C_mH_{2m} and C_kH_{2k} , respectively) by cleavage of the bond adjacent to branch carbon, leading to the formation of a_{0r} , respectively, b_{0r} ions, which are structural diagnostic ions.

The study of the ratio of relative intensity, a_{0r}/a_{0s} and b_{0r}/b_{0s} , respectively, leads to the conclusion that the rearrangement of ion involving elimination of olefinic group (of type C_iH_{2i}) depends on carbon number i from the radical branch and have maximum value for $i=6$, as can be seen in Fig. 4. This information is consistent with that fact that the stability of neutral olefin containing six carbon atoms is higher.

For each compound the $M^{+•}$ ion is around 10%, except for the 2-phenyl isomers where the molecular ion abundance is 16.2% (10-LAS), 18.0% (11-LAS) and 20% (12-LAS and 13-LAS).

The base peak of the 2-phenyl isomers (compounds 1, 5, 10 and 15) is the a_{0s} , m/z 199, produced by simple fission of the bond at branch carbon (elimination of longer alkyl radical). Other abundant ions are produced by elimination of the neutral CH_3OSO_2H , of the radical CH_3OSO_2 and of neutral CH_2OSO_2 from a_{0s} , respectively.

For 3-phenyl isomers (compounds 2, 6, 11 and 16), the base peak correspond to, m/z 185 produced in a secondary process. This ion is obtained from a_{0s} and b_{0s} by the loss of the other adjacent group through a rearrangement process.

The 4-phenyl isomers (compounds 3, 7, 12 and 17) have base peak at m/z 131, ion produced from a_{0s} after elimination of neutral CH_3OSO_2H . The transition was confirmed by MS/MS experiment. The other abundant ions are at m/z 195 and m/z 185 produced from a_{0s} by elimination of the neutral $HOCH_3$ and C_kH_{2k} (C_3H_6), respectively. The ion at m/z 185 can be produced also from b_{0s} by the same

