Analytical Methodology for Linear Alkylbenzene Sulfonate (LAS) in Waters and Wastes

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Analytical methodology has been developed for the measurement of linear alkylbenzene sulfonate (LAS) in a broad spectrum of water and wastewater samples. In addition to providing the homolog-isomer composition of LAS, the gas chromatographic procedure has been quantified by incorporation of an internal standard to provide a specific measurement of LAS. The applicability and sensitivity of the standard, but non-specific, methylene blue active substances (MBAS) method have been increased by concentration and clean-up steps that eliminate many of the known interferences. The gas chromatographic procedure has provided specific, as well as significant, information relative to the removal of LAS in the waste treatment process.

Approximately two decades have passed since the introduction of linear alkylbenzene sulfonate (LAS) as a major anionic surfactant used by the detergent industry. Numerous investigations concerned with the biodegradability and biodegradative mechanism of LAS have been carried out and published through the ensuing years. However, standardized analytical methodology for the measurement and characterization of LAS in a broad spectrum of water and waste samples has been slow to develop.

The routinely used method for the measurement of LAS in water and wastewater has been the colorimetric methylene blue active substances (MBAS) procedure (1). This method has been widely recognized as being nonspecific for LAS because it is subject to a number of positive, as well as negative, interferences (1,2). Further, because this method is calibrated in terms of a standard LAS, there has been a tendency to equate MBAS with LAS.

As early as 1963 Setzkorn and Carel (3) described a microdesulfonation procedure in which the LAS is desulfonated by boiling with concentrated phosphoric acid. The alkyl benzenes, isolated from the distillate, were then separated by gas chromatography. The specificity of the desulfonation-gas chromatography technique has been a key element in the elucidation of the biodegradation process of LAS by providing a clear picture of homolog-isomer compositional changes (2). Various modifications of this technique have been used by Swisher (4) and a number of other investigators for the examination of waters and wastewaters.

Waters and Garrigan (5) have described a desulfonation-gas chromatographic procedure for the determination of LAS in United Kingdom river water samples. In their procedure 1-phenyl isomers were used as internal standards for quantitation.

This paper presents analytical methodology that expands applicability of the MBAS and desulfonation-gas chromatographic procedures to primary and digester sludges, as well as to stream sediments. This extended applicability has made possible a comprehensive study of the fate of LAS from entry into the wastewater treatment process to final disposal.

EXPERIMENTAL-ANALYTICAL METHOD

Principle. The sample was carried through one of three preliminary operations, dependent upon sample type (Fig. 1). Following the initial step the sample was subjected to a standardized sequence of operations that led to measurement of interference limited MBAS (IL-MBAS) and LAS by desulfonation-gas chromatography.

Apparatus. Ion-exchange columns of conventional design were used that accommodate a resin bed of ca. 11 × 180 mm. The columns should be fitted with joints to accommodate a Teflon stopcock joint assembly and a 250 or 500-ml reservoir. Desulfonation apparatus, see Figure 2. The gas chromatograph was Varian Model 3700, and the chromatography data station was Perkin Elmer Sigma 10.

Reagents. The Amberlite XAD-2 resin (purified) was obtained from Applied Science Division, Milton Roy Company Laboratory Group, Cat. No. 17319. The anion exchange resin was Bio-Rex 9, 50–100 mesh, obtained from Bio Rad Laboratories. Solvents, acids and other reagents were reagent grade.

Solutions. Acidic (HCl) methanol (4N) was prepared by adding 40 vol of concentrated hydrochloric acid to 80 vol of methanol; it was mixed well and allowed to cool to room temperature.

Acetic acid in methanol was prepared by adding 2 vol of glacial acetic acid to 100 vol of methanol. Methanolic sodium hydroxide solution was prepared by dissolving 1.0 g of sodium hydroxide pellets in 500 ml of methanol. C-9 LAS, 100 $\mu g\ ml^{-1}$ in distilled water.

Preparation of ion-exchange columns. The XAD-2 resin column was prepared by placing a plug of glass wool near the bottom of the column and filling the column halfway with methanol. With the column stopcock partially open, a methanol slurry of the resin was added to the column slowly until a bed depth of 150–160 mm was obtained. A plug of glass wool was placed on top of the resin bed and a suction line from a water aspirator attached to the delivery tip of the column. The column stopcock was opened and the column inverted with the top of the column immersed in a 500 ml beaker of distilled water. Approximately 200 ml of water was pulled through the resin bed, the stopcock closed, and the column rapidly reinverted leaving the resin bed covered with water. A 500 ml reservoir was attached to the top of the column.

