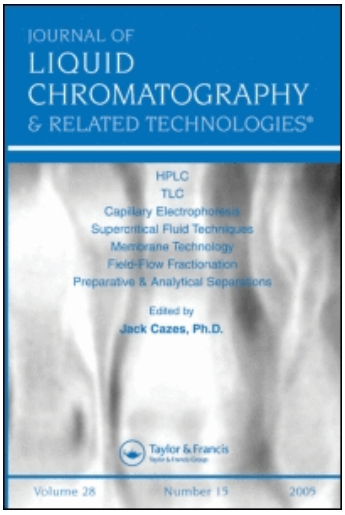

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Determination of Surfactant Sodium Lauryl Ether Sulfate by Ion Pairing Chromatography with Suppressed Conductivity Detection

Ming Y. Ye[a]; Ron G. Walkup[a]; Kim D. Hill[a]
[a] ManTech Environmental Research Services Corporation, Ada, Oklahoma

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DETERMINATION OF SURFACTANT SODIUM LAURYL ETHER SULFATE BY ION PAIRING CHROMATOGRAPHY WITH SUPPRESSED CONDUCTIVITY DETECTION

MING Y. YE, RON G. WALKUP, AND KIM D. HILL
ManTech Environmental Research Services Corporation
P.O. Box 1198
Ada, Oklahoma 74820

ABSTRACT

A method for the determination of the anionic Steol CS-330 surfactant is described. CS-330 is a complex mixture of oligomers due to the various sizes of fatty alcohols and the number of moles of the ethoxylation. The main component of CS-330 is sodium lauryl ether sulfate (SLES). Since a SLES molecule has a hydrophilic sulfate head and a hydrophobic alkyl ethoxyl tail, it is very difficult to separate these molecules with conventional reverse phase chromatography or ion exchange chromatography. This work uses ion pairing chromatography with suppressed conductivity detection. The separation of oligomers in CS-330 is achieved. SLES does not have UV-absorbing chromophores, therefore an optical detector is not very sensitive. Suppressed conductivity detection technique significantly increases sensitivity and a quantitation limit of 56.60 ppm is achieved.

INTRODUCTION

Recently, there has been considerable interest in using surfactants to remediate subsurface contamination, e.g., to immobilize contaminants for subsequent in situ treatment, to release contaminants from mineral surfaces, or to redistribute immobile

organic phases into the mobile aqueous phase. [1], [2], [3] Steol CS-330 is one of the surfactants under consideration for this application. ManTech Environmental has developed high performance liquid chromatography and supercritical fluid chromatography methods for the determination of various anionic and nonionic surfactants, such as T-MAZ (a registered trademark of PPG Industries, Inc.) ethoxylated sorbitan fatty acid esters, [4], [5] Dowfax (a registered trademark of Dow Chemical Company) 8390 monoalkylated disulfonated diphenyl oxide, sodium dodecylbenzene sulfonate, octylphenol polyether alcohols and polyethoxylated nonylphenols. [6]

Steol (a registered trademark of Stepan Company) CS-330 is an industrial chemical. CS-330 is derived from fatty alcohols, ethoxylated to an average of 3 moles, and sulfated via a continuous SO_3 process. This ionized surfactant consists of a saturated alkyl group, ethoxyl groups and a polar head, $-OSO_3$ Na (Figure 1a). As shown in Figure 1a, CS-330 can be a complex mixture of oligomers due to the various parent fatty alcohol and the number of moles of the ethoxylation. Because these molecules are amphipathic, i.e., contain both hydrophilic and hydrophobic moieties (Figure 1a), they are surface-active compounds and concentrate at oil-water interfacial regions. The major component of CS-330 is sodium lauryl ether sulfate (Figure 1b). According to the manufacturer, the content of sodium lauryl ether sulfate in CS-330 is 27.5 - 29.5% in weight.

Because of the amphipathic character of CS-330 molecules, it is very difficult to separate these molecules with conventional reverse phase chromatography or ion exchange chromatography. With reverse phase chromatography, the molecules cannot be retained by the column because the alkyl, ethoxyl and sulfate groups do not

(a) $(H_mC_n(OCHCH)_l)OSO_3^- Na^+$ n = 12, 13, 14, 15, ...

m = 2n+1

l = 1, 2, 3, 4, 5,

(b) $(H_{25}C_{12}(OCHCH)_3)OSO_3^- Na^+$

Figure 1 (a) The molecular formula of molecules in CS-330.

