Identification and Estimation of LAS in Waters and Effluents[1]

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Abstract

The detergent industry of the United States has replaced alkylbenzene sulfonate (ABS) derived from tetrapropylene by linear alkylate sulfonate (LAS) in its formulations in an effort to eliminate waste surfactants from the nation's pollution load. The effectiveness of this move will be assessed by the monitoring of sewage treatment plant effluents and receiving waters by numerous agencies during the next several years. Most of the analytical methods available respond to a whole range of surfactants and are not specific for LAS. This deficiency can be avoided by use of the desulfonation-gas chromatography technique, which gives unequivocal proof of the presence or absence of LAS and is readily applicable at the range of interest in the neighborhood of one part per million. Examples are given of examination of various samples for presence and semiquantitative estimation of LAS. A simple procedure is described for prepurification and separation of anionic surfactants from other components of the sample.

Introduction

IN JUNE 1965 THE DETERGENT industry of the United States completed the change of its most important surfactant, alkylbenzene sulfonate (ABS), to a new type, linear alkylate sulfonate (LAS). This change was made to reduce the undesirable foaming properties associated with sewage and sewage-polluted waters. The old material, tetrapropylene ABS (TBS), was quite resistant to bacterial action. It persisted a long time in treated sewage and in the receiving waters, and it contributed to their foaminess. In contrast, the new LAS is readily destroyed by bacteria; from now on detergents will play a very insignificant role in waste foam problems wherever adequate sewage treatment or other opportuntiy for aerobic bacterial action is provided.

For over a decade sewage effluents and receiving waters have been extensively monitored for surfactant content by many agencies. It is to be expected that monitoring will continue, and that the results thereof will be the primary basis for judging the success of LAS as a solution to the waste detergent aspect of the general pollution problem.

Background

Analytical methods specific for LAS are of course a prerequisite if such judgment is to be valid. The methylene blue method (1), which because of its simplicity and great sensitivity has been the most widely used up to the present time, does not meet this requirement. Many variants of the basic procedure have been developed using different solvents and different cationic dyes to minimize interference by nonsurfactant substances. However, considering the chemistry involved, a modification which would directly distinguish between LAS and other anionic surfactants, particularly nonlinear ABS, appears very unlikely.

Since the methylene blue reaction is not specific, it is important that results from it be reported in nonspecific terms, simply as "methylene blue active substance" (MBAS). This may be done either on a molar basis or in comparison with some standard such as TBS or the British Manoxol OT if a precise, arbitrary weight basis is necessary.

As an alternative to variations in the methylene blue test procedure itself, various prepurification procedures have been devised to improve specificity by removing interferences prior to running the test. For example, a preliminary acid hydrolysis treatment may be used to destroy alkyl sulfates. However, apparently no effective means for rejection of nonlinear ABS has been suggested, and the possibility seems remote.

An infrared (IR) technique, including prepurification, has been developed by Ogden, Webster and Halliday (O-W-H) (2), who found that the spectra of LAS and TBS differ in certain details. Their prepurification prior to the spectroscopy involves charcoal adsorption, desorption, hydrolysis, solvent treatment, conversion to the n-heptylamine salt and extraction. Frazee and co-workers have used similar procedures (3,4).

In the infrared method the amounts of LAS and TBS are calculated from the intensities of particular bands in comparison with known synthetic mixtures of the two components in pure form. Thus if the unknown contains other materials absorbing in the same spectral region, the calculated result will be in error. Although the prepurification steps reject many interfering materials, complete removal of all such components from an unknown wastewater cannot be guaranteed and thus identification of LAS may be uncertain.

A test specific for LAS is necessary if its presence is to be unequivocally proved. Simko, Emery and Blank (5) have recently approached this problem through mass spectrometry. The procedures described herein should also be useful to that end.

Principles

Presence of LAS in a waste-water or effluent at levels down to 0.1 mg/liter or lower can be demonstrated by desulfonation and gas chromatographic detection of the resultant phenyl-n-alkanes using techniques previously developed for study of surfactant biodegradation (6). If the original LAS is intact an unmistakable chromatographic pattern results; if partial biodegradation has occurred, some elements of the pattern may be diminished or missing—those corresponding to the more rapidly degraded components of the original LAS. The identity of the LAS components present may be verified and their quantity estimated by comparison with parallel samples to which known amounts of LAS have been added.

One microgram of LAS gives sufficient desulfonation product for one magnificent chromatogram (e.g., Fig. 1, bottom). However it is ordinarily more convenient to use a sample containing from a few tenths to a few milligrams of LAS (or MBAS) so that conventional techniques of handling, measuring and transferring can be used.

