

## **Degradation of LAS in Distilled, Tap and Sea Water**

### **Distile, Şebeke ve Deniz suyunda LAS'ın Parçalanması**

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#### **Abstract**

The degradation of LAS was investigated in distilled, tap and sea water. The analysis of LAS in HPLC showed that the number and size of peaks decreased during the test. Degradation began the first day and continued rapidly. LAS degraded in 20 days 84.8% in distilled water, in 14 days 84.8% in tap water and in 14 days 93.2% in sea water. The number of peaks were diminished and their areas reduced on HPLC chromatograms of LAS during the tests. The degradation of LAS was ranked as sea water > tap water > distilled water.

**Keywords:** LAS, degradation, distilled, tap, sea water.

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#### **Introduction**

The anionic group surfactants were mostly utilized in detergents (Gloxhuber, 1980). Of these the linear alkylbenzene sulfonate (LAS) is commonly used; but it is an important pollutant of seawater. LAS is toxic for marine organisms (Abel and Skidmore, 1972; Topcuoglu *et al.*, 1982; Koc *et al.*, Unpublished data). LAS is prepared by sulfonation of benzene ring of linear alkylbenzene (LAB) by Fridel-Crafts reaction. The final product is a relatively complex mixture and contains homologues with alkyl chain lengths usually varying from

C<sub>10</sub> to C<sub>14</sub> compounds. Commercially LAS may contain 10 - 18 carbon atoms depending on the source of LAB which is not also a uniform compound containing approx. 15-16 alkylbenzene compounds. During its sulfonation, various isomers are produced and oxidation, polymerization, decomposition of the molecules take place.

LAS amount is 20% in various ingredients of detergents.

The determination of LAS was made especially by spectrophotometric MBAS (Standard Methods) and metachromatic (Güven *et al.*, 1994) and HPLC methods (Marcomimi and Giger, 1987; Terzic and Ahel, 1993; Koç *et al.*, 2001) The problem of analysing LAS components in environment has not yet been resolved properly.

LAS are more rapidly biodegradable compounds used since 1970. It is not stable in water and degraded by  $\omega$ -oxidation of terminal methyl group through the alcohol, aldehyde to be carboxylic acid. It is followed by  $\beta$ -oxidation to a series of short chain sulfophenyl carboxylic acids as sulfophenyl butanoic acid and sulfophenyl pentanoic acid (Black and Howes, 1980). The second stage in LAS breakdown is loss of the sulfonate group. The mechanisms of the desulfonation is hydroxyative desulfonation, monooxygenase catalysis, reductive desulfonation. The loss of alkyl and sulfonate group from LAS leaves either phenylacetic acid or benzoic acid. Bacteria as a biological factor can degrade LAS further by removal of the sulfonate moiety, enabling degradation of the phenyl ring to occur. Various types of microorganisms were found to affect the degradation of LAS. Microbial oxidation of phenylacetic acid can result in fumaric and acetoacetic acid and benzene ring can be converted to catechol (Hachim *et al.*, 1992).

Biodegradation of LAS in sewage treatment plants is more rapid than its branched types (Okpokvasili and Olisa, 1991; Terzic *et al.*, 1992; Han and Yang, 1992).

LAS accumulates first on surface of the aqueous medium into which it is discharged. It has a notable capacity for adsorption by sediments and by matter in suspension. LAS disperses, together with its rate of degradation, depending to a large extent on the environmental conditions, principally on the salinity, temperature and above all, on the concentration of oxygen (Gonzalez-Mazo and Gomez-Parra, 1996; Rubio *et al.*, 1996).

Illumination, aeration, agitation, temperature and salinity are external factors of degradation of LAS (Quiroga and Sales, 1990). The concentration of LAS in medium also influenced the degradation.

Speed of biodegradation of LAS is strongly influenced by the alkyl chain length and the point of phenyl attachment to the alkyl chain (Swisher, 1963). The degradation of LAS in different waters was investigated and found that LAS of C<sub>10</sub> - C<sub>11</sub> slightly decreased and those of C<sub>12</sub> - C<sub>13</sub> increased as compared with the river and the estuary water. More than 97% of the LAS degraded after 34 days in bay water. C<sub>12</sub> and C<sub>13</sub> LAS began earlier than those of C<sub>10</sub> and C<sub>11</sub>. The degradation of the same LAS was 71% in estuary water and 67% in river water in 14-17 days exposure. The degradation was 86% after 22 - 29 days exposure. These findings seem to show that LAS of the 22-29 days has been degraded significantly in the bay water. The degradation rate of LAS at the high concentration in seawater was slower than in river water (Hon-Nami and Hanya, 1980).