The Bio-Rex 9 resin column was prepared by placing a plug of glass wool near the bottom of the column and filling the column halfway with methanol. With the stopcock partially open, a methanol slurry of the anion exchange resin was added to the column to a bed depth of approximately 180 mm. The resin bed was kept covered with methanol at all times.

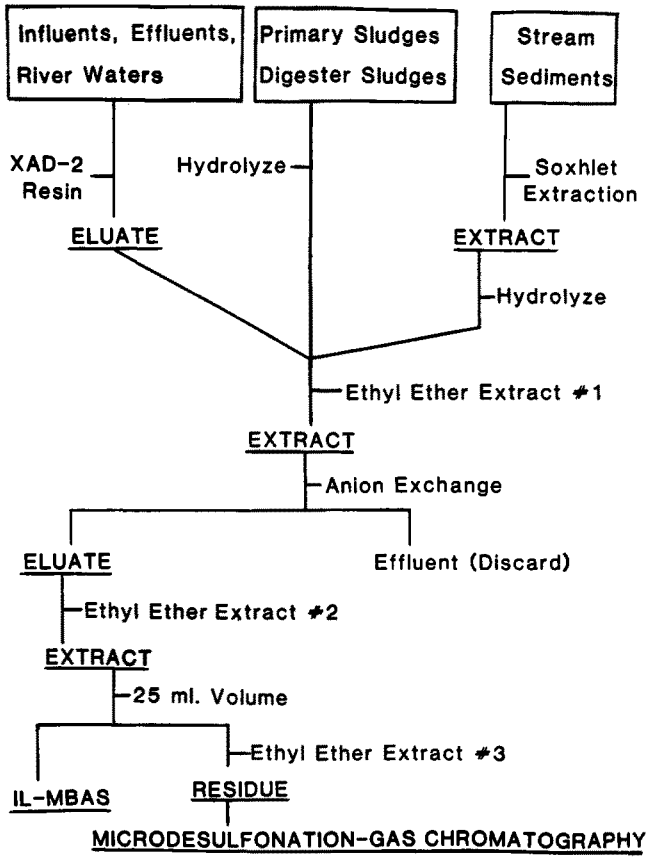

FIG. 1. Analytical schematic.

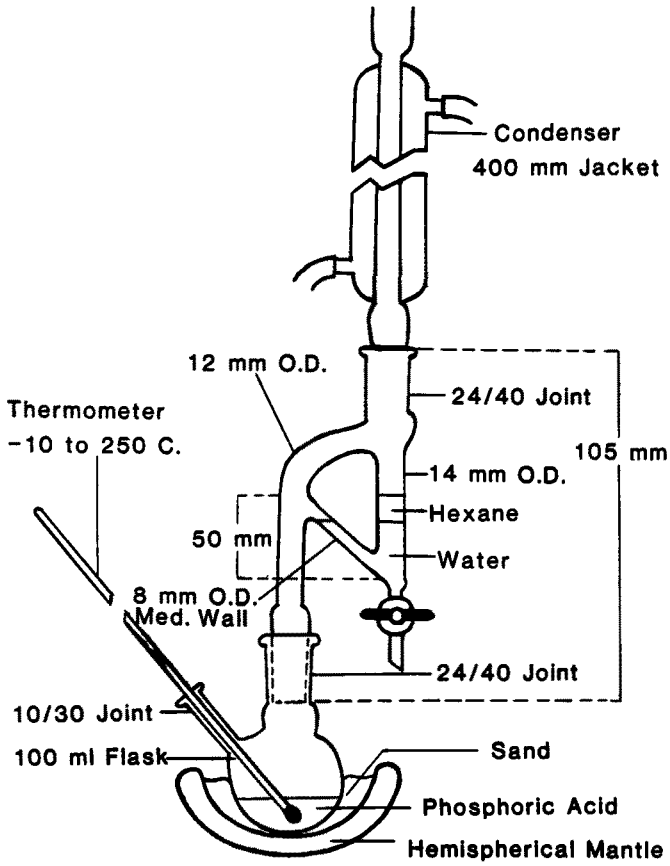

FIG. 2. Desulfonation apparatus.

Procedure, XAD-2 resin concentration (Operation A). A sample volume, estimated to contain 300–1000 μg of LAS, was passed through the XAD-2 resin bed at a rate not exceeding one drop per second. Typical sample volumes were in the following range:

Sample type	*Sample volume*
Influent	250–1,000 ml
Final effluent	2–4 liters
River water	4–8 liters

Following passage of the sample, the reservoir and resin bed were rinsed with two 25-ml portions of distilled water. Water was removed from the column by passing 30–40 ml of ethyl ether through the resin bed. This usually required application of pressure with a suction bulb, the pressure being applied in such a manner that discharge from the column was drop by drop. When the ether reached the level of the upper glass wool plug, the stopcock was closed and the contents of the receiving vessel discarded.

