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The influence of salinity of seawater on the determination of LAS by MBAS methods

MBAS metoduna göre LAS'ın tayininde deniz suyu tuzluluğun rolü

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Abstract

The determination of LAS in seawater by MBAS method presents some difficulties. Many factors influence on this method. Some of them, salinity have an important role. In this work LAS was determined in various seawater surrounded Turkey as salinity of 16-18 ‰ (the Black Sea), 24 ‰ (Sea of Marmara) and 36 ‰ (Mediterranean Sea). All the solutions were prepared with similar salinity of examined water and the blank used was prepared with similar salinity of seawater described in calibration curve omitting LAS. The other modification was made on the blank. It was prepared with similar salinity of seawater described in calibration curve omitting LAS.

It was found that salinity of seawater is effected on the results as the LAS amount found by Standard Methods is found 5-8.5 % lower than this proposed method.

Keywords: LAS determination, blank, pure chloroform, saline.

Introduction

LAS[*] linear alkyl benzene sulfonate is an anionic surface active substance and is widely used in detergents formulas. Its precursor LAB (linear alkyl benzene) has usually a linear alkyl chain varying from C8 to C16 carbon atom. Commercially available products of LAS are not unique compound. It is complex mixtures containing several alkyl homologues and positional isomers of phenyl group.

LAS is an important pollutant of sea water and cause many disturbance to marine life. The effect of surface active substances on marine life was extensively investigated. The determination of LAS is important for seawater. Several determination methods have been proposed. MBAS (Methylen Bleu Active Substances) method is widely used for the determination of LAS (Standard Methods 1995). Many organic (organic sulfate, sulfonate, carboxylate, phenol, amine, quaterner ammonium) and inorganic compounds (chlorure, sulfate, phosphate, thiocyanate) interfere with this method. These compounds showed positive or negative effect on the assay.

The other determination methods are based on metachromatic reaction (Güven *et al.,* 1994, Akıncı and Güven, 1997, Bektaş and Güven, 2004), IR (Hellman, 1978), GC/MS (Hon-Nami and Hanya, 1978; 1980, Raymundo and Preston, 1992), HPLC (Terzic *et al.,* 1992, Terzic and Ahel,

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1993, Mancomimi and Giger, 1987, Koç *et al.*, 2001; Sarrazih *et al.*, 2005), AAS (Crips *et al.*, 1978; 1980).

Minimum detectable quantity of LAS per liter is 10 μg for MBAS (Standard Method) and metachromatic method, 0.1 μg (Kikuchi *et al.*, 1986), 1 μg (Terzic and Ahel, 1993) for HPLC, 40 μg for IR spectrophotometry (Hellman, 1978), 3 μg for AAS (Crips *et al.*, 1976), 3 μg for GC/MS (Hon-Hami and Hanya, 1978). GC/MS analysis gave individual components in a mixture and the isomers of anionic surfactants. But it is difficult to apply for the determination in the environment (Hon-Hami and Hanya, 1978).

The salinity of water is a major factor controlling the determination of LAS concentration in the marine environment. The influence of salinity of water on MBAS method is indicated by Standard Methods (1980) (Marcomimi *et al.*, 1987; Hon-Nami and Hanya 1980; Gonzales-Mazo and Gomez-Parra, 1996). The influence of various origins of sodium chloride added in distilled water for different salinities on LAS determination was investigated by Çetintürk and Güven (unpublished data). Rubio *et al.* (1996) proposed a method to eliminate the salt in the seawater evaporation at 60^0C until the salinity approached 75. Hypersaline water was then filtered, through a 0.45 μm filter and the required salinity obtained by subsequent dilution with Milli-Q water.

LAS adsorbs on river sediments in estuary and the settling rates of sediments increase with salinity when the river water mixes with the seawater (Scott and Johns, 2000). LAS accumulates in sediments in hypersaline water (Rubio *et al.*, 1996).

The other factors influencing on the determination of LAS are the adsorption on the suspended matter in water. The degradation of LAS in seawater depends on bacterial population. The bacterial contamination of the samples greatly increases during the storage time.

Thus many factors are important for determination of LAS in seawater. The degradation of LAS depends on environmental condition as well as salinity, temperature, concentration of oxygen and existence of bacterial population.