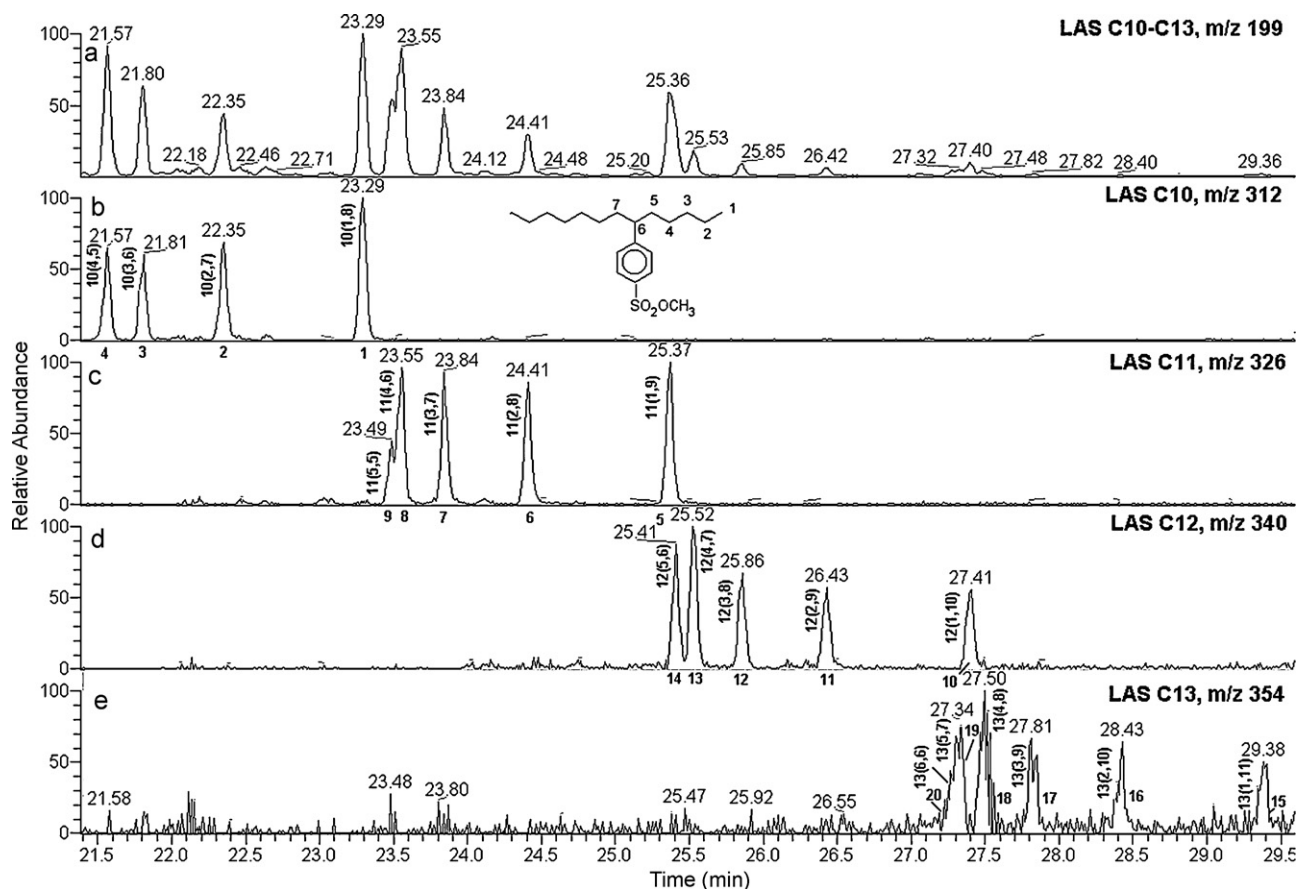


Fig. 3. GC/MS chromatogram of LAS isomers from a real sample: (a) m/z 199 (main ion for LASs), (b) 312 (M^+ for C_{10} -LAS), (c) 326 (M^+ for C_{11} -LAS), (d) 340 (M^+ for C_{12} -LAS), and (e) 354 (M^+ for C_{12} -LAS).

mechanisms but after elimination of C_6 , C_7 , C_8 and C_9 olefin group, respectively, for compounds **3**, **7**, **12** and **17**. From m/z 185, are produced the ions at m/z 91 (60%) and m/z 121 (65%) by elimination of neutral CH_2SO_3 and SO_2 , respectively.

The 5-phenyl isomers (compounds **4**, **8**, **13** and **18**) have as base peak the ion at m/z 145, produced also from a_{0s} after elimination of neutral CH_3OSO_2H followed by the ions at m/z 91 (65%) and m/z 121 (70%) which are produced by similar mechanisms like that of the 4-phenyl isomers from ion at m/z 185 (produced from a_{0s} by elimination of olefin C_4H_8).

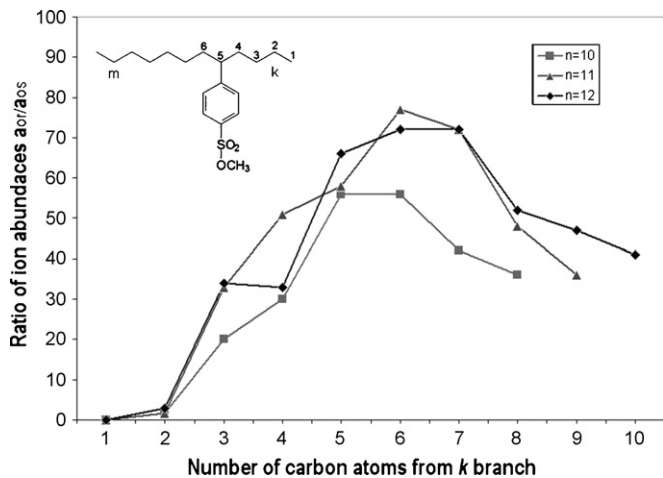


Fig. 4. The relative abundance of the ion a_{0r} (rearrangement) to a_{0s} (simple fission) as a function of carbon number from involved branch.

For 6-phenyl isomers (compounds **9**, **14** and **19**) the base peak was at m/z 199 produced by elimination of neutral C_4 olefin from a_{0s} (m/z 255). Other important ion observed is at m/z 185 (50%), resulting from a_{0s} by elimination of C_5H_{10} olefin group.

For 7-phenyl isomer (compound **20**) the base peak was at m/z 199 produced by elimination of neutral C_5 olefin from a_{0s} or b_{0s} (in this case a_0 and b_0 are at the same m/z 269). Other important observed ion is at m/z 213 produced from a_{0s} by elimination of C_4 olefin (65%).

For each compound the diagnostic ions for determination of the branch position on alkyl chain are the ions a_{0s} , b_{0s} and a_{0r} and b_{0r} , respectively.

3.2. Study of LAS removal in WWTP using absorption on zeolites

For removal of organic compounds, many attempts were made via adsorption process using various adsorbents [47] or advanced oxidation processes (AOPs) using ozone or hydrogen peroxide [48]. Zeolites are excellent compounds with great absorption capacity, which are naturally produced in mines but can also be synthesized by artificial processes. Zeolites were found to be cost efficient adsorbents. They are often used as water purification materials due to their good ion-exchange capacity [49]. Total cation-exchange capacity in natural zeolites varies from 25 to 300 meq/100 g [50].

The zeolite selected for sewage treatment as additive in the sedimentation basin was Szedimentin-MW (GEOPRODUCT KFT. 3909 MÁD, Hungary) with chemical composition of mineral component known [51]. The analyzed samples were taken from the compartments of WWTP as described in Section 2.1. The amount of each LAS compounds was measured from GC/MS base peak

Table 4
LAS concentration (ng/l) measured in the zeolites WWTP compartments and removal rate relative to reference line.