A clean 250-ml extraction flask was placed under the column and the resin eluted sequentially, at a rate of approximately one drop per second, with 25 ml methanol, 40 ml of methanolic sodium hydroxide solution, 25 ml methanol, 55 ml of 25:25:5 methanol:chloroform:conc. HCl and 25 ml of methanol. The eluate was then evaporated to near dryness on a steam bath under a stream of nitrogen or clean, dry air.

Acid hydrolysis (Operation B). A representative sample of well-mixed primary or digester sludge was homogenized in a blender and 8–20 g of sample rapidly transferred into a tared 20-ml liquid scintillation vial (or equivalent) and reweighed. The weighed sample was washed into a 150-ml extraction flask with approximately 60 ml of distilled water. Two boiling stones and 10 ml concentrated HCl were added and the flask placed on an electric hot plate (medium heat). The acidified sample was boiled slowly until the volume was reduced to approximately 25–30 ml.

Soxhlet extraction (Operation C). A 10–40 g sample of dry sediment was weighed into a 33 × 94 mm cellulose extraction thimble, covered with a plug of glass wool and extracted for 16 hr with methanol using a Soxhlet extraction apparatus.

The methanol extract was transferred into a 150-ml extraction flask and evaporated to dryness on a steam bath under a stream of nitrogen or clean, dry air. To the residue was added 60 ml distilled water, two boiling stones, and 10 ml concentrated HCl, following which the solution was boiled gently on a hot plate (medium heat) until the volume was reduced to 25–30 ml.

Ethyl ether extraction #1 (Operation D). The eluate residue from Operation A or the hydrolyzed solution from Operation B or C was transferred into a 250-ml separatory funnel with distilled water to a total volume of approximately 60 ml. Following the addition of 20 ml of concentrated HCl, the funnel was stoppered and the acidified solution mixed by inverting the funnel several times. The solution in the funnel was allowed to cool to room temperature, following which the extraction flask from

Operation A, B or C was rinsed with 65 ml ethyl ether into the separatory funnel. The funnel was shaken vigorously for one minute, the layers allowed to separate, and the lower acid layer drained into a second 250-ml separatory funnel. The first funnel was swirled and the lower layer again drained into the second funnel. The ethyl ether layer was decanted into a clean, dry 150-ml extraction flask and evaporated on a steam bath under a stream of nitrogen. The first funnel was rinsed with 65 ml of ethyl ether which was added to the second funnel and the extraction described above repeated. The acid layer was discarded and the ether layer decanted into the 150-ml extraction flask. The combined ether extracts were evaporated to dryness.

For sludge samples (Operation B) a total of four ether extractions were made to effectively achieve separation of the ether layers from the acid layer, which contained a high level of particulate matter.

Anion exchange (Operation E). The ether extract residue from Operation D was dissolved in approximately 5 ml of chloroform and 10 ml of methanol and passed through the Bio-Rex 9 resin bed at a rate of one drop per second. The extraction flask was rinsed two times with 10-ml portions of methanol, each portion being added to the column when the solvent level was 1–2 cm above the resin bed. The resin was then washed with 100 ml acetic acid in methanol solution using a 250-ml column reservoir. The reservoir was then removed and the resin bed washed with two 10-ml portions of methanol. The column effluent was discarded.

A clean, dry 150-ml extraction flask was placed under the column and the resin eluted with 120 ml of the 4N acidified methanol, followed by 20 ml of methanol. The eluate was then evaporated to near dryness on a steam bath under a stream of nitrogen or clean, dry air.

For ether extractables from sludge samples the initial transfers into the Bio-Rex 9 column were made with three 10-ml portions of equal parts of chloroform and methanol.

A newly prepared Bio-Rex 9 resin column must be used for each sample.

Ethyl ether extraction #2 (Operation F). Operation D was repeated with the concentrated eluate from Operation E using two 65-ml ethyl ether extractions. The ether extractables residue was then transferred into a 25-ml volumetric flask with ethyl ether, made to volume with ether and mixed well by shaking.

Interference limited MBAS (Operation G). A 2.0-ml aliquot of the ether solution from Operation F was pipetted into a 150-ml extraction flask and the ether removed by evaporation under a stream of nitrogen. The residue was dissolved in 10 ml of chloroform and added to a 250-ml separatory funnel containing 200 ml distilled water and 25 ml of the methylene blue reagent. The MBAS determination was then carried out as described in Method 512A of *Standard Methods for the Examination of Water and Wastewater* (1). The 150-ml extraction flask was rinsed with each of the three subsequent 10-ml portions of chloroform before addition to the separatory funnel.

