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Note

Determination of sodium linear dodecyl benzene sulfonate and sodium cumene sulfonate in mixtures by liquid chromatography

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The sodium salts of linear dodecylbenzene sulfonate (NaLAS) and cumene sulfonate (NaCS) are used, at times, in combination in liquid household cleaning products. Heretofore, an analytical method did not exist for the accurate measurement of these components in a full-formula mixture. The mixed-indicator titration method[1,2] for anionic surfactants was not specific for either of the components in a mixture. NaCS-type compounds were identified by Dunn and Robson[3] with reversed-phase thin-layer chromatography. Nake[4] developed a high-speed liquid chromatographic method to measure lower alkylbenzene sulfonates, but higher alkylbenzene sulfonates were strongly held by the anion-exchange resin.

To meet this need, a liquid chromatographic method was developed for individually measuring NaLAS and NaCS in samples of this type. Separation was achieved with a paired-ion solvent system and a custom-packed, low-efficiency, reversed-phase radial-compression cartridge. The cartridge, coupled with the tailored solvent and gradient elution program, provided for the elution of NaLAS analogues as one chromatographic peak. High-resolution analytical columns separated the two surfactant species but also partially resolved many of the NaLAS analogues into a chromatographic peak pattern which could not be integrated accurately. This problem was eliminated with the lower-efficiency cartridges, and accurate measurements of NaLAS and NaCS were made possible. Quantitation relative to an internal standard is reported.

EXPERIMENTAL

Instrumentation

The liquid chromatograph was a Hewlett-Packard 1084B, equipped with a 79850BLC data system, a 79841A autoinjector, a 79842 sample module, and a 79875A variable-wavelength UV detector which was set at 222 nm for detection of the analytes and at 310 nm for reference purposes.

A Waters Assoc. radial-compression module fitted with a cartridge custom-packed with 37–50 μm Bondapak Corasil I C_{18} reversed-phase packing was used for the chromatographic separation. The solvent flow-rate was 1.5 ml/min. A gradient elution program with the profile shown in Table I was used.

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TABLE I

GRADIENT ELUTION PROGRAM

Run time (min)	*Solvent B (%)*
0	5
1.5	40
2.25	70
2.40	100
5.00	100
5.5	5.0
10.0	Stop run and inject next sample

Slight variations in the solvent program were needed to compensate for minor variations in performance between different cartridges. Linear gradient ramps were used between the percentage concentrations of solvent B shown in Table I.

Reagents and samples

Samples of NaLAS and NaCS were obtained from Pilot Chemical Co. and Stepan Chemical Co., respectively. Tetramethylammonium hydroxide (1.0 *M* aqueous solution) was obtained from Southwestern Analytical Chemicals (Austin, TX, U.S.A.). Methyl paraben (methyl *p*-hydroxybenzoate) was ordered from Pflatz and Bauer (Stanford, CT, U.S.A.). Distilled water was passed through a Milli-Q water purification system to obtain high-purity water for solvent preparation. Acetonitrile and methanol were chromatographic-grade solvents from Fisher Scientific.

The radial-compression cartridge was custom packed by Waters Assoc. with 37–50 μm Corasil I C_{18} reversed-phase packing. Bondapak Corasil I C_{18} reversed-phase packing was obtained from Waters Assoc. for preparation of the hand-packed, low-efficiency experimental column.

Solvent A was water–acetonitrile–paired-ion solution (900:50:50). Solvent B was water–acetonitrile–paired-ion solution (50:875:50). The paired-ion solution consisted of 0.2 *M* aqueous tetramethylammonium hydroxide (TMAH) that was adjusted to pH 4.6 with phosphoric acid. The water and TMAH solutions were premixed before adding acetonitrile to prevent precipitation of TMAH. Solvents A and B were vacuum-filtered through 0.45 μm Millipore FHUP 04700 discs to remove particulates and to degas.

Calibration standards

The analytical method was calibrated for three different product formulations as shown in Table II. Each calibration standard was prepared in 50 ml of methanol–water (1:1).

Sample preparation

Experimental product solutions were prepared to obtain concentrations of 500 mg of product and 40.0 mg of the methyl paraben in 50 ml of methanol–water (1:1). These concentrations of product gave levels of the analytes that were near the calibration standard concentrations.

TABLE II

CALIBRATION STANDARD SOLUTIONS

Material	*Solution (mg per 50 ml)*		
	A	*B*	*C*
NaCS	40.0	35.0	30.0
NaLAS	25.0	11.5	15.0
Methyl paraben	40.0	40.0	40.0

All calibration standards and experimental product sample solutions were filtered with a Swinney filter through a 0.45 μm Millipore FHLP 01300 paper before injection on to the chromatographic column.