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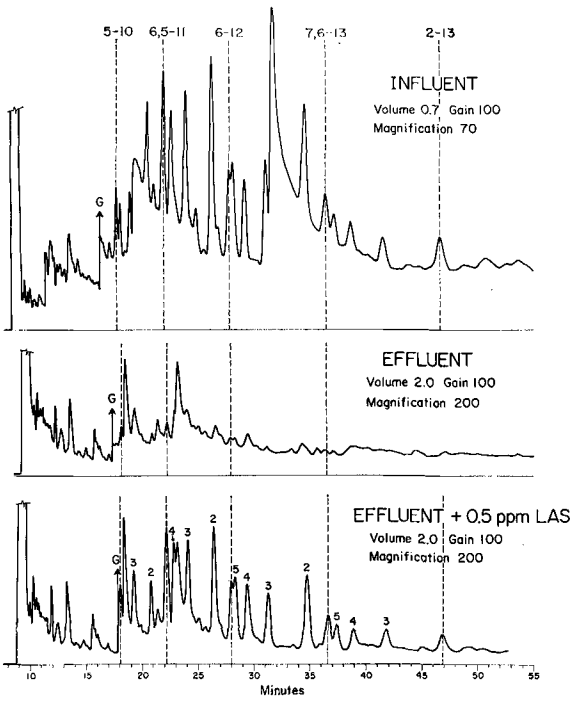

FIG. 1. Gas chromatograms of desulfonation products from samples evaporated directly. Dotted lines locate selected phenylalkanes, numbered at top, from 5-phenyldecane (5–10) to 2-phenyltridecane (2–13). Remaining phenylalkane isomers of each homolog indicated by numbering of peaks in bottom chromatogram. Instrument gain increased from 30 to indicated value at 15–20 min as shown by arrow and G. Volume indicated is milliliters of original water sample corresponding to injected sample reaching column (Table I). Large peak at 9–10 min is hexane solvent.

Inasmuch as the desulfonation is done in a medium of concentrated phosphoric acid, the water must be removed from the sample. Simple evaporation and desulfonation of the entire residue is often to be preferred, since there is then no possibility of LAS loss such as might occur in the malfunction of a more complex isolation procedure. However if the waste-water sample contains large amounts of other materials which may also contribute to the final chromatogram (e.g., sewage), preliminary purification or isolation may be helpful. The O-W-H prepurification (2) is suitable, and a simpler procedure has also been developed based on the methylene blue analytical method.

The amount of LAS present in a sample may be quantitatively estimated by comparsion of its gas chromatogram with one obtained under similar circumstances from a known amount of LAS, giving appropriate consideration to sample size and to instrument sensitivity. However, accidental or uncontrollable variations in the processing or the gas chromatography may introduce large errors. Use of suitable internal standards would give warning when this has occurred; such assurance is provided by adding known amounts of LAS to parallel samples of the water being investigated and processing them all side by side. The non-LAS features of the resulting chromatograms serve as the internal standard; if these match, the LAS content of the original sample can be estimated with confidence by direct comparison of its LAS peaks with those from the spiked samples.

Applications

The examination of waters from a field test of LAS biodegradation, the Kettle Moraine test (7), provides illustrative examples. For some time after beginning

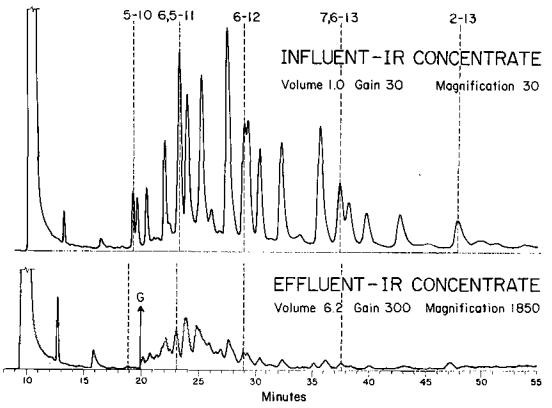

FIG. 2. Gas chromatograms of desulfonation products from samples prepurified for infrared examination. See Figure 1 for explanation.

the LAS phase of that operation, the sewage entering the treatment plant contained 5–10 ppm of MBAS and the effluent showed about 1 ppm. Use of the gas chromatographic technique made it possible to prove that the LAS content of the effluent at that time was well below 0.1 mg/liter. Thus the LAS was being essentially completely degraded, but some other material in the effluent was responding in the methylene blue test. (The nature of the other material was not determined, but after a few more days operation it was no longer appearing in the effluent and the MBAS had dropped to around 0.1 ppm.)

Samples

The influent and effluent composites examined had been collected from 8:00 AM to 1:30 PM on July 7, 1964. The effluent sample thus came from influent entering the plant some time prior to the influent sample actually examined; however, there was no reason to suppose that any significant change in the influent had occurred over that period of time. The composites were preserved by adding 5 ml of formalin per liter when collected, and two days later were evaporated for subsequent desulfonation.