(b) The molecular formula of sodium laureth sulfate.

have strong enough interactions with a C_{18} reverse phase column to be retained. With ion exchange chromatography, CS-330 molecules are retained in the ion-exchange resins for a very long time due to the hydrophobic nature of the alkyl group. Reverse phase ion pair chromatography is ideal for the separation of ionic organic compounds, such as sodium laureth sulfate. A reverse phase column is used and an ion pairing reagent is added to the eluent. This reagent adsorbs onto the neutral, hydrophobic resin forming an ion-exchange surface on which the organic ions are differentially retained and separated. [7], [8], [9] Sodium laureth sulfate does not have UV-absorbing chromophores and therefore, an optical detector is not very sensitive. Suppressed conductivity detection significantly increases sensitivity and a quantitation limit of 56.60 ppm is achieved.

MATERIALS AND METHODS

CS-330 was from Stepan Company (Northfield, IL,U.S.A.), tetrabutylammonium hydroxide (55% aqueous solution, TBAOH) from Southwestern Analytical Chemicals,

Inc. (Austin, TX, U.S.A.), acetonitrile from Burdick and Jackson (Baxter Healthcare Corporation, Muskegon, MI, U.S.A.). 18 MΩ water was obtained from a Millipore Milli-Q system (Marlborough, MA, U.S.A.).

Instrumentation included a Waters (Waters Associates, Milford, MA, U.S.A.) 6000A HPLC pump, a Waters 717 autosampler, and a Waters 431 conductivity detector. Separations were accomplished using a Dionex (Dionex Corporation, Sunnyvale, CA, U.S.A.) IonPac NS1 column (4 mm x 250 mm) and a NG1 guard column. A Dionex anion micro membrane suppressor (AMMS-MPIC) and 25 mM sulfuric acid solution were used to suppress the background conductivity of the mobile phase. The mobile phase was 50% acetonitrile and 5 mM TBAOH in water with a pH value of 11.8. A silica based reverse phase column cannot be used with this strong basic eluent because a silica based column usually has an operating pH range from 4 to 7.5. Organic polymer packings, such as IonPac NS1 column, have a wide pH range (0 to 14) and they are ideally suited for the separation of molecules in CS-330. The injection volume was 400 µl at an eluent flow rate of 1.0 ml/min. Data acquisition and processing was accomplished with a Waters Maxima 820 chromatography workstation, which included a system interface module and an NEC PowerMate SX/16 computer.

RESULTS AND DISCUSSION

The eluent used in the ion pairing chromatography must maintain the analytes in their ionic states so that the ion pairing reagents can form ion pairs with the sample ions. The 50% acetonitrile and 5 mM TBAOH eluent has a pH value of 11.8 and the cation (TBA^+) can form an ion pair with the sample anion ($ROSO_3^-$). The conductivity

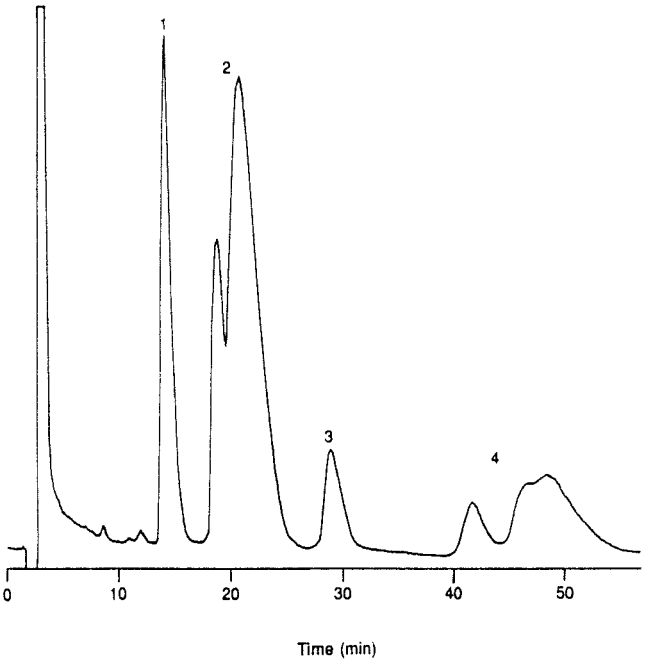

Figure 2 Chromatograms of Steol CS-330

Injection volume: 400 µl; concentration : 800 ppm. Detection: suppressed conductivity; Mobile phase: 50% acetonitrile and 5 mM TBAOH; Flow rate: 1 ml/min.

