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The effect of sodium chloride concentration on the assay of LAS in seawater by MBAS methods

MBAS metodu ile deniz suyunda LAS tayininde sodyum klorun konsantrasyonunun etkisi

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Abstract

The effect of salinity in seawater on methylene blue active substance (MBAS) method for LAS determination was investigated. To reproduce the salinity of the Black Sea (18 ‰), Sea of Marmara (24 ‰) and Mediterranean Sea (34 ‰), we used sodium chloride from Aegean Sea, Merck and Baker products. Standard curve of LAS was drown in seawater reproduced in the same salinity. It was found that the purity and concentration of sodium chloride have an effect on the LAS level determined by Standard Methods in sample tested. Merck and Baker sodium chloride give similar results but using common salts, the results are more reliable.

In this work we proposed a modification improve MBAS assay in seawater as follows:

1. Standard LAS solution must be prepared with common salts with the same concentration as seawater tested.
2. The blank chloroform used was prepared applying the procedure of calibration curve of LAS determination by MBAS method omitting LAS.
3. The extraction with chloroform was made 6 times instead of 3 times.
4. The calibration curve of LAS was plotted using common salts instead of distilled water, with the same salinity of seawater examined.
5. Correlation equation were calculated from the equations of different salinity of seawater (18, 24, 34 ‰)

Key Words: LAS, sodium chloride, MBAS method.

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Introduction

Detergents are important pollutants for seawater. They cause many disturbances to marine life. It contains condensed phosphates (tripoly, pyro, etc.), silicates, carbonate, carboxymethylcellulose sodium, sorbitol and many types of surfactants. The widely used detergents are anionic surfactant, LAS (linear alkylbenzenesulfonates). Commercial LAS is not a unique compound. It is a complex mixture containing approximately 26 isomers and homologues with the general structure: $R^{1}.C_6H_4SO_3$ Na. It was characterized by a lipophilic moiety (R^1) and hydrophilic group (sulfonic).

Linear alkyl chain R^1 contains C_8-C_{16} carbon atoms and several positional isomers of phenyl group. The manufacturing process of LAS defines the mixture. Thus, LAS contains many isomers depending on the number of carbon of alkyl group, the benzene link and sulfonation process applied. The exact composition of commercial LAS is not known.

LAS is not stable in marine environment and is degraded in approximately 20 days (Hon-Nami and Hanya 1980, Koç et al. 2002).

LAS is used in large amounts for cleaning and pollutes the aquatic environment through waste water sewage to the rivers and seawater. For this reason the determination of LAS in seawater is important.

Various methods were proposed to determine anionic detergent, LAS concentrations in town, rivers and seawater. The determinations are based on spectrophotometric methods (Standard Methods 1995), IR (Hellman 1978), GC/MS (Hon-Nami and Hanya 1978, 1980, Raymundo and Preston 1992), HPLC (Terzic et al. 1992, Terzic and Ahel 1993, Marcomimi and Gifer 1997, Koç et al. 2001), and AAS (Crips et al. 1978).

In MBAS method, the complex formed between methylene blue (MB) and LAS. Its color is blue and soluble in chloroform and the concentration can be determined by measuring the absorbance at λ_{max} 652 nm.

Another spectrophotometric method is based on metachromasy of dye with LAS (Güven *et al.* 1994, Akıncı and Güven 1997, Bektaş and Güven 2004). Similarly to MBAS method, a complex is formed between metachromatic dye and LAS. It is soluble in chloroform and the absorbance can be measured at metachromatic β band and also λ_{max} of dye. MBAS and metachromatic methods gave the same results (Güven et al. 1994).

MBAS method is relatively simple but some substances such as organic sulphonates, sulfates, carboxylates and phenols and inorganic substances as thiocyanates, cyanates, nitrates, chloride and sulfates may transfer more or less methylene blue into the chloroform phase. Positive and negative interferences with the organic and inorganic substances were demonstrated with methylene blue (Srivastava et al. 1977). The aqueous back wash step removes these positive interferences. Negative interference was due to the presence of cationic surfactants, other cationic materials and particular matter. The latter was eliminated by filtration. The presence of sulfides in waste water may react with methylene blue to form a colorless reduction product. The existence of interfering substances in river, town and seawater influences the assay. The determination of anionic detergents with methylene blue depends on the pollution of seawater and results vary depending on the pollution of sampling regions. Thus MBAS results are due to the total anion active compounds plus interfering substances reacting in this assay. The methylene blue method has been successfully applied to the examination of the anionic sulfactant content in drinking water supplies. But numerous material present in sea water, industrial waste and sludge can seriously interfere with the determination and lead to incorrect results (Standard Methods, 1995).

The salinity of the water is a major factor controlling the LAS concentration by MBAS method in marine environment (Standard Methods 1995, Marcomimi et al. 1987, Hon-Nami and Hanya 1980, Gonzales-Mazo and Gomez-Para 1996, Scott et al. 2000).