The biodegradability of shorter chain length homologues is less than for higher homologues (Perales *et al.*, 1999). The loss of C<sub>12</sub> alkylsulfate in test condition was quick (Guckert *et al.*, 1996)

Terzic *et al.*, (1992) showed that the efficient biodegradation of short chain LAS homologues was significantly lower. For instance, degradation efficiencies were 26% and 89% for C<sub>10</sub> and C<sub>13</sub> LAS respectively.

Biodegradation of LAS in river water and sea water under aeration and dark condition, the rate was faster at lower concentration (0.1-10 mg /L). It was found that the degradation rate of LAS at the high concentration in sea water was slower than in river water. It was faster at lower concentration (Wakabayashi *et al.*, 1989).

Microbial population size affects the degradation of LAS in lake water in time 0 to 72 h (Yediler *et al.*, 1989). LAS was almost completely degraded by microorganisms (96.8%) (Visottiviseth *et al.*, 1988), and 60-80% at 37°C and pH 3 in concentration of 50 mg/L in mixed bacteria culture (Han and Yang, 1992).

In the waste water pond the highest biodegradative activity was associated with detrius, cattail rhizosphere, algal-bacterial materials and saturated suboil beneath the pond and nearby topsoil. In the

control pond LAS was degraded in aerobic sediments, cattail rhizosphere, detrius and saturated sub soil immediately beneath the pond. Biodegradation of  $^{14}\text{C}$ -labeled LAS in waste water ponds and a pristine control pond. Generally biodegradative activity in waste water pond was higher than in corresponding control pond (De Federle *et al.*, 1992).

The rate of biodegradation of LAS was rapid provided the flow conditions in the river were adequate (Ferrer *et al.*, 1991).

In this work degradation of LAS was determined in distilled, tap and sea water in laboratory condition.

## **Materials and Methods**

### *Material*

LAS sample was obtained from Lever, Gebze-Turkey.

The tank volumes were 5 L.

LAS concentration in tanks was 50 mg/5L.

Tested waters;

- 1) Distilled,
- 2) Tap (Tap water in Istanbul, dechlorinated by aeration and filtration on charcoal).
- 3) Sea (taken from coast of Kumkapı, Sea of Marmara, Istanbul).

### *Method*

Determination of LAS was made by MBAS method (Standard Methods, 1995) and HPLC method (HP1100) (Koç *et al.*, 2001).

LAB (Solventas) was obtained from LEVER, Turkey and analysis by GC/MS (HP6890).

LAS solution was prepared in tested water in a concentration of 50 $\mu\text{g}/\text{ml}$ . The content of LAS in tanks was measured by Standard Methods and HPLC method.

## **Results and Discussion**

The equations of the standard curves of LAS are:

for MBAS method;

$$y = 0.038 \times C + 0.0196 \quad r^2 = 0.9988;$$

for HPLC

$$y = 62.134 \times C + 15.554 \quad r^2 = 0.9988$$

LAB which is precursor of LAS was analysed by GC/MS. Its chromatogram and corresponded compounds are shown in Fig. 1.