In those cases where the micrograms of MBAS were greater than the upper limit of the calibration curve, the determination was repeated using a smaller volume of the ether solution.

Sample volumes or weights used for calculations of IL-MBAS results were: Original volume or weight × Aliquot volume/25.

Ethyl ether extraction #3 (Operation H). This operation was carried out for the purpose of adding the C-9 LAS internal standard used to quantitate LAS by the desulfonation-gas chromatographic procedure. Into a 250-ml separatory funnel were added, in turn, 45 ml distilled water, 1.00 ml of the C-9 LAS solution (100 $\mu g\ ml^{-1}$) and 15 ml concentrated HCl.

The $\mu g\ ml^{-1}$ of ether in the volumetric flask was calculated from the results of the MBAS determination (Operation G). If the MBAS concentration was 50 $\mu g\ ml^{-1}$ or less, the remaining 23 ml of ether solution was transferred into the separatory funnel, using 40–45 ml of fresh ethyl ether to rinse the volumetric flask into the separatory funnel. When the MBAS concentration of the ether solution was greater than 50 $\mu g\ ml^{-1}$, the volume of ether solution required to provide not more than 1000 μg of MBAS was calculated and this volume pipetted into the separatory funnel. Fresh ethyl ether was added to make a total ether volume of 65 ml.

Two ether extractions were carried out as described in Operation D, following which the residue of the ether extractables was transferred into a 100-ml microdesulfonation flask (Fig. 2) with three 10-ml portions of ethyl ether. The ether was removed by evaporation. Sample volumes or weights used for desulfonation-gas chromatography were calculated as shown under Operation G.

Microdesulfonation (Operation I). The thermometer was inserted into the thermometer neck of the desulfonation flask from Operation H, and two small boiling stones and 25 ml of 85% phosphoric acid were added to the flask. The trap, with stopcock closed, was attached to the flask and distilled water added to nearly overflow level of the lower return tube of the trap, following which 1.0–1.5 ml of hexane was added on top of the vertical column of water. The trap was attached to the condenser and the assembled apparatus lowered into the hemispherical heating mantle. Dry Ottawa sand was used to fill the mantle around the flask. The stopcock was then opened cautiously and water removed drop by drop until the bottom of the hexane layer was approximately 1.0 cm above the lower return tube.

The heating mantle control Powerstat, set at 80 volts, was turned on and, when reflux caused the return tube to reach the point of overflow, several drops of water were drained from the trap; care was taken to keep the bottom of the hexane layer approximately 1.0 cm above the lower return tube. Water removal was continued in this manner until a temperature of 215 C was reached. From this point reflux was continued for 3 hr. At the end of the 3-hr reflux period, the heat was turned off and the flask allowed to cool.

All but 0.5 ml of water was drained from the trap, the condenser walls rinsed with three 1.0-ml portions of n-pentane, and the water layer again cautiously drained until the hexane-pentane layer reached the stopcock plug. The delivery tip of the trap was dried with a tissue, following which the solvent layer was drained into a 2-dram screw cap vial containing a bed depth of approximately 1.0 cm of anhydrous sodium sulfate crystals. The vial was covered with aluminum foil, capped tightly, mixed by gentle shaking and allowed to stand for at least 10 min.

The hexane-pentane solution was transferred, in in-

crements, with a Pasteur disposable pipet from the 2-dram vial into a 3-ml micro reaction vial. Each increment was evaporated to approximately 1.0 ml, without heat, under a gentle stream of nitrogen before addition of the next increment. Following transfer of all the hexane-pentane solution, the sodium sulfate was rinsed with 2 ml of pentane which also was transferred into the reaction vial. The contents of the vial were evaporated, the evaporation being discontinued immediately upon removal of the solvent. The reaction vial was covered with aluminum foil and tightly capped with a septum screw cap.

Gas chromatography (Operation J). Typically 500 μl of toluene was injected into the 3-ml reaction vial from Operation I and briefly agitated on a vortex mixer to effect complete dissolution of the alkylbenzenes in the toluene.

The chromatographic analysis was carried out on a Varian 3700 chromatograph fitted with a flame ionization detector. A Supelco-DB-1 fused silica capillary column (15 m, 0.32 mm i.d., film thickness 1.0 micrometer) was used. A sample injection of 1.4 μl of the toluene solution was generally used, using a 25:1 split with injector and detector zones at 300 C. A helium carrier gas pressure of 10 psi and detector hydrogen and air pressures of 30 psi were used. The analysis was programmed from 100 to 170 C at 5 C/min with a final temperature hold time of 25 min. An amplifier range of 10 and attenuation setting of X2 were used. A Perkin Elmer Sigma 10 data station was used to record the chromatogram and integrate the individual LAS isomer peaks.

