J. Black Sea/Mediterranean Environment
Vol. 24, No. 3: 306-313 (2018)

REVIEW ARTICLE

A review on the problems of LAS determination methods in sea water

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Abstract

In this paper, the research made on the factors which influence the determination of LAS in sea water by MBAS and HPLC methods was summarized. These factors are purity of LAB and LAS, degradation, light, storage time, salinity and methods used for analysis. These factors were discussed and a modification on the MBAS method was proposed.

Keywords: LAB, LAS, factors, purity, degradation, MBAS

Received: 12.09.2018, **Accepted:** 15.10.2018

Introduction

Linear alkylbenzene sulfanoates (LAS) are mainly used as anionic surfactant and therefore they are one of the main pollutants in sea water. The toxicity of LAS in marine organisms was investigated by several authors (Abel 1974; Unlu and Topçuoğlu 1977; Spehar *et al.* 1979; Topçuoğlu and Birol 1982; Koç and Guven 2002).Various methods were used for LAS determination including methylene blue active substances assay (MBAS assay) (Epton 1948; Barr *et al.*1948; Evans 1950; Degens *et al.* 1953; Güven *et al.* 2010; Güven and Coban 2013), IR spectroscopy (Hellman 1979), mass spectrometry (GC-MS) (Hon-Nami and Hanya 1978; 1980; Raymundo and Preston 1992), HPLC (Marcomini and Giger 1987; Terzic *et al.* 1992; Koç *et al.* 2001; Villar *et al.* 2009;), API-MS (Ceglarek *et al.* 1999), AAS (Cripps *et al.* 1978), potentiometric (Ivanov and Prashin 1985), fluorometric (Sablayrolles *et al.* 2009), and polarographic (Cosovic e*t al.* 1985).

The most commonly used method is MBAS (Standard Methods 1992) using commercial LAS reference material based on metachromasy which was found by Ehrlich (1887) in histological staining of cells and this phenomenon was elucidated by Lison (1935). Instead of methylene blue dye other metachromatic dyes including Nile blue, toluidine blue, Azur A, (α, β bands) were examined for

LAS determination, but no significant difference was found (Akıncı and Güven 1997; Güven *et al.* 1994; Bektaş and Güven 2004; Güven and Cumalı 2007). Many compounds interfere the result of this method (Standard Methods 1992). HPLC method based on peaks C10-C14 or total peak areas of LAS, which differ according to the producer of LAS used as reference. This in turn creates variations in the results of the measurements depending on the source of the reference. GC-MS method has a difficult extraction stage, derivatization steps for methylsulfonate derivatives and tedious application to the apparatus.

In this paper, the researches made on the LAS determination by various laboratories were summarized and the solutions are proposed. The factors affecting LAS determination were investigated as follows: purity of LAS, degradation, light, storage time, salinity and methods used.

Purity of LAS

Commercial LAS products are not a uniform compound. Its content depends on the precursor (LAB) that contains many isomers and sulfonation process. The GC/MS analysis of LAB products (Tol Runner and Isochem) were shown in Table 1 as peak areas on the chromatogram. This indicates that each lot of product in the table has different peak areas depending on the source of the LAB producer.

Table 1. The peak areas for the LAB compositions of two different brands.

Peaks	LAB Composition	Peak areas	
		Isochem[1]	Tol Runner[2]
1	$C_{10\text{-}5}$	95.844.477	38.651.102
2	$C_{10\text{-}4}$	80.145.146	39.151.510
3	$C_{10\text{-}3}$	76.202.934	35.011.249
4	$C_{11\text{-}5}$	279.002.917	260.824.893
5	$C_{11\text{-}4}$	208.428.771	171.279.483
6	$C_{11\text{-}3}$	122.970.354	116.625.274
7	$C_{12\text{-}5}$	320.566.266	260.147.870
8	$C_{12\text{-}4}$	243.951.002	215.292.886
9	$C_{12\text{-}3}$	94.703.996	81.360.858
10	$C_{13\text{-}6}$	162.724.965	100.673.318
11	$C_{13\text{-}5}$	81.851.068	53.967.883
12	$C_{13\text{-}4}$	64.657.217	38.175.033
13	$C_{12\text{-}2}$	89.701.204	89.844.619
14	$C_{13\text{-}3}$	57.454.976	34.258.725
15	$C_{13\text{-}2}$	55.593.644	35.037.289

Cx-y: "x" indicates the number of carbon atoms, "y" indicates the position where the benzene ring is attached.

