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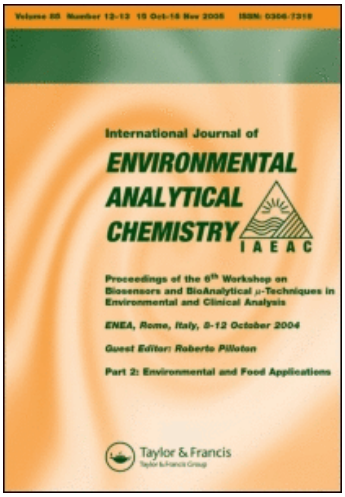

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Determination of Branched and Linear Alkylbenzene Sulfonates (Basand Las) in Water Using Hplc

S. L. Tong[a]; C. B. Tan[b]
[a] Institute for Advanced Studies, University of Malaya, Kuala Lumpur, Malaysia [b] The Analytical Laboratories (M), OffJalan Sungei Besi, Kuala Lumpur, Malaysia

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DETERMINATION OF BRANCHED AND LINEAR ALKYLBENZENE SULFONATES (BAS AND LAS) IN WATER USING HPLC

S.L. TONG

Institute for Advanced Studies, University of Malaya, 59100 Kuala Lumpur, Malaysia

C.B. TAN

The Analytical Laboratories (M), Off Jalan Sungei Besi, 57100 Kuala Lumpur, Malaysia

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Analytical methodology has been developed for the simultaneous determination of branched and linear alkylbenzene sulfonates (BAS and LAS) in river water and wastewater samples. The samples were purified and concentrated by solid phase extraction, followed by HPLC separation and quantification using a C_{18} column. The LAS homologues were well separated with prominent peaks corresponding to the different alkyl groups with carbon chainlengths from C_{10} to C_{14}. The elution of BAS shows a slightly broadened major peak with the same retention time as the C_{11} peak of LAS. The C_{12} peak, with no significant contribution from BAS components, has been chosen for the direct determination of LAS whereas the concentration of BAS can be calculated from the composite peak height of BAS after correcting for the C_{11} contribution from LAS. The method has been applied for the determination of the levels of specific LAS and BAS in some river water and wastewater samples. Comparison with the anionic surfactant concentrations measured in terms of the standard MBAS (methylene blue active substances) values is presented.

KEY WORDS: Branched alkylbenzene sulfonate, linear alkylbenzene sulfonate, HPLC, solid phase extraction.

INTRODUCTION

Alkylbenzene sulfonates (ABS) have been the major surfactant for synthetic household detergents worldwide since the 1950's. Depending on the manufacturing process, a highly branched ABS called branched alkylbenzene sulfonates or BAS, and an ABS with a linear side chain called LAS are available. The BAS are regarded as "hard" detergents because of its relatively slow biodegradation rate as compared to the "soft" LAS detergents which are more quickly degraded by common microorganisms. Presence of significant levels of these detergents in sewage and the waterways has been known to cause foaming problems in sewage and water treatment plants operations. The persistence of these detergents in river water can also cause adverse effects to aquatic life. The foaming problem has led the

industrial countries to switch in the 1960's from BAS to LAS which has since been found to be a satisfactory solution.[1]

In Malaysia, BAS is still in common use in the main types of detergents although in recent years the use of LAS is in a moderately increasing scale. Analytical methodology is therefore required for the specific determinations of BAS and LAS in waste water and ambient water both for research studies and pollution monitoring as the existing detergent pollution data available are measured in terms of the non-specific MBAS level.

Various chromatographic methods have been reported for the specific determination of LAS. These include the methods of derivatisation followed by gas liquid chromatography (GLC) reported by Swisher[2], Sullivan *et al*[3], Hon-Nami *et al*[4], and Osburn[5]. These methods require intensive sample pretreatment and derivatisation which makes it rather tedious and time-consuming.

High performance liquid chromatographic (HPLC) methods have been developed and reported by Linder and Allen[6], Smedes *et al*[7], Nakae *et al*[8], Matthijs and De Henau[9], where the separation of the main LAS homologues is sufficient for the specific determination of LAS although lacking the high specificity of derivatisation-GLC technique. The HPLC technique which normally includes a clean-up step using solid phase extractor is relatively simple and suitable for routine applications.