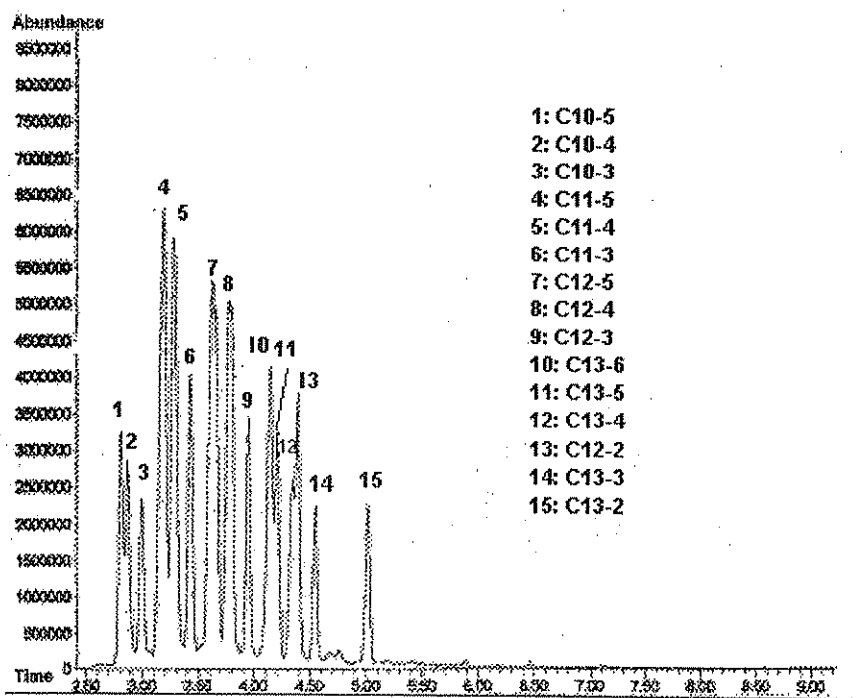


Fig 1. GC/MS Chromatogram and corresponded compounds of LAB.

1:C10-5; C10: Carbon number, 5: indicates carbon number where phenyl group is bonded.

The losses of LAS in distilled, tap and sea water are shown in Table 1.

Table 1. The degradation of LAS (added 50mg /L) in distilled, tap and sea water.

Days	Distilled water		Tap water		Sea water	
	found	loss %	found	loss %	found	loss %
0	48.13	-	47.66	-	48.10	-
4	44.18	11.64	39.12	21.76	16.63	66.74
9	35.44	29.12	26.99	46.02	8.15	83.07
14	-	-	7.6	84.08	3.4	93.02
20	16.71	66.58	-	-	-	-

The results showed that LAS degraded 66.58% in distilled water in 20 days, 84.08% in tap water in 14 days and 93.02% in sea water in 14 days. The degradation of LAS was ranked as sea water > tap water > distilled water. According to Hon-Nami and Hanya (1980) LAS degraded in 22-29 days in bay water and degradation rate was higher than river water. Wakabayashi *et al.*, (1989) and Hon-Nami and Hanya (1980) found that LAS degraded faster in bay water than in sea water. We found that LAS degraded more in sea water than in the others.

HPLC chromatograms showed LAS in distilled, tap water and seawater (Fig.2, 3 and 4).