Phenyl position	Compound concentration (ng/l)			Removal rate (%)	
	P1	P2	P3	R(P2)	R(P3)
C₁₀-LASs (M = 312)					
(5)	653 ± 6.2	454 ± 3.6	283 ± 2.1	30.5 ± 2.8	56.7 ± 11.1
(4)	516 ± 4.8	386 ± 3.4	247 ± 2.5	25.2 ± 3.0	52.1 ± 2.8
(3)	606 ± 5.3	463 ± 4.2	351 ± 3.2	23.6 ± 3.4	42.1 ± 6.3
(2)	798 ± 6.1	608 ± 6.2	455 ± 4.3	23.8 ± 2.3	42.9 ± 5.0
				Mean = 25.9 ± 2.8	Mean = 48.4 ± 6.2
C₁₁-LASs (M = 326)					
(6)	220 ± 2.9	152 ± 7.3	110 ± 5.3	31.5 ± 4.0	50.0 ± 3.8
(5)	510 ± 4.2	372 ± 4.6	270 ± 8.3	27.1 ± 2.2	47.1 ± 5.0
(4)	435 ± 4.7	345 ± 8.1	220 ± 6.4	20.6 ± 3.0	49.4 ± 5.4
(3)	477 ± 3.8	330 ± 7.6	250 ± 5.1	30.8 ± 2.7	47.6 ± 5.9
(2)	525 ± 6.1	417 ± 4.2	395 ± 7.3	20.6 ± 1.4	49.5 ± 4.1
				Mean = 26.1 ± 2.6	Mean = 48.7 ± 3.8
C₁₂-LASs (M = 340)					
(6)	185 ± 7.1	128 ± 8.1	86 ± 4.3	30.1 ± 2.4	53.5 ± 9.6
(5)	232 ± 13.8	159 ± 7.7	103 ± 8.6	31.4 ± 3.2	55.6 ± 8.2
(4)	182 ± 5.4	125 ± 6.7	94 ± 4.7	31.3 ± 2.8	48.3 ± 4.3
(3)	124 ± 10.1	93 ± 6.4	68 ± 3.5	25.0 ± 3.7	45.2 ± 4.5
(2)	134 ± 9.6	98 ± 4.9	63 ± 6.3	26.8 ± 2.8	52.0 ± 6.7
				Mean = 28.9 ± 2.9	Mean = 50.9 ± 6.6
C₁₀ + C₁₁ + C₁₂*				Mean = 26.9 ± 2.7	Mean = 49.3 ± 5.5

P1: reference line (no zeolites); P2: line with 9 g/m³; P3: line with 15 g/m³. The compounds from homologue series C₁₃-LAS were not measured.

area. The removal rate was obtained by comparison of concentration in different compartments, with the concentration in a reference line (line without zeolites). The results are shown in Table 4.

The average removal rates obtained were 26.9% for a zeolite concentration of 9 g/m³ and 49.3% for 15 g/m³. The values were obtained by comparison with quantity from reference line (no zeolites) and are closed to those reported in other studies on LAS removal from wastewater, by physical processes (e.g. 30–35% by sorption and sedimentation) [22]. The average removal values of C₁₀-, C₁₁- and C₁₂-LAS groups show a better absorption for longer LAS (C₁₂-LAS). No discrimination was seen for isomers in the same homologue series. The results are in agreement with those reported on sludge experiments [7,25,26].

4. Conclusions

In samples collected from a sewage treatment system was detected a number of 20 compounds from LASs family. The EI mass spectrum of homologue series C₁₀-, C₁₁-, C₁₂- and C₁₃-LAS as methyl esters derivatives, strongly depends on the position of branched carbon. The main ions observed in the mass spectra of LAS isomers, produced by simple fission processes are of type: [M–C_iH_{2i+1}]⁺. The structure of compounds can be obtained by comparing the relative intensity of the ion produced by rearrangement and fission processes. The ion corresponding to bond fission adjacent to branched carbon (*i* = *m* and *i* = *k*) can be recognised from the ratio of ions (A + 1)/A. The ratio is more than 30%, due to the ions produced by rearrangement processes. The molecular distribution of LAS isomers in water samples can be described by the profile of the characteristic ion chromatograms (*m/z* 199 as common ion for all compounds and molecular ion 312, 326, 340 and 354 corresponding to each homologue series).

The LASs compounds detected in WWTP contain chains with the number of carbon atom between 10 and 13, having concentration of: 47% (C₁₀-LAS), 40% (C₁₁-LAS), 11% (C₁₂-LAS) and 2% (C₁₃-LAS). The measured removal of 14 compounds depends on

zeolite amount. The average removal rate was 26.9% (for 9 g/m³) and 49.3% (for 15 g/m³). A positive discrimination was observed in the removal process of C₁₂-LASs relative to C₁₀-LASs and C₁₁-LASs chain homologues.

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