However, no method for the specific determination of BAS has been reported, probably because of the complete stop in use of BAS in industrial countries. Recognising the simplicity and potential of HPLC technique and the HPLC-based method reported for LAS measurement by Matthijs and De Henau[9], a method for the simultaneous determination of both BAS and LAS has been developed. The method involves a simple solid phase extraction and clean-up followed by HPLC separation using a reversed-phase C_{18} column. Quantification for LAS is based on the peak heights of C_{12} peak which is specific to LAS, whereas the composite peak making up of the major components of BAS and the C_{11} component of LAS is used for the estimation of BAS after correcting for the LAS fraction. Results obtained from the analysis of river water and wastewater samples in comparison with the standard MBAS values for anionic surfactants are discussed.

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EXPERIMENTAL

Materials

Solid phase extraction columns packed with octyl reversed-phase silica (C_8) were purchased from Supelco (40μm porosity, bonded silica, 500 mg/3 ml per column). The columns were conditioned with 10 ml methanol and 10 ml water successively before use.

Technical grade LAS and BAS were obtained rom PETRESA ESPANOLA, S.A., Madrid, Spain as 10.06% and 10.20% active solution respectively. Aqueous standard solutions were prepared from these stocks by serial dilution in distilled water. Analytical grade reagents and chromatographic grade acetonitrile were used in all preparations.

Treatment of LAS and BAS standards

The LAS and BAS standard stocks were prepared at concentration of approximately 20 mg/l in deionized water. A series of LAS and BAS standards were then prepared by passing 5-50 ml of the LAS or BAS standard stocks over the C_8 reversed-phase silica column respectively. The column was washed with 5 ml of deionized water and 3 ml of 40% methanol solution in water. The retained materials were then eluted with 5 ml of methanol. The final eluate, containing LAS or BAS, was transferred into a vial and dried on a steambath. The samples were kept in a dry state until analysis by HPLC. The residue was reconstituted to 50 ml in an acetonitrile/water (55/45) solvent mixture prior to HPLC injection.

Treatment of mixed LAS/BAS standards

The mixed LAS/BAS standard stocks were prepared at total concentration of 50 mg/l in deionized water. LAS and BAS were mixed in concentration ratios of 0:1; 1:5; 1:3; 1:1; 3:1; 5:1; and 1:0 and passed through C_8 column and treated as described above before injection into the HPLC column.

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Detergent and water samples

Environmental water samples were taken from the Klang River Basin. Eight sampling points were selected and the locations are shown in Figure 1 map. In addition, water samples from the influent and effluent of Pantai Sewage Treatment Plant, Kuala Lumpur were also collected during the same period of the study.

The water samples (2L) were collected in polyethylene containers, preserved on site with 1% formaldehyde solution, and stored in a refrigerator at <4°C. The samples were also tested for MBAS, pH, conductivity, turbidity, chemical oxygen demand (COD) and biochemical oxygen demand (BOD), following the methods in *Standard Methods for the Examination of Water and Wastewater*[10].

A total of ten common brands of commercial detergents were obtained consisting of four in liquid form and six marketed as powder detergents. Solutions of the samples were prepared in deionized water.

Isolation and concentration procedures

The water samples were adjusted to pH 7.0 using 0.1 M sodium hydroxide and filtered through 47-mm diameter 0.45 μm membrane filter. A 100 mL aliquot of the filtrate was passed over a C_8 reversed-phase silica column. The column was washed with 5 ml of water and 3 mL of 40% methanol in water. The LAS/BAS retained was eluted with 5 ml of methanol and collected in a vial. The eluate was dried on a steambath and kept in the dry state. Prior to HPLC analysis, the residue was redissolved in 1.00 ml of an acetonitrile/water (55/45 solvent mixture).