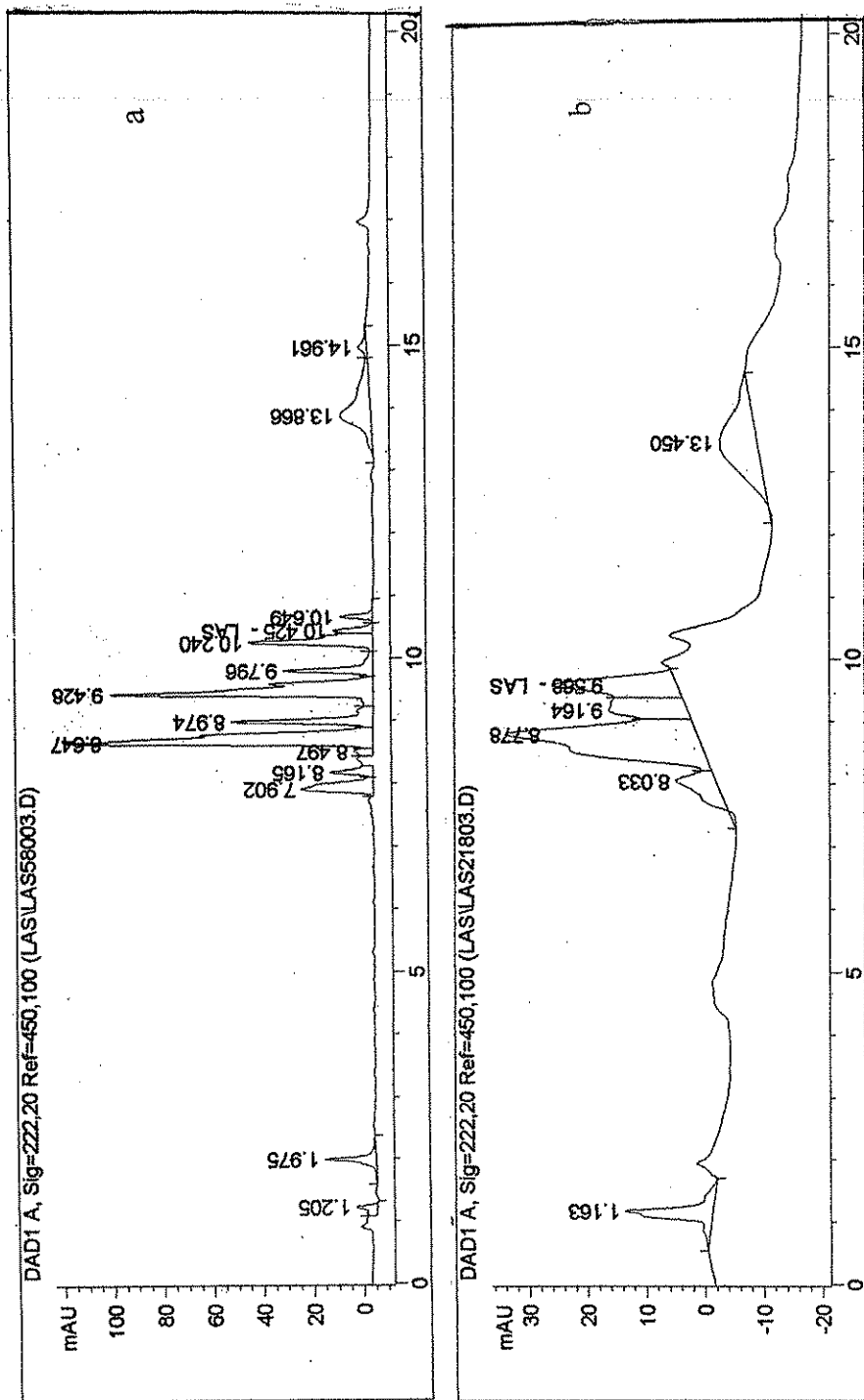


Fig 2. HPLC chromatogram of LAS in distilled water.  
 a) 0 time (found 47.66 mg/L) b) After 20 days (found 16.71 mg/L)

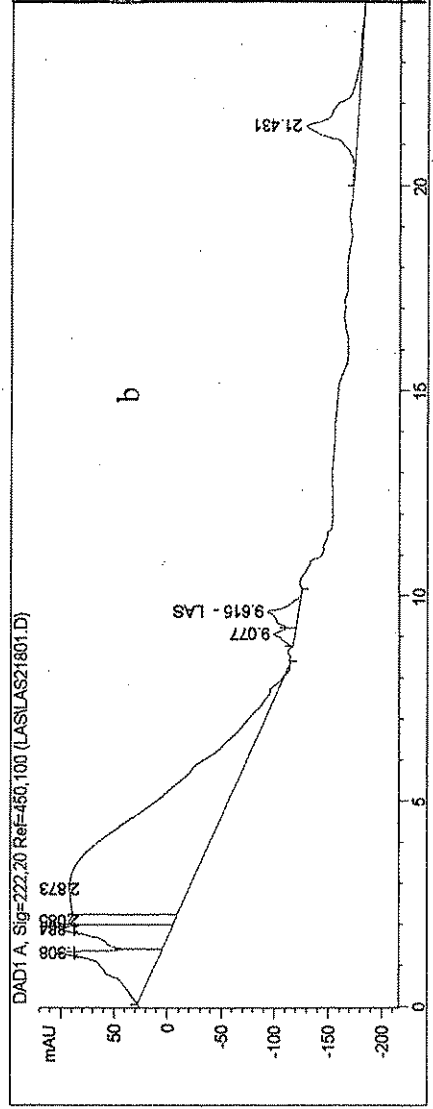
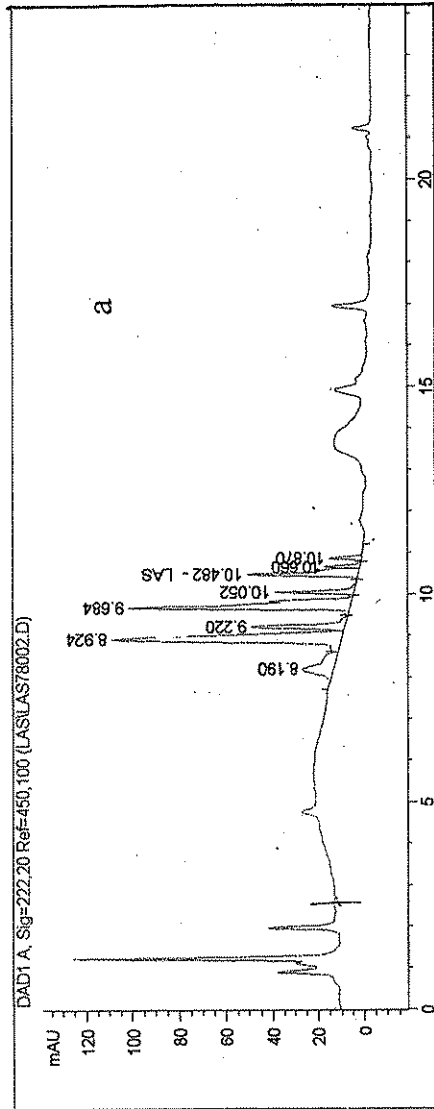


Fig.3. HPLC chromatogram of LAS in tap water  
a) 0 time (found 48.13 mg/L) b) After 14 days (found 7.2 mg/L).