In this work we investigated the influence of different salinities of water prepared with sodium chloride from various origins on the determination of anionic detergent by MBAS method.

Material and Methods

LAS (98%) was supplied by Lever, Izmit, Turkey. Sodium chloride is Merck (Darmstadt, Germany) and J.T.Baker (USA) product. Common salt (prepared in Tuzla, Izmir from Aegean Sea) was purchased from market. Chloroform is Merck (Darmstadt, Germany) product.

Seawater samples are taken from the Black Sea, Bosphorus, Golden Horn and Marmara Sea. Mediterranean Sea sample was taken from deep water of Bosphorus. Turkish Straits seawater contains two flows, the upper current is the Black Sea water and the under current of Mediterranean Sea water. The sampling stations are shown in Figure 1 and Figure 2.

Figure 1. Sampling station in the Black Sea, Bosphorus and Sea of Marmara.

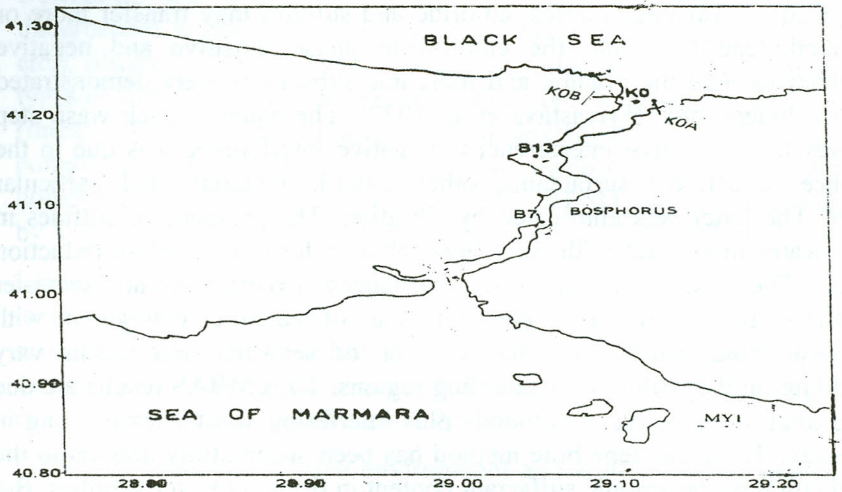
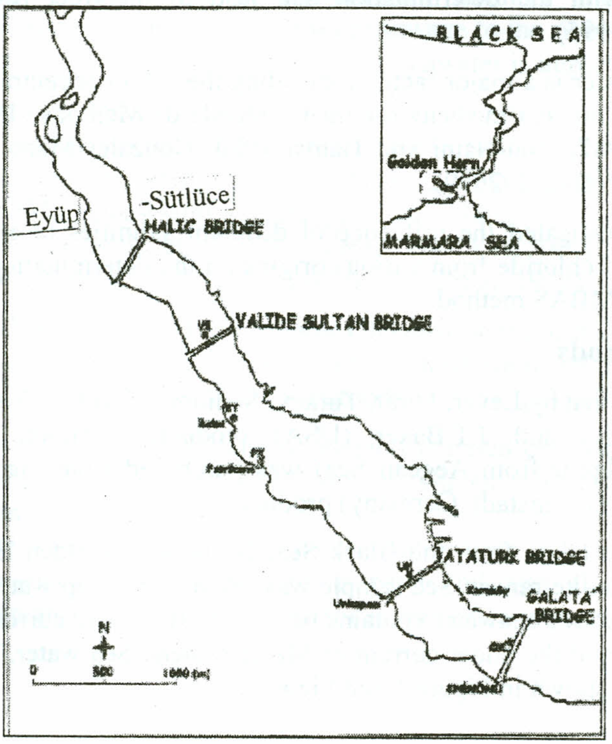


Figure 2. Sampling station of Golden Horn



In this work the modification MBAS method for LAS determination in seawater was made as.

1. Extraction time with chloroform from seawater was changed 6x15 ml instead of 3x15 ml as described by Standard Methods, 1995.

2. The blank is treated as sample omitting LAS addition instead of pure chloroform.

3. The modification of calibration curve: LAS solution was prepared with distilled water and various type of sodium chloride to imitate natural conditions of seawater. For the control, standard curve was also drown through Standard Methods with distilled water.

The determination of LAS

700 ml seawater or 18, 24, 34 ‰ salt added distilled water sample are transferred to a separatory funnel. The solution is alkalinized by dropwise addition of 1 N NaOH, using phenolphthalein indicator, shaken and treated 1 N H_2SO_4 until pink color disappear. 10 ml chloroform and 25 ml methylene blue reagent were added and shaken vigorously for 30 sec. The chloroform layer was filtered through glass wool into a 100 ml volumetric flask. The volume was adjusted to 100 ml with chloroform.