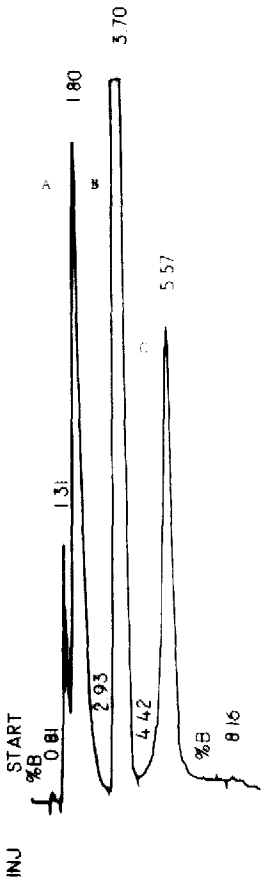

Fig. 1. Chromatogram of NaCS, methyl paraben (internal standard) and NaLAS. Column: 37–50 μm Bondapak Corasil I C_{18} radial-compression cartridge. Peaks: A = NaCS; B = methyl paraben; C = NaLAS.

Quantitation

The liquid chromatographic system was calibrated by chromatographing 20 μl of the appropriate calibration standard and monitoring the response of the effluent at 222 nm with the UV detector. Retention time and peak area data for the analytes and the internal standard were collected by the data system. Final calibration was then achieved by following the instructions for the internal standard method calibration described in the data system operation manual.

The experimental sample solutions were analyzed by adding internal standard (methyl *p*-hydroxybenzoate), chromatographing with the same instrument conditions and calculating analyte levels with the data system.

RESULTS AND DISCUSSION

Effect of column packing on the separation

High-resolution analytical columns containing, for example, 10 μm Bondapak C_{18} packing resolved numerous analogues of NaLAS to produce a series of chromatographic peaks that could not be integrated accurately. More accurate measurements were believed possible if the analogues could be eluted and integrated as one chromatographic peak. Experiments performed by varying the solvent composition and chromatographing NaLAS on an analytical column (10 μm C_{18} packing) were also unsuccessful in obtaining a system which coeluted the NaLAS analogues. Experiments with a less efficient experimental column, hand-packed with 37–50 μm Bondapak Corasil I C_{18}, showed the analogues could be coeluted and measured accurately. Radial compression cartridges containing this type of packing, were also found applicable and were used to generate all of the following data. Fig. 1 shows a typical chromatogram.

Effect of ion-pair reagent on retention time

Excellent separation between NaCS and the NaLAS analogues peak was achieved with both tetramethylammonium hydroxide (TMAH) and tetrabutylammonium hydroxide (TBAH). Longer retention times were experienced with TBAH relative to TMAH and, therefore, the latter was chosen.

Effect of solvent composition on the separation of NaLAS, the internal standard and NaCS

The initial composition of acetonitrile in the solvent gradient program was important in order to separate these compounds. Too high a concentration of acetonitrile resulted in the coelution of the internal standard and analytes. Too little acetonitrile resulted in broad chromatographic peaks for NaCS, the internal standard, and NaLAS. The gradient solvent profile was optimized by adjusting the initial concentration of acetonitrile to provide separation of the NaCS and internal standard into sharp chromatographic peaks and then rapidly increasing the B solvent concentration to elute the NaLAS.

Applications

The method was applied to measure the levels of NaLAS and NaCS in solutions of three different experimental product formulations, each of which contained known levels of the analytes. The recovery data are shown in Table III.

TABLE III

NaLAS AND NaCS IN PRODUCT SOLUTIONS

NaLAS (mg/50 ml)			*NaCS (mg/50 ml)*		
Theoretical	*Measured*	*Recovery (%)*	*Theoretical*	*Measured*	*Recovery (%)*
Product A					
27.5	27.6	100.4	42.5	42.5	100.0
25.0	24.9	99.6	40.0	39.7	99.2
22.5	22.8	101.3	37.5	37.3	99.5
Product B					
13.0	12.9	99.2	37.5	37.7	100.5
11.5	12.0	104.0	35.0	35.1	100.3
10.0	10.5	105.0	32.5	32.8	100.9
Product C					
16.3	15.8	96.9	35.0	35.0	100.0
15.0	14.8	98.7	30.0	30.3	101.0
13.8	13.6	98.6	25.0	25.1	100.4
Overall average recovery (%)		100.4 ± 2.6			100.2 ± 0.6

These data show that levels of NaLAS and NaCS were measured accurately in the experimental products investigated. The NaCS levels were measured with somewhat better precision than the lower concentrations of NaLAS. The method currently is being applied to analyze other types of products which contain both NaLAS and NaCS.

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