Evaporation, Desulfonation, Gas Chromatography

The procedure already described for use with river water (6) is directly applicable to waters in general, using a sample containing 1 to 10 mg of MBAS (much smaller or much larger amounts may be used with appropriate modifications). Briefly, a one liter sample was evaporated to dryness, the entire residue was subjected to desulfonation by boiling with concentrated phosphoric acid, and the volatile products were trapped in hexane. The hexane solution was evaporated in a stream of air, made up to a volume of 50 μl and examined by gas chromatography. A Barber-Colman Model 20 instrument was used with a 150 ft × 0.02 in. (46 m × 0.05 cm) stainless steel capillary column, silicone rubber (SE-30) substrate, strontium 90 detector, column temperature 190C, argon pressure 4 psi (0.3 kg/cm^2). Injection of 0.5–1 μl of the hexane concentrate usually gave a good response at a split ratio of 10:1 and a gain of 30–300.

As indicated in Figures 1 and 2, each of the gas chromatograms represents a certain volume of the original sample. For example, the second entry in Table I shows that the desulfonate from 980 ml of effluent was made up to 50 μl of hexane solution, of which 0.1 μl reached the column (1 μl injected, 90% discarded in the split). This corresponds to 1.96 ml

TABLE I
Material Balance into Gas Chromatography

	MBAS, ppm	Sample, ml	Desulfn. prod., mg[a]	Hexane soln., μl		Sample equiv., ml[b]
				Total	Injected	
Influent	6.5	1000	130	150	1	0.67
Effluent	1.0	980	5	50	1	1.96
Effluent + 0.5 ppm LAS	1.5	950	5	50	1	1.90
Influent-IR	6.5	970	2	50	0.5	0.97
Effluent-IR	1.0	6150	1	50	0.5	6.15

[a] Estimated by evaporation of hexane solution to approximately constant weight.
[b] Split ratio about 10:1, i.e., about 90% of injected sample discarded.

of the original effluent, rounded off to 2.0 ml.

During the gas chromatography, shortly before expected emergence of the phenylalkanes the instrument gain was set at either 30, 100 or 300 to get suitable peak heights. Multiplying the sample volume by the gain gives the magnification factor which must be kept in mind when comparing the different chromatograms.

Also included in Table I are the MBAS values of the original samples as determined by the Hellige method using color standards calibrated in terms of ppm of TBS (8). Values determined by the Standard method (1) on similar samples were in reasonable agreement. Addition of 0.5 mg/liter of actual LAS (SDA reference sample 1–1) to the effluent increased the MBAS value from 1.0 to 1.5 ppm as would be expected (third entry in Table I).

Estimation of LAS Content

Figure 1 shows chromatograms from the raw sewage influent, the effluent, and the effluent to which 0.5 mg/liter of fresh LAS had been added. The dashed lines locate the peaks of the central isomers of each homolog, 5-phenyldecane through 7-phenyltridecane. The 2-phenyltridecane position is indicated in like manner to show the limit of the C_{13} range, while the other isomers of each homolog are indicated by the numbering of the peaks in the bottom chromatogram of Figure 1.

Examining the middle and bottom chromatograms in Figure 1, it is evident that their earlier features, from 10–18 min, are substantially equivalent. This gives assurance that comparable recoveries have indeed been achieved from these two samples throughout desulfonation and gas chromatography, and that the estimate of LAS content of the original sample can thus be made with all confidence. Visual comparison of the phenylalkane peaks in the bottom chromatogram, produced by 0.5 mg/liter of added LAS, with those in the middle chromatogram indicates that no more than a trace of LAS was present in the original effluent sample, considerably less than 0.1 mg/liter.

In contrast, the top chromatogram of Figure 1 shows that a considerable amount of LAS was present in the influent, the characteristic pattern of peaks being superimposed upon a very high background arising from other components of the sewage. Comparison of net peak heights and magnification with the bottom chromatogram leads to an estimate of around 2 mg/liter of LAS content in the influent. This of course may be subject to considerable error as discussed above, in the absence of an internal standard such as would have been provided by a parallel run using a sample of the same influent spiked with a known amount of LAS.

O-W-H Prepurification

Direct evaporation and desulfonation of one liter of sewage influent as described above should yield at most about 4 mg of alkylbenzenes, assuming that the 6.5 ppm of MBAS was entirely ABS. Actually about 130 mg of desulfonate was obtained (Table I), arising from the other materials present in the sewage and giving rise to the relatively enormous area under the chromatogram in Figure 1, top. Even though this did not interfere with the detection of the LAS present, still in certain circumstances a cleaner chromatogram might be desirable.