Calibration curve was plotted with LAS in a concentration of 10, 50, 100, 150 ug/L. Each the results are the mean of nine determinations.

Measurement: The absorbance of chloroform extract was measured at 652 nm against a blank of pure chloroform (through Standard Method) and the modified blank.

The LAS samples were prepared with various origin sodium chloride as salinity of 18, 24 and 34 ‰ in water.

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

LAS solution: 1 ml stock LAS solution was diluted to 100 ml with distilled water.

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

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

Methylene blue (MB) solution: 30 mg MB in 50 ml same salinity water tested.

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

Eq.1. Correlation equation was calculated from the calibration curve equations of each sodium chloride (common salt, sodium chloride pure (Baker and Merck) added in seawater in a concentration of 18, 22, 34 ‰ and through Standard Methods (omitting sodium chloride).

Eq.2. Correlation equations calculated from the standard curve equations of 18, 22, 34 ‰ common salt, Baker and Merck sodium chloride.

Results and Discussion

The equation of the calibration curves using different techniques are:

1. Through Standard Methods with 3x15 ml chloroform

   $y = 0.1923xc + 0.0231$ $r^2 = 0.998$

2. Modified Standard Methods

   Extraction with 6x15 ml chloroform

   $y = 0.2280xc - 0.0212$ $r^2 = 0.997$

The standard curve equation of LAS in different salinity is shown Table 1.

Standard curve of LAS by MBAS method was drown using distilled water. But the LAS was determined in rivers and especially in sea water. The problem in this subject is the influence of positive and negative interferences on this assay.

The modifications were also applied to calibration curve. Calibration solutions were prepared with distilled water added various type of sodium chloride to imitate natural conditions of sea water. For the control standard curve was drown through Standard Methods with distilled water.

The method used by LAS determination is MBAS method (Standard Method, 1995).

Table 1. The calibration curve equation of LAS in water with different salinities and correlation equations (1, 2) (µg/mL).

Origin of salt concentration	Salinity 18 ‰	Salinity 22 ‰	Salinity 34 ‰	Correlation Equation 1	Correlation Equation 2
Common Salt	y=0.2705xc-0.0051 r^2 = 0.998	y=0.2640xc-0.0072 r^2= 0.999	y=0.2250xc-0.0010 r^2 = 0.999	y=0.2424xc-0.0058 r^2 = 0.9991	y=0.2473xc-0.0008 r^2 = 0.9992
J.T.Baker	y=0.2648xc+0.0226 r^2= 0.9951	0.2460.c+0.0278 r2= 0.9982	y=0.2727.c+0.0278 r^2= 0,997	y=0.2534xc+0.0140 r^2= 0.9994	y=0.2611xc+0.0266 r^2=0.9982
Merck	y=0.2645xc+0.0215 r^2 = 0.9951	y=0.2460xc+0.0300 r^2 = 0.990	y=0.2727xc+0.039 r^2 = 0.997	y=0.2573xc+0.0250 r^2= 0.9989	y=0.2605xc+0.0302 r^2=0.9984

As can be seen in this Table standard curve equation of LAS in sodium chloride Merck and Baker products are similar but its differ in common salt.

The effect of extraction time 3x15 or 6x15 and modified blank and also correlation equations on the results in Bosphorus seawater and Golden Horn are shown in Table 2.

Table 2. The effect of extraction times on the assay calculated from MBAS and correlation equations (1, 2) in Bosphorus and Golden Horn seawater. (µg/mL)

Equation / Sample	Ext 3x15 Standard Method	Modified Standard Method Ext 6x15		Salinity18‰ with Common salts		Correlation equation	
		$CHCl_3$	MBC	$CHCl_3$	MBC	1	2
Baltalimanı termoclin	41.21	71.54	60.30	52.86	40.80	56.69	56.13
Golden Horn Surface	77.45	101.97	90.73	78.51	66.45	87.79	83.53
Golden Horn Deep	46.02	94.90	83.66	72.55	60.49	81.26	77.16
Eyüp-Sütlüce Surface	95.59	179.55	168.31	143.90	131.83	159.43	153.39

MBC:Modified Blank Chloroform, Ext: Extraction.

LAS amount found in the Golden Horn prepared with various origins of sodium chloride and correlations equations calculated from these equations are shown in Table 3 (µg/mL).

Table 3. LAS amount found in the Golden Horn calculated from modified method and correlations equations.