[1] (Koç *et al.* 2002)

[2] (Gezgin and Güven unpublished results)

Degradation

LAS is a fast-degrading product (Black and Howes 1980). Various factors affect LAS degradation such as: light, aeration, salinity (Quiroga and Sales 1990; Gonzalez-Mazo and Gomez Parra 1996; Gezgin and Guven 2012), microbial

population (Okpokwasili and Olisa 1991; Han and Yang 1992; Hashim *et al.* 1992) and storage time of the sample (Güven *et al.* 2008). The speed of degradation of LAS is strongly influenced by alkyl chain point of phenyl attachment (Swisher 1987). Losses of LAS depend on the contaminant in the sea water (Hon-Nami and Hanya 1980). The degradation of LAS was ranked as sea-water > tap-water > distilled-water (Koç and Güven 2002). The degradation time for LAS in tap water was previously estimated to be 22-29 days by Hon-Nami and Hanya (1980) or 20 days by Koç *et al.* (2002) and its degradation time in the environment varies. LAS degraded 66.56 % in Tokyo Bay water (with 0.3 % salt content) in 20 days (Hon-Nami and Hanya 1980), 91 % in Golden Horn water over 22 days and 89.9 % in Samsun, Black Sea water in 10 days (Güven and Cumalı 2007).

Influence of Light
The influence of the color of glass bottles in which the water samples were stored was studied and results are as follows. The loss of LAS in 15 days in colorless glass bottle was 90 %, whereas the loss in brown glass bottle was 33 % (Gezgin and Güven Unpublished data).

Storage of the sample
Degradation of LAS in the sea water depending storage time was studied for the different stations. In five days, LAS was 60 % degraded in sea water collected from Zonguldak, in comparison to the sea water from Bartın where the LAS degradation occurred only 30 %. In 10 days, sea water samples from two different locations in Samsun were compared and 58 % and 89 % LAS losses were calculated (Güven *et al.* 2008).

Salinity of seawater
Salinity is also a major factor on the determination of LAS (Marcomini *et al.* 1987; Rubio *et al.* 1996; Srivastava *et al.* 1977). The effect of salinity on the LAS in the sea water was investigated. Artificial sea water samples with different salt contents from commercial (Merck and Baker) pure salts were prepared (Wood and Ayres 1977) and measurements using MBAS method varied. For the elimination of salt effect, the MBAS method was modified and details were given in the conclusion (Güven *et al.* 2007; Çetintürk and Güven 2009).

Method used
The most commonly used method for LAS determination is MBAS and less frequently HPLC and GC-MS methods. MBAS and HPLC methods were compared and results found were 10.68 $\mu g\ L^{-1}$ and 12.45 $\mu g\ L^{-1}$, respectively (Koç *et al.* 2001).

Modification of MBAS method
In the MBAS method, the standard curve of LAS was plotted by using LAS solutions prepared in distilled water. This creates deviations in the results because of the salinity of the samples. The method was modified as preparing the LAS

solutions in water at the same salinity of the examined sea water for the standard curve calculation by using pure salts (Güven and Cumalı 2007; Çetintürk and Güven 2009). Standard curves were plotted with these solutions prepared in different salinities like 16‰, 27‰, 38‰, according to Wood and Ayres (1977). The results were presented obtained from this proposed method versus standard method in Table 2.

Table 2. The comparison LAS determination in sea water by using the modified MBAS and standard BAS methods. Standard curves were plotted according to the standard solutions prepared with distilled water with different salinity.

Salinity of standard solution (‰)	Modified method	Standard MBAS
16	263.06	238.64
27	239.26	227.00
38	247.50	226.47

As a result of this study, a modification of MBAS method was outlined (Güven and Cumalı 2007; Çetintürk and Güven 2009). All the solutions for the standard curve must be prepared with similar salinity of sea water examined. The blank should also be prepared with the same salinity. The sea water samples should be extracted with 6 × 15 mL of chloroform for 30 seconds and combine the chloroform phases. Absorbance was read at 652 nm against the modified blank which was treated as sample omitting LAS addition instead of pure chloroform.

Conclusion

The factors mentioned above created problems in analyses in the literature were discussed (Güven *et al.* 2010; Güven and Coban 2013). Prevention of degradation may be provided by doing the analysis quickly right after collection of the samples which should be kept in dark and a cool place, the standard-curve should be plotted by using water at the same salinity of the seawater to be analyzed instead of distilled water.

Deniz suyunda LAS'ın analizindeki problemlere ait bir inceleme

Öz

Bu çalışmada deniz suyunda LAS'ın MBAS ve HPLC metotlarıyla analizini etkileyen faktörler üzerine araştırmalar özetlenmiştir. Bu faktörler: LAB ve LAS'ın saflığı, parçalanması, ışık, örneğin bekletme zamanı, tuzluluk ve kullanılan analiz metodudur. Bu faktörler literatürle tartışılmış ve MBAS'ye göre LAS miktar tayini için bir modifikasyon önerilmiştir.

Anahtar kelimeler: LAB, LAS, faktörler, saflık, bozunma, MBAS

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