Another problem is pretreatment of samples before analysis. Many analysis particularly earlier records, are suspect of inadequate precaution against contamination from external sources.

The results of LAS determination show high difference among laboratories independently analyzing the same material; there is often a wide discrepancy between their results. The quality of analytical data can be controlled by the use of reference materials.

In this paper the influence of salinity of seawater on the determination of LAS was investigated and a modification was proposed to eliminate the effect of salts on the MBAS assay.

Material and method

In this work the artificial seawaters used were prepared through Wood and Ayres (1977). The salinity level chosen was guided by the level in sea water surroundings of Turkey. The concentrations of salinity are for the Black Sea 16 ‰, Sea of Marmara 24 ‰ and Egean Sea/Mediterranean Sea 36 ‰ (Table 1).

The method used by LAS determination is MBAS method (Standard Methods, 1995) is:

Preparation of calibration curve: prepare a series of 10 separatory funnels with 0, 2.00, 3.00, 5.00, 7.00, 9.00, 11.00, 13.00, 15.00 and 20.00 ml of the standard LAS solution. Add sufficient water to make the total volume 100 ml in each separatory funnel. Plot a calibration curve of micrograms LAS versus absorbance.

Extraction and color development:

1) Add the sample solution to a separatory funnel. Make the solution alkaline by drpwise addition of 1 N NaOH, using phenolphthalein indicator. Discharge the pink color by dropwise addition of 1 N H_2SO_4.
2) Add 10 ml chloroform and 25 ml methylene blue reagent. Rock funnel vigorously for 30 sec and let the phases separate. Excessive agitation may cause emulsion trouble. Some samples require a longer period of phase separation than others. Before draining the chloroform layer, swirl the sample gently, then let it settle.
3) Draw off the chloroform layer into a second separatory funnel. Rinse delivery tube of the first separatory funnel with a small amount of chloroform. Repeat the extraction three times, using color in the water phase becomes faint and disappears, discard the sample and repeat the determination, using a smaller sample size.
4) Combine all chloroform extracts in the second separatory funnel. Add 50 ml wash solution and shake vigorously for 30 sec. Emulsions do not form at this stage. Let settle, swirl the contents and then draw off the chloroform layer through glass wool that has been pre-extracted with chloroform into a 100 ml volumetric flask. Extract wash solution twice with 10 ml chloroform, adding these to the volumetric flask. Rinse the glass wool and the funnel with the chloroform. Collect the washing in the volumetric flask, dilute to the mark with chloroform, and mix well.

Measurement: Determine the absorbance of the solution at 652 nm against a blank of chloroform pure and modified blank.

The process applied and all the solutions used were prepared according to Standard Methods. The modifications were made only on the blank. The blank chloroform was prepared with the same salinity of seawater in the calibration curve preparation procedure omitting LAS.

The solutions for calibration curve

Standard curve of LAS: Reference substances of LAS (97.7%) were obtained from Lever (Gebze, Turkey).

All the solutions are prepared with salinity of 16, 24 and 36 ‰ water (SSW).

Stock LAS solution was prepared with 0.100g LAS in 100 ml of SSW.

LAS solution: 1 ml stock LAS solution was diluted to 100 ml with SSW examined.

Phenolphthalein solution 1/100 (v/v) in alcohol.

Base and acid solution: 0.1N NaOH, 1N H_2SO_4 and 6N H_2SO_4.

Methylene blue (MB) solution: 30 mg MB in 50 ml SSW.

Washing solution: 50 g Na_2HPO_4 H_2O was dissolved in 500 ml SSW 41 ml, 6N H_2SO_4 added and the volume adjusted to 1000 ml with corresponding salinity.

Chloroform (pro analysis, Merck) and all chemicals used were Merck products (Darmstad).

The salinity of investigated seawater was prepared with artificial sea water (Wood and Ayres, 1977)(Table 1).