Sample \ Equation	18‰ Baker		Correlation Equation		18‰ Merck		Correlation Equation	
	$CHCl_3$	MBC	1	2	$CHCl_3$	MBC	1	2
Valide Sultan Deep	48.95	40.55	55.40	47.73	49.53	40.45	49.21	46.11
Haliç Bridge Surface	67.13	58.72	74.38	66.16	67.72	58.64	67.92	64.59
Haliç Bridge Deep	61.04	52.63	68.02	59.99	61.63	52.55	61.65	58.40
Eyüp-Sütlüce Surface	133.92	125.52	144.19	133.90	134.59	125.52	136.64	132.49

Ext: Extraction, MBC: Modified blank chloroform

LAS amount found in the Black Sea, Bosphorus, Sea of Marmara and the Mediterranean Sea using pure and modified chloroform calculated from the various equation curves are shown in Table 4.

Table 4. LAS amounts found in sea water through different calibration curve equation. (µg/mL)

Sea water	Station	Blank		Added NaCl	18‰		22‰		34‰		C .eq	
		PC	MBC		PC	MBC	PC	MBC	PC	MBC	1	2
Black Sea	K2 Surface	42.43	31.20	C.S	28.33	16.27	30.02	15.20	31.78	23.06	31.97	28.81
				B	15.86	7.46	13.72	1.63	13.02	1.19	20.82	14.17
				M	16.40	7.33	13.31	1.63	8.39	1.19	15.16	12.48
Bosphorus	KoA	71.05	59.81	C.S	52.45	40.93	54.73	39.91	60.78	52.06	58.89	55.20
				B	56.50	32.10	40.24	28.15	36.95	25.12	46.57	39.16
				M	41.07	31.99	39.84	28.15	32.32	25.12	40.52	37.25
	KoB	99.34	88.10	C.S	74.29	64.23	79.17	64.35	89.44	80.72	85.50	81.28
				B	64.86	56.46	66.46	54.37	60.60	48.77	72.02	68.66
				M	65.45	56.38	66.06	54.37	55.97	48.77	65.58	62.28
	B13 Surface	46.98	35.75	C.S	32.16	20.10	33.95	19.13	36.39	27.67	36.25	33.06
				B	19.78	11.38	17.94	5.84	16.82	5.0	24.91	18.14
				M	20.32	11.25	17.53	5.84	12.19	5.0	19.91	16.46
Sea of Marmara	M23 Surface	153.45	142.22	C.S	121.90	109.85	125.90	111.08	144.28	135.56	136.40	131.17
				B	111.45	103.05	116.62	104.52	105.84	94.01	120.71	111.12
				M	112.10	103.02	116.21	104.52	101.21	94.01	113.53	109.65
	MY1 Surface	103.89	92.65	C.S	80.13	68.07	83.10	68.28	94.06	85.33	89.78	85.47
				B	68.78	60.38	70.68	58.59	64.40	52.58	76.11	67.84
				M	69.38	60.30	70.27	58.59	59.77	52.58	69.62	66.27
Mediterranean Sea	B7 Deep	137.12	125.89	C.S	108.13	96.07	111.79	96.97	127.72	119.0	121.03	116.16
				B	97.38	88.98	101.47	89.38	92.18	80.50	106.01	96.85
				M	98.08	88.94	101.07	89.38	87.55	80.35	99.06	95.35

PC: Pure chloroform, MBC: Modified blank chloroform, CS: Common salts, B: NaCl Baker, M: NaCl Merck, C.eq: Correlation equation 1, 2

As can be seen in this Table 2, 3, 4 the LAS amount in seawater were changed through the method applied. When pure chloroform used as blank the amount of LAS in the sample was found high.

Table 5 shows the difference of LAS amount found between the methods used.

Table 5. The difference (%) between the method applied.

Salinity / Station	PC/MBC	Common salts	B/M salts	Eq.1/Eq.2
K_2	23	42	50	10
K_0A	14	22	56	15
K_0B	11	15	55	16
B13	27	38	39	10.1
M23	40	17	3	6
MY1	10	17.9	32.9	4.9
M7 deep	8	7	5	4

PC:Pure chloroform, MBC: Modified blank chloroform, B/M: Baker/Merck, Eq.1/ Eq. 2: correlation equation

Another observation is linearity was broken for concentrations of in:

Common salt ‰ 22

Baker NaCl ‰ 32

Merck NaCl ‰ 32

Conclusion

The role of extraction time

The discoloration of the sample in the assay was obtained after 6 extractions with chloroform and the amount of the LAS found was increased.

The effect of blank chloroform

When pure chloroform is used the calculated LAS amount is increased, compared to the modified blank.

The effect of salinity

When calibration curve is prepared in distilled water, LAS amount were higher. The results were also changed depending on the salt type.

It was found that the results of common salts and correlation equation 1 are similar.

The results were found reliable with commercial salt which was obtained from seawater and contained all the factors influencing on the assay.

The results of correlation equation (eq. 1) give more reliable results. Thus one equation can be used to prevent inconveniences practiced in the determination of anion active substances by MBAS method.

Hence the proposed modifications can help to obtained more reliable results.

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