Calculations. μg C10–C14 LAS = 100 μg C9LAS × ΣC10–C14 peak areas/ΣC9 peak areas. LAS (Mgl^{-1} or μg g^{-1}) = μg C10–C14 LAS/ml or g of sample desulfonated. Isomer distribution, normalized to 100%, was calculated as shown below. % Individual isomer = peak area of isomer × 100/ΣC10–C14 isomer peak areas.

DISCUSSION

IL-MBAS. The interference limited connotation given to the MBAS determination in this methodology means that some known interferences have been eliminated by the concentration and clean-up steps employed. Acid hydrolysis was employed to eliminate the positive interference of organic sulfates as well as to facilitate the ethyl ether extraction of LAS adsorbed on solids. The anion exchange step was necessary for the elimination of the negative interference of quaternary ammonium compounds and long chain amines. In addition, lipophilic substances, particularly from sludges, were removed by this step.

The XAD-2 resin concentration step successfully eliminated interferences due to inorganic salts, such as metal chlorides. The elimination of inorganic salts has made the MBAS determination just as applicable to ocean and estuarine waters as to non-saline waters. Although this methodology has successfully eliminated most known interferences, many unidentified MBAS interferences remain, particularly in river water and sewage effluent samples. For this reason the IL-MBAS method cannot be considered as providing a specific measurement of LAS.

Desulfonation-gas chromatography. Swisher (2) has presented a thorough discussion of the formation of tetralones and indanones upon desulfonation of certain products of LAS biodegradation. These cyclized materials have chromatographic retention times overlapping the linear alkylbenzene isomers and could result in some interference with the quantitation and compositional analysis of LAS by gas chromatography. Fortunately, this possible interference has been eliminated because the intermediates of LAS biodegradation are not extracted into ethyl ether from acid solution.

Microdesulfonation procedures (3,5) generally have called for distillation of the alkylbenzenes for 1.5 hr at 215 C. The 3-hr reflux period used in this procedure is the result of the finding that not all of the alkylbenzenes are distilled and collected in the trap in a 1.5-hr time frame, particularly the isomers of the C13 and C14 homologs. Figure 3 shows the incompleteness of the distillation in 1.5 hr. Chromatogram A resulted from microdesulfonation of an LAS having an average mol wt corresponding to C13 LAS for 3 hr. Chromatogram B was obtained following a desulfonation period of 1.5 hr, after which the desulfonation flask was allowed to cool to room temperature and a new trap attached. The alkylbenzenes recovered by an additional 1.5 hr distillation are shown in Chromatogram C, consisting primarily of additional C13 and C14 isomers.

The use of C9 LAS as an internal standard for the quantitation of LAS has been most satisfactory and has appeared to have several advantages over internal standards producing a single peak. First, the four C9 isomers all have retention times less than the following C10

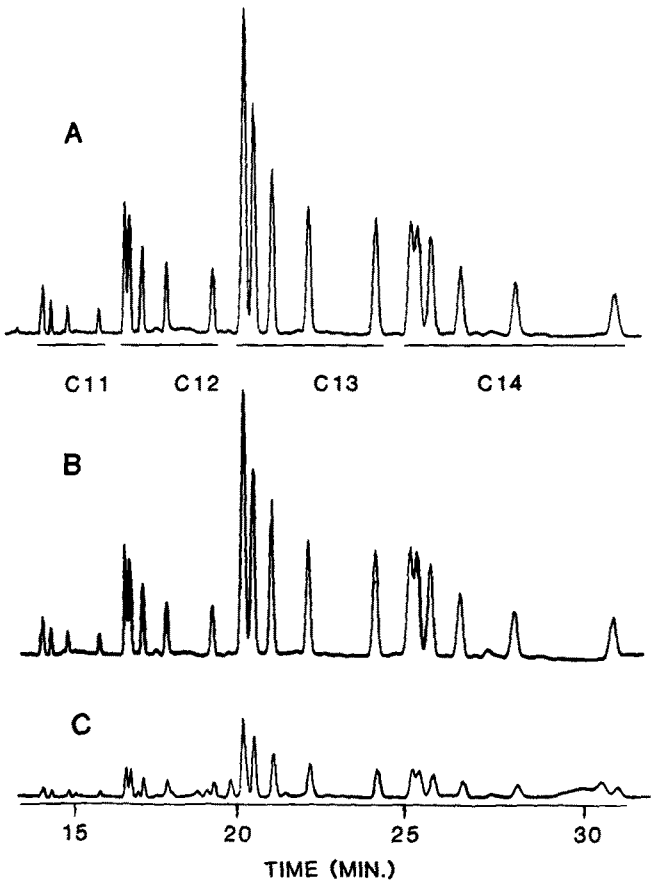

FIG. 3. Validation of 3-hr desulfonation reflux time.