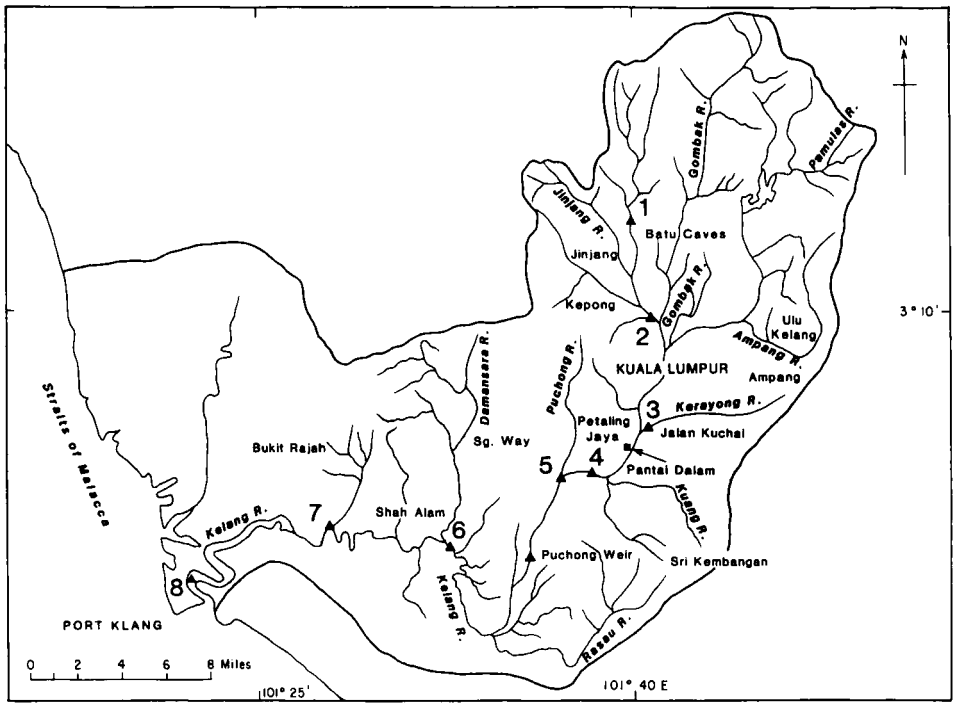

Figure 1 Location map of Klang River water quality sampling points (1 to 8).

HPLC Measurements

The liquid chromatograph employed (Shimadzu Corporation) consists of a dual pump system (LC6A), an injector (Rheodyne 7161) with a 20-µl loop, a variable wavelength UV-Vis detector (SPD-6AV) and an integrator (CR6A chromatopac).

The HPLC separation was achieved on a 7 µm, 250 mm × 4.6 mm i.d. PHENOMENEX ZORBAX C_{18} column. The mobile phase consists of 55% of acetonitrile and 45% of 0.33 M $NaClO_4$ in water and the LAS/BAS elution was done isocratically for 20 minutes at the column temperature, 40°C. The column effluent was monitored using UV detection at 230 nm. The flowrate was maintained at 1 ml/min. The chromatographic system was washed extensively with water at the end of each day to prevent crystallisation of the inorganic salt present in the mobile phase. The column was subsequently rinsed with pure acetonitrile for regeneration.

RESULTS AND DISCUSSION

LAS and BAS calibration: Peak height versus peak area

Typical chromatograms of LAS and BAS standards are shown in Figure 2. The LAS chromatogram shows the complete distribution of the LAS homologues by their alkyl

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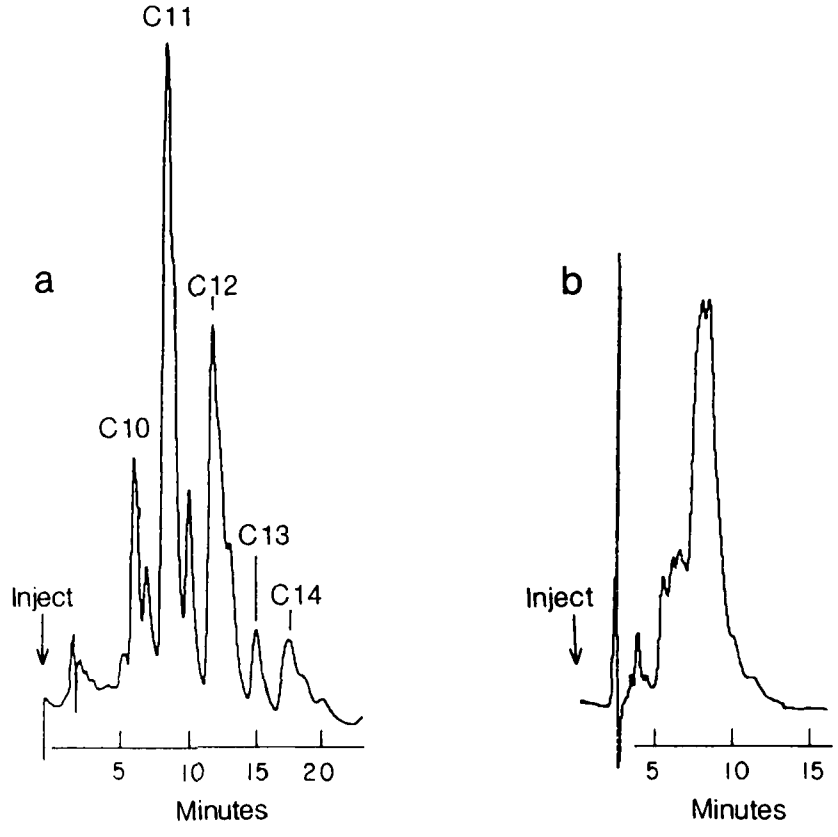