Table 1. The composition of artificial sea water for salinity of 16 ‰, 27 ‰ , 38 ‰ (g/L).

for 16 ‰	g/L	for 27 ‰	g/L	for 38 ‰	g/L
NaCl	11.31	NaCl	21.08	NaCl	24.7
KCl	0.36	$MgSO_4$	5.18	$MgCl_2$	13.0
$NaHCO_3$	0.17	$MgCl_2$	4.12	$Na_2SO_4.10H_2O$	9.0
$MgSO_4.7H_2O$	2.39	$CaCl_2$	1.06		
$MgCl_2 . 6H_2O$	1.97	KCl	0.50		
$CaCl_2$	0.54	$NaHCO_3$	0.31		

Results and Discussion

The absorption values obtained for different concentrations of LAS in different salinity are shown in Table 2.

Table 2. The absorption values of LAS at different concentrations at 652 nm.

Salinity Conc. μg/ml	16 ‰	27 ‰	38 ‰
20	0.0423 ±0.007-0.02	0.059±0.0104-0.00682	0.0657±0.016-0.012
100	0.0285 ±0.0083-0.0105	0.222±0.001-0.0037	0.2282±0.078-0.011
150	0.0323±0.0295-0.00128	0.3243±0.032-0.011	0.2944±0.085-0.0076
200	0,0402±0.0132-0.0084		0.3861±0.0015-0.0161

The equations of calibration curves obtained for different salinity are shown in Table 3.

Table 3. The standard curve of equations for different salinity against blank modified in the present work (a) with chloroform pure by Standard Method (b).

	for 16 ‰	for 27 ‰	for 38 ‰
a)	y= 0.0017x + 0.0379 R^2= 0.991	y= 0.0019x + 0.0305 R^2= 0.995	y= 0.0018x + 0.0396 R^2=0.99
b)	y= 0.0017x + 0.0794 R^2= 0.993	y= 0.0019x + 0.0538 R^2= 0.998	y= 0.0017x + 0.1094 R^2= 0.9727

For the comparison of the results obtained from MBAS with the modified method proposed in this work are shown in table 4. The LAS concentrations were calculated in Baltalimanı sample (Istanbul Strait).

Table 4. The results obtained from proposed method, Standard Methods and metachromatic methods.

Salinity	Present work	MBAS method	Metachromatic Methods	
			Azur A	Nil Blue
16 ‰	263.06	238.64	264	244
27 ‰	239.26	227.00	-	-
38 ‰	247.50	226.47	-	-

- ; not tested.

The results showed that salinity of sea water has an effect on the level of detergent amount in sea water. The level found is depended on salinity degree of sea water.

The finding of LAS is lower through Standard Methods than this modified method. The important point is determined LAS level decreases when salinity increases.

This work showed that the analysis of LAS is particular has suffered several problems such as the temperature, salinity, ions, organic compounds and especially storing time of the samples. Another problem is the sample collection or pretreatment before analysis.

Conclusion

The effect of salinity on the determination of LAS in seawater was indicated by MBAS methods but not demonstrated quantitatively. In this work the effect of salinity on the determination of LAS was lower as 5-8.5 %.

Özet

Bu çalışmada MBAS metodunda bir modifikasyon önerilmiş ve MBAS metodundaki tuzluluk problemi tartışılmıştır. LAS'ın deniz suyunda MBAS metodu ile tayininde değişik zorluklar vardır. Birçok faktör bu metodu etkilemektedir. Tuzluluk gibi bunlardan bazıları önemli role sahiptir. Bu çalışmada Türkiye'yi çevreleyen Karadeniz, Marmara Denizi ve Akdeniz'in tuzluluklarına (‰ 16, 24 ‰ ve 36 ‰) sahip suni deniz suyunda LAS tayini yapılmıştır. Bu çalışmada modifiye edilmiş Standart Metot ile aynı tuzluluk miktarlarında hazırlanan blanklerin kullanımı esas alınmıştır. Standart eğrisinin blank saf kloroform yerine aynı tuzluluğa sahip deniz suyu ile işlem görmüş kloroform blank olarak kullanılmıştır.

Elde edilen bulgular deniz suyunun tuzluluğunun LAS miktarı tayini üzerine etkisi olduğunu göstermiştir. Standart metot ile belirlenen LAS miktarının teklif edilen modifiye edilmiş metottan % 5-8.5 daha düşük olduğu bulunmuştur.

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