TABLE 1

Average Percentage of Various C9 LAS Isomer Combinations

C9 isomer combination	%C9 added	C9 isomer—average % 5	4	3	2
5,4,3,2	100	11.0	23.0	24.1	41.9
5,4,3	58	18.9	39.6	41.5	—
5,4,2	76	14.5	30.3	—	55.2
5,3,2	77	14.3	—	31.3	54.4
4,3,2	89	—	25.8	27.1	47.1
5,4	34	32.3	67.7	—	—
5,3	35	31.3	—	68.7	—
5,2	53	20.8	—	—	79.2
4,3	47	—	48.8	51.2	—
4,2	65	—	35.4	—	64.5
3,2	66	—	—	36.5	63.5
2	42	—	—	—	100.00

TABLE 2

Comparative Inter-Laboratory Results

Laboratory	#1		#2	
Sample type	Influent	Influent	Influent	Influent
Sample number	1	2	1	2
IL-MBAS (Mgl^{-1})	6.1	5.9	6.5	6.0
GC-LAS (Mgl^{-1})	6.2	6.0	6.5	5.7
% Homolog				
C-10	11.2	11.3	10.6	11.3
C-11	33.9	34.0	33.3	33.5
C-12	39.2	39.6	39.5	38.5
C-13	12.5	12.0	12.8	12.8
C-14	3.2	3.1	3.6	3.8
Sample type	P. sludge	P. sludge	P. sludge	P. sludge
Sample number	1	2	1	2
IL-MBAS ($\mu g\ g^{-1}$)	110	115	111	126
GC-LAS ($\mu g\ g^{-1}$)	107	121	122	127
% Homolog				
C-10	3.2	3.1	2.4	2.0
C-11	17.1	16.8	14.3	13.5
C-12	37.5	37.7	34.7	35.0
C-13	28.7	28.6	31.1	33.0
C-14	13.5	13.8	17.5	16.5

isomers and fall in an area of the chromatogram that is usually free of extraneous (interfering) peaks. Second, the predetermined isomer composition of the C9 LAS may be used to determine if the sum of the C9 isomer peak areas in a sample chromatogram may be used for quantitation. The possibility exists that any one isomer peak may be intensified in area by an extraneous peak having the same, or nearly the same, retention time. The practice in this investigation has been to normalize to 100% the isomer composition of the C9 homolog, with the requirement that the percentage of each isomer be ±12 relative % of the predetermined percentage. Table 1 has been used to determine the combination of C9 isomer peak

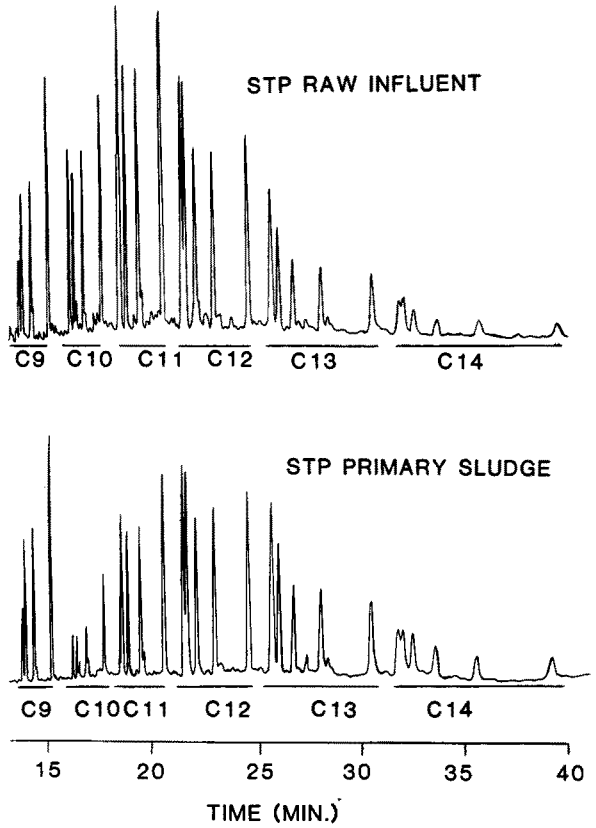

FIG. 4. Comparison of raw influent and primary sludge chromatograms.

areas that are summed for quantitation purposes. In those cases where the sum of all four isomer areas could not be used, the 100 g of C9 LAS used in Calculations was adjusted to reflect the μg of the isomer combination used.