Figure 2 Typical HPLC chromatograms of (a) separation of LAS; and (b) elution of BAS on a C_{18} column.

chainlength from C_{10} to C_{14} as four well-resolved peaks in similar pattern as those reported by Matthijs and Henau[9]. However, the chromatogram for standard BAS shows a group of minor peaks with retention time of less than 7.5 minutes and a slightly broadened major peak with retention time which coincides with the C_{11} peak of LAS. The major peak represents the elution of the major components of BAS.

Linear calibration curves been obtained for LAS using peak heights as well as peak area for both C_{11} and C_{12} peaks for LAS standard solutions form 2 to 20 mg/l. the C_{11} and C_{12} peaks represent the two principal homologues of LAS and the best sensitivity is obtained using these two peaks.

For the quantification of BAS using the HPLC chromatograms, the calibration curve for BAS based on the peak height of the major peak was linear from 2 to 20 mg/l. Calibration for BAS based on peak areas was sensitive to the peak width parameter used in the integration which may result in significant deviation from linearity.

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LAS and BAS contents in commercial detergents

Table 1 presents the results of the LAS and BAS contents in some common brands of commercial detergents obtained from the market. The results were based on HPLC determinations using separate LAS and BAS standard calibrations. The detergent samples were also analysed and cross-checked by the Laboratory of Petresa Madrid in Spain[11] using the derivatisation-GLC method. This method gave much higher resolution and specificity in the analysis of the distribution of the homologues according to the carbon chainlength for both LAS and BAS. The data obtained by the two laboratories were in good agreement within the standard deviation limits of the analytical results.

The derivatisation-GLC method showed that all ten types of detergents analysed were based on either single LAS or BAS as the active constituent. The content of LAS in the four types of liquid detergents tested ranges from 13 to 19%. The six types of household powder laundry detergents studied contains 20 to 31% of BAS as the active ingredient.

The distribution of the LAS homologues among the various brands of liquid detergents are also shown in Table 1. The percentage of C_{11} homologues shows significant variation ranging from 9 to 39.1%, whereas the C_{12} components are within a narrower range from 22 to 35%. An average C_{12} content of 29.1% has been adopted as representative of the common LAS-based detergents for the estimation of LAS level in river water samples in Malaysia.

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Table 1 (a) LAS and BAS content in household detergents and (b) LAS composition.

(a) No.	*Sample Marking*	*LAS,%*	*BAS,%*
1	Dy	13	0
2	Su	17	0
3	Zi	18	0
4	Gl	19	0
5	Ec	0	26
6	Bp	0	27
7	Tr	0	21
8	Fp	0	20
9	Fb	0	28
10	Bb	0	31

(b) Detergent Type	*LAS Homologue Composition, %*					
	$<C_{10}$	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
DY	0.1	1.9	12.0	31.5	39.2	15.3
Su	0.9	2.6	9.0	27.0	42.5	18.0
Zi	—	8.5	36.7	35.5	16.5	2.8
Gl	5.5	21.4	39.1	22.3	8.4	3.3
Average	1.6	8.6	24.2	29.1	26.6	9.9