TABLE 1 Peak Area/Peak Height and Average Relative Response

Concentration	Peak Area/Peak Height [a]				Relative Response [b] (peak area)			
(ppm)	1	2	3	4	1	2	3	4
60	61	195			0.30	1.00		
80	54	172			0.32	1.00		
160	54	178	94		0.33	1.00	0.10	
200	63	180	106	372	0.33	1.00	0.10	0.31
320	56	189	98	408	0.32	1.00	0.11	0.34
800	66	220	105	460	0.32	1.00	0.10	0.34
1600	76	240	122	496	0.32	1.00	0.10	0.35

[a] Data of peak area and peak height were averaged from three injections.
[b] Relative response of the peak area was averaged from three injections.

TABLE 2 Analytical Precision and Detection Limit

Peak Group	Concentration		Detection Limit (ppm)
	160 ppm	640 ppm	
1	n = 3	n = 3	16.98
	$\bar{x}$ =163.91	$\bar{x}$ = 671.16	
	SD = 5.66	SD = 2.18	
	RSD = 3.5%	RSD = 0.3%	
2	n = 3	n = 3	13.05
	$\bar{x}$ = 164.01	$\bar{x}$ = 665.92	
	SD = 4.35	SD = 9.73	
	RSD = 2.7%	RSD = 1.5%	

n: Number of standard solutions analyzed
$\bar{x}$: Mean solution concentration (ppm)
SD: Standard deviation
RSD: Percent relative standard deviation (= 100 x (SD / $\bar{x}$))
Detection limit was calculated as three times the standard deviation of the mean (3 x SD).

background of this eluent is 650 μS due to the high concentration of TBAOH. With such a high conductivity background, the ratios of signal to noise by a conductivity detector are poor. The micromembrane suppressor removed cations in the column eluent after the oligomer separation was accomplished, reducing the background conductance to 92 μS.

Figure 2 shows the chromatogram of the oligomer separation of CS-330. The concentration of CS-330 in the chromatogram was 800 ppm with 400 μl injection. The peak areas were integrated as four groups, from 13.05 to 16.95, 17.46 to 26.44, 26.78

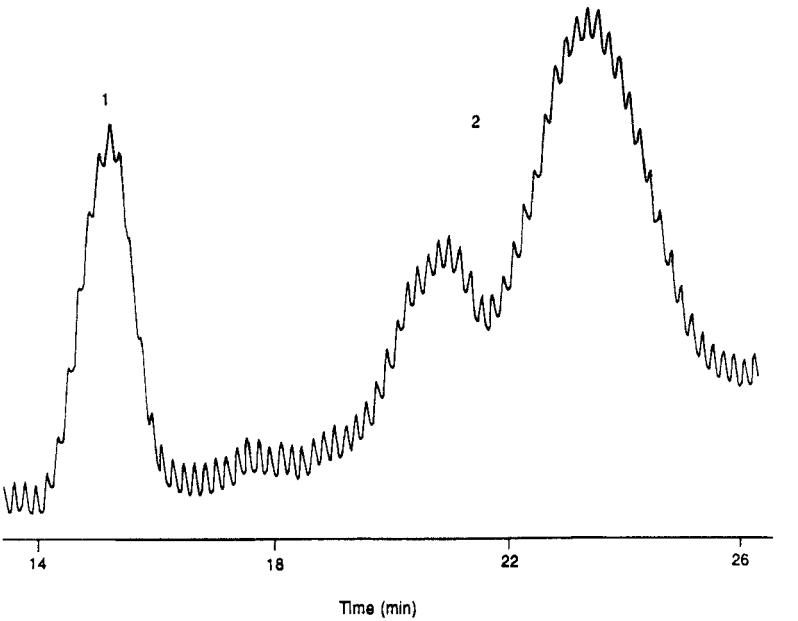

Figure 3 Chromatogram of Steol CS-330.

Injection volume: 400 µl; concentration : 60 ppm. Detection: suppressed conductivity; Mobile phase: 50% acetonitrile and 5 mM TBAOH; Flow rate: 1 ml/min.

to 33.05 and 38.81 to 56.80 minutes. Peak 3 and peak group 4 were not detectable at concentrations below 160 ppm. The ratio of the peak area to the peak height (TABLE 1) shows that peak group 4 is a very broad peak due to the long retention of 49 minutes. The averaged relative response of peaks and peak groups 1, 2, 3 and 4 is 0.32 : 1.00 : 0.10 : 0.33 (TABLE 1), which indicates that the peak 3 has the lowest response. Since peak 3 has the lowest response and peak group 4 is the broadest, it was determined to use peak 1 and peak group 2 to quantify CS-330.