Results. The analytical methodology presented in this paper has been both intra- and inter-laboratory tested over a period of several years. However, the results are not purported to represent any particular study but, rather, to show the precision and accuracy that were achieved using the IL-MBAS and desulfonation-gas chromatographic procedure described. In addition, results are given that effectively demonstrate the non-specificity of the MBAS method as a measure of actual LAS.

Figure 4 graphically shows the quality of a chromatogram of the LAS in a primary sludge sample. Comparison of this chromatogram with that from the raw influent sample, taken at the same treatment plant, indicates the homolog-isomer compositional changes that may be measured by gas chromatography.

Table 2 presents typical inter-laboratory results for duplicate influent and primary sludge samples. Intra-laboratory results for representative influent and effluent samples are given in Table 3. As shown, results by both the IL-MBAS and chromatographic procedures were usually in good agreement for influent and sludge samples as shown in Tables 2 and 3. Typically, the specific level of LAS in effluent samples, as measured by gas chromatography, was significantly lower than the level measured by IL-MBAS.

TABLE 3

Comparative Intra Laboratory Results

Sample type	IL-MBAS (Mgl^{-1})	GC-LAS (Mgl^{1})
Influent	5.2	4.9
Influent	3.7	3.8
Influent	3.9	3.8
Effluent	1.02	0.60
Effluent	0.44	0.21
Effluent	0.39	0.14
Effluent	0.60	0.39

TABLE 4

LAS in River Water by Gas Chromatography

Sample		A	B	C	Mean
LAS added (μgl^{-1})		50	50	50	
GC-LAS (μgl^{-1})		58	60	58	59
% Homolog	C-10	16.5	15.2	17.8	16.4
	C-11	42.2	40.8	44.1	42.3
	C-12	34.9	36.7	33.9	35.3
	C-13	6.4	7.3	4.2	5.9
Sample		D	E	F	
LAS added (μgl^{-1})		100	100	100	
GC-LAS (μgl^{-1})		90	107	96	98
% Homolog	C-10	18.1	16.8	17.3	17.4
	C-11	44.7	44.0	44.4	44.4
	C-12	32.2	33.7	32.9	32.9
	C-13	5.0	5.5	5.4	5.3
Composition of LAS added					
% Homolog	C-10	16.5			
	C-11	43.0			
	C-12	34.3			
	C-13	6.2			

TABLE 5

Effect of Distance Downstream on IL-MBAS and GC-LAS Levels in River Water Samples

Miles downstream	IL-MBAS (μgl^{-1})	GC-LAS (μgl^{-1})
0.5	400	270
4.4	300	150
7.4	250	120
15.8	240	100
30.0	130	40
55.0	100	10

The accuracy and precision, as well as sensitivity, of the gas chromatographic procedure for the analysis of river water are shown in Table 4. Levels of 50 and 100 μg l^{-1} of LAS were added to river water collected many miles below a sewage treatment plant outlet and containing no detectable level of LAS. They were analyzed in triplicate.

Table 5 demonstrates the increasing difference between IL-MBAS and the specific gas chromatographic measure-

TABLE 6

Stream Sediments (Comparative Results)

Month	Miles downstream	IL-MBAS ($\mu g\ g^{-1}$)	GC-LAS ($\mu g\ g^{-1}$)
1	0.5	178	166
	4.4	7.8	2.0
	7.4	7.5	1.3
2	0.5	118	107
	4.4	4.1	2.7
	7.4	7.8	4.4
3	0.5	317	322
	4.4	6.9	2.2
	7.4	8.1	1.4
4	0.5	171	100
	4.4	19	5.1
	7.4	10.6	1.8

TABLE 7

Recovery of Added LAS

Sample type	Initial	Added	Calculated	Found
	IL-MBAS (mgl^{-1})			
River water	0.02	0.10	0.12	0.11
River water	0.49	0.40	0.89	0.88
Influent	2.0	0.8	2.8	2.9
Influent	11.0	2.0	13.0	13.0
Influent	6.8	2.5	9.3	9.8
Influent	11.0	2.0	13.0	13.0
Influent	5.8	1.5	7.3	7.3
Influent	10.0	2.5	12.5	13.0
Effluent	6.0	2.0	8.0	8.5
Effluent	0.12	0.52	0.64	0.58
Effluent	0.16	0.52	0.68	0.67

TABLE 8

Recovery of LAS Added to Sludges

Sample type	Initial	Added	Calculated	Found
	IL-MBAS ($\mu g\ g^{-1}$)			
Primary sludge	92	52	144	153
Primary sludge	113	48	161	147
Digester sludge	109	54	163	157
Digester sludge	125	52	177	176
Digester sludge	125	52	177	159
Digester sludge	82	51	133	121
	GC-LAS ($\mu g\ g^{-1}$)			
Primary sludge	73	52	125	157
Primary sludge	97	48	145	156
Digester sludge	102	54	156	142
Digester sludge	106	52	158	165
Digester sludge	107	52	159	154
Digester sludge	63	51	114	110

ment of LAS in river water with increasing distance downstream from a sewage treatment plant outfall. Table 6 shows a similar pattern for IL-MBAS and GC-LAS levels in four monthly samplings of stream sediments, with the data showing a much more rapid decrease of both levels with increasing distance downstream.