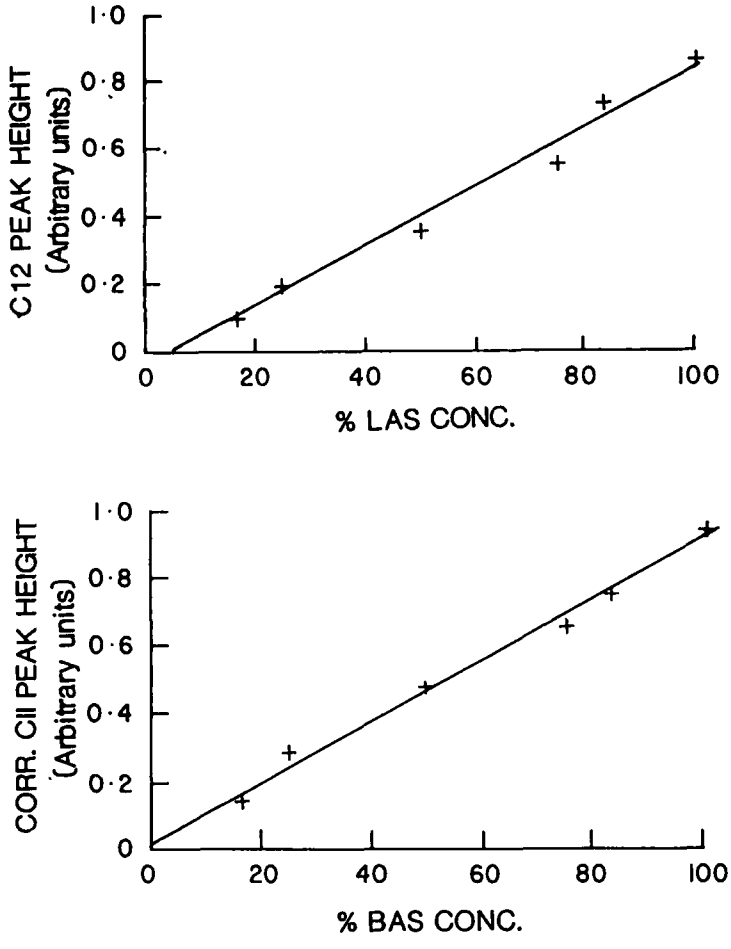

Figure 3 Specific LAS and BAS peak height versus percentage concentration in mixed LAS/BAS standards of constant total concentration.

Calibration for simultaneous determination of LAS and BAS

To study the possibility of using HPLC separations for the simultaneous determination of LAS and BAS in water samples, chromatograms have been obtained for mixed LAS/BAS standards under the same conditions established for LAS separation. The mixtures were prepared in LAS:BAS ratios of 0:1; 1:5; 1:3; 1:1; 3:1; 5:1 and 1:0 with a constant total concentration of 50 mg/l. The peak height ratio of the C_{11} to C_{12} peaks ($LASC_{11}/LASC_{12}$ obtained from the standard LAS HPLC chromatogram is used in the estimation of the LAS contribution to the C_{11} peak in the mixture chromatogram.

The quantification of LAS in a mixture chromatogram is based on the calibration curve plotted as:

Peak height C_{12}vs. [(conc LAS)/(conc LAS + conc BAS)].

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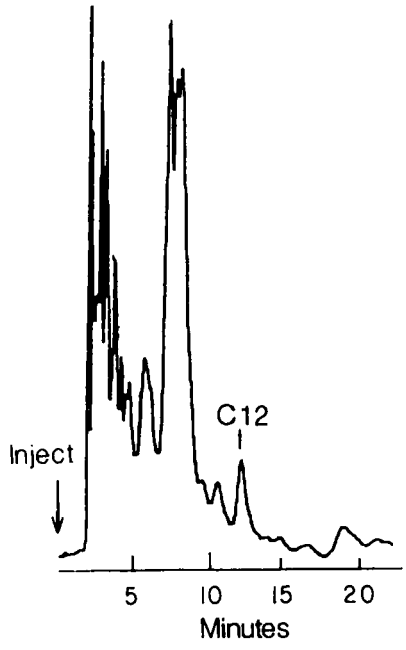

Figure 4 HPLC chromatogram of a purified and concentrated river water sample.

The concentration of BAS is then calculated from a plot of:

[Peak height C_{11} - peak height $C_{12} \times (LASC_{11}/LASC_{12})$] vs. [(conc BAS)/(conc LAS + conc BAS)].

The two calibrations obtained are as shown in Figure 3. Since the total concentration has been kept constant, the results implied that linear curves are obtained for the calibration based on (a) peak height C_{12} vs conc LAS; and (b) [peak height C_{11} - peak height $C_{12} \times (LASC_{11}/LASC_{12})$] vs. conc BAS.

This approach has been employed for the simultaneous determination of LAS and BAS concentrations in water samples based on the measured peak heights corresponding to the C_{12} and C_{11} peaks. A typical HPLC chromatogram of the extract from a river water sample is shown in Figure 4. In this example, the concentrations of LAS and BAS calculated were 0.12 and 0.44 mg/l, respectively.