The O-W-H isolation procedure developed for sewage (2) (with a few minor variations of no importance in the present context) had been applied to these same Kettle Moraine samples for the purpose of infrared examination. The purified products had been deposited on rock salt plates as the heptylamine salts for the spectroscopy and were subsequently rinsed directly into the desulfonation flask with chloroform. After evaporation they were desulfonated and chromatographed as described below.

The O-W-H cleanup procedure was eminently satisfactory; one liter of the sewage influent using such treatment gave only about 5 mg of desulfonate, compared to 130 mg without the treatment, and its chromatogram (Fig. 2, top) was hardly distinguishable from virgin linear alkylate. Comparison of peak heights and magnification with Figure 1, top, suggests that there was little if any loss of LAS in the purification.

The bottom chromatogram in Figure 2 is from the effluent purified in the same manner. Most of the peaks fall in the alkylbenzene region and probably originate principally from TBS or other nonlinear ABS. These peaks (e.g., 6-phenyldodecane) are only slightly higher than in Figure 1, middle, despite the 9 times greater magnification. This does not necessarily mean loss of ABS in the prepurification, but equally likely may arise from losses in the desulfonation or gas chromatography; in any event it illustrates the importance of internal standards in making quantitative estimates.

The MBAS balance across this prepurification step was consistent with the conclusions drawn from the gas chromatographic results. One liter of influent contained 6.5 mg of MBAS and gave an infrared concentrate containing 2.9 mg. In contrast, 8 liters of effluent contained 8 mg of MBAS, but little or none of this was LAS (or ABS) since only about 0.02 mg survived the prepurification.

Prepurification via Methylene Blue

Principles

The methylene blue analytical method provides the basis for a relatively simple cleanup procedure: in the presence of an excess of methylene blue the anionic surfactant is extracted into chloroform as the methylene blue salt. The chloroform phase may be evaporated and the residue desulfonated for gas chromatography. The ABS moiety of the methylene blue salt desulfonates in the normal manner, while the

methylene blue portion does not given any products detectable under the gas chromatographic conditions used. Similar results are obtained using heptylamine instead of methylene blue, but the latter is preferred because it makes the completeness of the extraction so easily checked visually.

In addition to the MBAS, the chloroform phase will also contain any chloroform extractable components present in the original sample. Although such materials do not interfere with the colorimetric measurement of the MBAS (unless highly colored themselves), they may well show some gas chromatographic response. Accordingly it may be desirable to remove such materials by preextraction with chloroform prior to addition of the methylene blue. Comparative experiments indicate that some of the MBAS may be lost in such a treatment, perhaps by interfacial adsorption in the emulsion layer which usually forms. This possibility should be recognized if a preextraction procedure is used.

Even when chromatographically interfering substances are absent from the initial sample the methylene blue isolation procedure may be preferred to simple evaporation of the entire sample. The extraction step is reasonably rapid, and the chloroform phase can be readily evaporated directly in the desulfonation flask; the main uncertainty is whether the MBAS, or more particularly the LAS, has in fact been brought into the chloroform. Simple evaporation of the original aqueous sample leaves no such doubt, but has its own disadvantages: a large sample requires considerable elapsed time to evaporate, and the residue is distributed over the surface of a large vessel with associated difficulties of quantitative removal and transfer.

Procedure

Methylene blue reagent was prepared as described in Standard Methods, p. 247 (1). A sample containing around 1 mg of MBAS (much larger or smaller amounts may be used with appropriate changes) and 150 ml of methylene blue reagent was shaken with 50 ml of chloroform. In order to break the emulsion which usually formed to some extent, the chloroform layer and the emulsion layer were both forced through a 2 cm bed of glass wool packed into a 2 cm diameter glass tube and the resulting chloroform layer was placed in the desulfonation flask. The original aqueous mixture was further extracted with a second 50 ml portion of chloroform, which was then passed through the glass wool and into the desulfonation flask in the same manner, acting as a rinse. The combined chloroform layers were evaporated for desulfonation and gas chromatography as described previously.

Glass equipment should be used for the extraction and for any other steps involving chloroform; polyethylene ware may contain extractives contributing to the gas chromatogram.

The amount of water present in the original sample is not critical; one liter containing 1 mg MBAS (i.e., 1 ppm) is quite satisfactory and it seems likely that no trouble would be encountered at considerably higher dilutions. MBAS removal is substantially complete in the first extraction, as may be verified by visual comparison of the second chloroform extract with the first (intensity of blue color), or by running an actual methylene blue analysis on the spent aqueous layer. If an unexpectedly large amount of MBAS is present, insufficient methylene blue will be indicated by decolorization of the aqueous phase; in such a case more reagent should be added to maintain an excess of methylene blue in the system.

The methylene blue reagent is formulated to give a pH around 2–3 during extraction. The initial pH of the sample does not appear to be critical, at least in the range 5–7, but samples of large size or high buffering capacity might require acidification with sulfuric acid to maintain the desired pH during extraction.

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