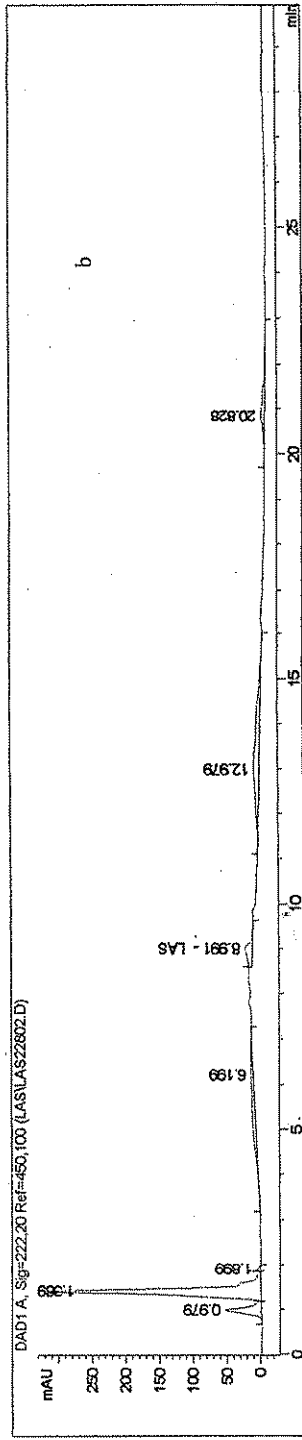
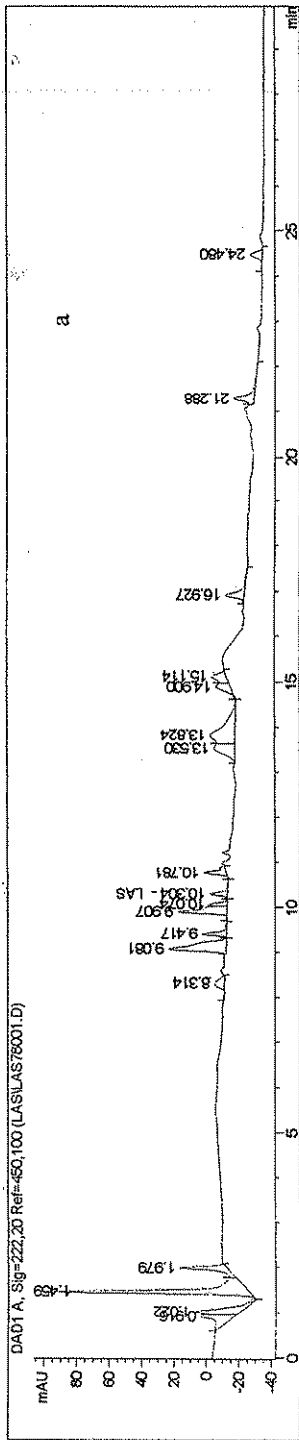


Fig.4. HPLC chromatogram of LAS in sea water  
 a) 0 time (found 48.10 mg/L) b) After 14 days (found 3.4 mg/L).  
 As can be seen in these chromatograms the number of peaks of LAS is 17 and the number of peaks and its areas decreased in time.

Finally LAS was decomposed in sea water faster than tap and distilled water.

## Özet

LAS'ın distile su, çeşme suyu ve deniz suyunda sebatlılığı incelenen bu çalışmada tayinler MBAS ve HPLC metodu ile yapılmıştır. Bulunan sonuçlara göre LAS distile suda 20 günde %66.58, şebeke suyunda 14 günde %84.08, deniz suyunda 14 günde %93.02 parçalandığı tespit edilmiştir. Buna göre LAS, denenen sularda parçalanma sırası deniz suyu > şebeke suyu > distile suyu şeklindedir.

HPLC ile yapılan incelemede 14 günlük deneme süresince kromatogramlarda LAS'ın homologlarına ait piklerin sayısının gittikçe azaldığı ve küçüldüğü saptanmıştır.

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