Solid phase extraction

Solid phase extraction is a simple and effective way for the clean-up, isolation and concentration of LAS and BAS from sample matrices as compared to the solvent extraction and ion exchange procedure recommended in standard MBAS method for surfactants determination. The conditions adopted are similar to those reported for LAS by Metthijs and Henau[9]. In this study, both LAS and BAS have been found quantitatively retained on

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Table 2 Recovery of spiked LAS and BAS in river water samples.

Sample No.	*Conc.Found (Unspiked Sample)*		*LAS Spiked Recovery (Spiked: 0.48 mg/l)*		*BAS Spiked Recovery (Spiked:0.62 mg/l)*	
	LAS mg/l	*BAS mg/l*	*LAS mg/l*	*%*	*BAS mg/l*	*%*
1	0.00	0.04	0.50	104.2	0.66	103.2
2	0.00	0.07	0.44	91.7	0.67	96.7
3	0.32	0.52	0.79	98.8	1.04	91.2
4	0.00	0.22	0.45	93.8	0.88	104.8
5	0.41	0.59	1.01	113.5	1.35	109.1
Ave.% Recovery				100.4		101.7

the C_8 column from aqueous samples. No detectable loss of either of these species is encountered in the rinsing step using 40% methanol in water. Complete recovery is achieved with 100 % methanol subsequently for both species.

Table 2 summarises the recovery of LAS and BAS from water samples spiked separately with LAS and BAS. Two of the samples were found to contain significant level of LAS in addition to the higher level of BAS as expected in river water. Percentage recovery of 100.4% and 101.7% has been obtained for LAS and BAS respectively.

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Specific LAS and BAS levels in environmental water samples and comparison with MBAS values

Analytical results obtained in applying the methodology developed to water samples taken from Klang River and the influent and effluent from a wastewater treatment plant are shown in Table 3. Also shown for comparison are the MBAS values and other parameters, including pH, conductivity, turbidity, COD and BOD.

In the river water, LAS was only detectable at a point where the river is receiving the

Table 3 Concentrations of LAS and BAS in river and wastewater samples in comparison with other parameters*.

SAMP. POINT	*LAS*	*BAS*	*MBAS*	*pH*	*COND*	*TURB*	*COD*	*BOD*
1	ND[§]	0.20	0.41	6.80	131	96.8	24	9
2	ND	0.17	0.18	6.90	68	321.8	52	15
3	ND	0.40	0.70	6.95	340	115.7	68	50
4	ND	0.32	0.68	7.20	240	143.4	68	14
5	0.20	1.11	2.18	7.00	379	29.0	164	53
6	ND	0.30	0.28	7.05	181	327.1	96	16
7	ND	0.22	0.25	7.15	141	368.4	172	33
8	ND	0.41	0.96	7.10	9700	17.8	80	41
9	0.40	1.01	1.67	6.90	435	66.5	256	150
10	0.14	0.63	1.09	6.85	344	19.0	72	52

*All concentrations in mg/l except for pH, COND (Conductivity, μmhos/cm) and TURB (turbidity, NTU).
[§]Not detectable.

industrial and domestic wastewaters via its tributaries passing through the major parts of industrial town Petaling Jaya. However, significant detergent pollution in terms of BAS level in the river water is noted. The highest level of BAS of 1.11 mg/l was observed at point 5. The concentrations of BAS found in other points are in the range from 0.17 to 0.41 mg/l. These values are close to the limits of ambient water quality standards of 0.3 to 0.5 mg/l commonly adopted for the protection of aquatic life.

In the influent and effluent water from the sewage treatment plant, the levels found were 1.01 and 0.63 mg/l for BAS, and 0.40 and 0.14 mg/l for LAS, respectively. The percentage reduction of LAS of about 65% is comparable to the decrease in BOD in the effluent water, whereas the reduction in BAS is significantly less (about 38%).

A comparison between the MBAS data and the combined BAS and LAS concentrations shows that the MBAS values represent an over estimation of the actual detergent level in most of the river water samples. The higher levels of MBAS found have been attributed to the non-specific nature of the methylene blue reagent which responds to, in addition to LAS and BAS, other anionic materials also[10].

The present study has shown that BAS can be determined simultaneously with LAS in water and wastewater samples using solid phase extraction for sample clean-up followed by HPLC separation for quantification. The specific BAS and LAS levels obtained will allow a more accurate assessment of the actual detergent pollution due to the anionic detergents in river water than the standard MBAS method normally adopted in water pollution monitoring. The proposed method also can be adopted for the evaluation of the relative biodegradability of BAS and LAS in the aquatic environment. The method is simple, efficient and suitable for routine applications.

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