The IL-MBAS results shown in Table 7, although not necessarily specific for actual LAS, demonstrate that LAS was quantitatively carried through the concentration and clean-up steps of the methodology described in this paper.

Table 8 provides a comparison of the IL-MBAS and GC procedures applied to sludge samples. The results again show that LAS was quantitatively carried through the various operations of the described procedure. Converse to the findings for river water, stream sediment and effluent samples, the IL-MBAS results on sludge samples were essentially the same as the specific measurements of LAS provided by gas chromatography.

ACKNOWLEDGMENT

The internal standard used in this work was provided by R. D. Swisher. J. Quinlisk and B. Goodlander performed the chromatographic analyses.

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[Received June 24, 1985]

New Amphoteric Surfactants Containing a 2-Hydroxyalkyl Group VIII. Synthesis and Surface Activities for Amphoteric Oligomeric or Polymeric Surfactants of β-Alanine Type

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A series of amphoteric oligomeric and polymeric surfactants of poly(iminoethylene) (PIE) containing both a 2-hydroxyalkyl group (C_{12}-HA or C_{14}-HA) and a 2-carboxyethyl (CE) group as N-substituents was studied as follows: PIE having 1,000 or 20,000 molecular weight was treated with 1,2-epoxydodecane or 1,2-epoxytetradecane and subsequently methyl acrylate. The adducts were saponified to obtain amphoteric oligomeric surfactants (AO) or amphoteric polymeric surfactants (AP), poly{[N-(2-carboxyethyl)-N′-(2-hydroxyalkyl)]iminoethylene}. Various adducts of which the ratios of CE/HA for one unit of iminoethylene group are 2, 3.5, 8, 17 and 89 were synthesized.

Surface activities such as surface tension, solubilization of orange OT, and foaming power, and physicochemical properties such as turbidity, isoelectric point, and the dissociation constant, were studied. Particular attention was paid to the dependence of solubilization, viscosity and turbidity on pH value.

A series of amphoteric surfactants containing both β-alanine and hydroxyalkyl groups has been published by the authors (1-6). Because the application of the surfactants for commercial usages was restricted due to low molecular weights, we have developed new amphoteric high molecular surfactants containing both β-alanine and 2-hydroxyalkyl groups. Although a few papers have been reported on polyampholytes having polyethylenepolyamine skeletons and carboxylic groups, e.g. poly-N-ethyleneglycine (7), polyaminopolypropionic acid (8) and polydimethylaminoalkyl acrylates and similar polymers (9), these exhibit no or poor surface activities.

For this paper, new amphoteric oligomeric or polymeric surfactants, the sodium salts of poly {[N-(2-carboxyethyl)-N′-(2-hydroxyalkyl)]iminoethylene} were prepared. Poly(iminoethylene) was treated with 1,2-epoxyalkane and methyl acrylate, followed by saponification. The surface activities and physicochemical properties for these surfactants were studied.

EXPERIMENTAL

Three series of amphoteric oligomeric surfactants (C_{12}-AO and C_{14}-AO) and amphoteric polymeric surfactants (C_{12}-AP) were synthesized as shown in the following scheme. The notations C_{12}- and C_{14}- placed in front of these abbreviations denote a 2-hydroxydodecyl group and a 2-hydroxytetradecyl group.

Scheme. Two series of oligomeric surfactants, C_{12}-AO or C_{14}-AO, were prepared by the addition of both 1,2-epoxydodecane or 1,2-epoxytetradecane and methyl acrylate to poly(iminoethylene) (PIE) having 1,000 molecular weight (iminoethylene unit number = ca. 23). Both C_{12}-AO and C_{14}-AO have an average calculated molecular weight of 2,500-3,500. While a series of polymeric surfactants (C_{12}-AP) was prepared similarly by the addition of 1,2-epoxydodecane and methyl acrylate to PIE having 20,000 mw (iminoethylene unit number = ca. 465). The average calculated mw of C_{12}-AP is 51,000-66,000. Where the additional molar ratios of CE/HA for one unit of the iminoethylene group are changed to be 0.6/0.3 = 2, 0.7/0.2 = 3.5, 0.8/0.1 = 8,

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