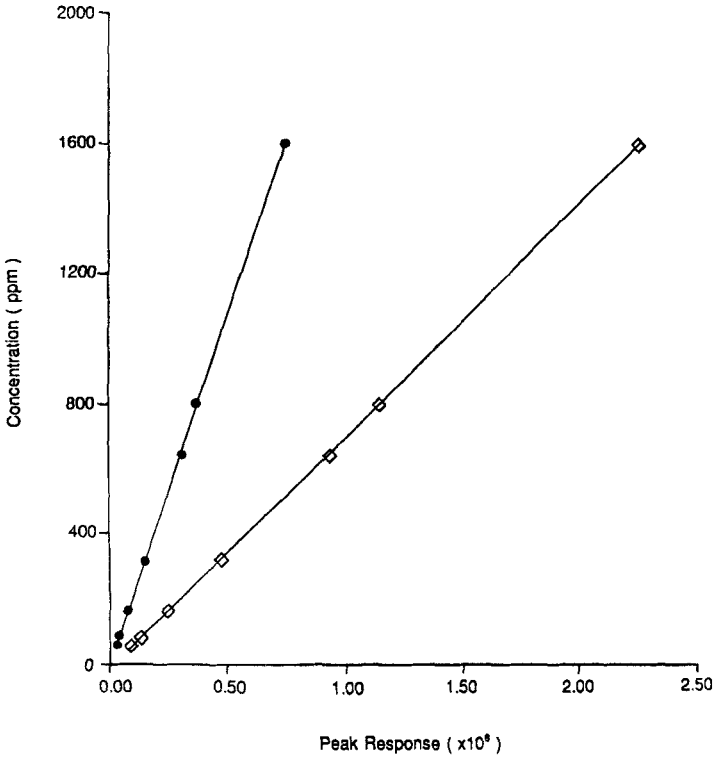

Figure 4 The calibration curves of the peak 1 (●) and peak groups 2 (■), in which quadratic curves were used to fit the data.

CS-330 was analyzed quantitatively with a good degree of precision and accuracy (TABLE 2). CS-330 standards in the concentration range from 60 to 1600 ppm were analyzed four times, and 160 and 640 ppm standards were used to determine the detection limit. The detection limits were 16.98 ppm for the peak 1 and 13.05 ppm for the peak group 2, calculated as three times the standard deviation of the mean. From the detection limit of 16.98 ppm for the peak 1, a quantitation limit of 56.60 ppm was estimated, calculated as ten times the standard deviation of the mean. Figure 3 shows the chromatogram of 60 ppm standard, which demonstrates that CS-

TABLE 3 Average Peak Area, Relative Standard Deviation, Calculated Concentrations and Relative Error

Concentr. (ppm)	Ave. Peak Area (x 10^{-7})[a]				Cal. Concentr.		Relat. Error (%)	
	1	(%RSD)	2	(%RSD)	1	2	1	2
60	0.3156	(6.5)	1.0389	(4.4)	59	63	-1.15	4.73
80	0.4001	(6.3)	1.2358	(4.8)	80	76	-0.06	-4.66
160	0.8057	(3.2)	2.4525	(3.2)	164	164	2.44	2.51
200	0.9644	(0.8)	2.9545	(2.2)	198	197	-1.01	-1.18
320	0.1613	(3.6)	4.8988	(1.9)	334	331	4.26	3.46
800	3.9986	(0.7)	12.337	(0.6)	852	856	6.47	6.95
1600	7.9483	(0.2)	24.589	(0.7)	1749	1742	9.29	8.88

[a] The peak areas were averaged from three experimental data.
RSD: Relative Standard Deviation = 100 x (Standard Deviation / Average Peak Area)

330 can be easily quantified at this concentration, confirming the estimated quantitation limit of 56.60 ppm.

Four standards of each concentration (60, 80, 160, 200, 320, 800 and 1600 ppm) were analyzed. A standard from each concentration was randomly selected to generate calibration curves for the peak 1 and peak group 2. Figure 4 shows the calibration curves of the peak 1 and peak group 2, in which a quadratic equation was used to fit the data. The three standards of each concentration, which were not used in the calibration curves, were used as unknowns and their concentrations were calculated independently with the calibration curves of the peak 1 and peak group 2 as shown in TABLE 3. As demonstrated by the relative error, the calculated concentrations are in a good agreement with the known concentrations. These results demonstrate that both the peak 1 and the peak group 2 can be used independently to

quantify CS-330 concentration. In a routine analysis, one can choose to use either one of the groups for quantification.

To insure that no components of CS-330 with high molecular weights were retained in the column, the column eluent was monitored for 90 minutes and no peak was found after 55 minutes with area counts higher than 315600, which corresponds to the lowest standard of 60 ppm for the peak 1 in the calibration curve (TABLE 3).

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DISCLAIMER

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QA/QC REQUIREMENTS

All QA/QC aspects of this work were performed in accordance with the requirements of the Quality Assurance Program Plan of the ManTech Environmental Research Service Corporation.

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