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Journal of Chromatography A, 804 (1998) 233–239

JOURNAL OF  
CHROMATOGRAPHY A

## Recent developments in surfactant analysis by ion chromatography

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### Abstract

A simple and sensitive method for analysing surfactants by ion chromatography (IC) is described. The method uses ion-pair separation with gradient elution and suppressed conductivity detection. Two types of suppressor devices are used. The electrochemically regenerated ion suppressor (ERIS; patent pending) is ideal for continuous unattended operation. It uses an electrochemical process to self-regenerate the suppressor cells. No regenerant reagent or system is required and no chemical waste is generated. This suppressor is compatible with up to 30% organic solvents in the mobile phase. For mobile phases containing higher organic concentration, the solid-phase chemical suppressor (SPCS) was used. The SPCS uses disposable suppressor cartridges as the suppression device. No regeneration or maintenance is needed with this suppressor since the cartridges are disposable. The SPCS cartridges are compatible with up to 80% organic solvents. Separation of surfactants was based on ion-pair interaction on a reversed-phase column. Both anionic and cationic surfactants can be determined using this method. The detection limits for the surfactants are in the parts-per billion and low parts-per million ranges. © 1998 Elsevier Science B.V.

*Keywords:* Surfactants; Alkanesulfonates; Alkyl sulfates; Alkyl benzenesulfonates, linear

### 1. Introduction

Surfactants have hydrophilic and hydrophobic centers both of which affect their physical and chemical properties. They are widely used in many industries due to their ability to reduce surface tension and can be classified as anionic, cationic or nonionic surfactants, depending on the charge of the hydrophilic group. Anionic surfactants are classified as alkanesulfonates, alkyl sulfates, and alkylbenzenesulfonates that are commonly used in commercial detergents, cleansing agents, cosmetics, and hygienic products. The cationic surfactants are quaternary ammonium compounds being used in cosmetics, disinfectants, antistatic agents, foam depressants, and textile softeners. Both of these surfactants are used in large quantities and discharged into

the environment, which can affect the ecological equilibrium due to the toxic nature of surfactants [1]. Therefore, the determination of surfactants is important for product control and for environmental monitoring.

Several analytical methods have been reported for analysing surfactants. They are colorimetric methods, planar chromatography, gas chromatography, high-performance liquid chromatography (HPLC), and capillary electrophoresis (CE) [2–6]. The HPLC separation with UV detection is the most common method in practice, however this method is not sensitive enough to detect low level determination of surfactants in environmental samples. A more sensitive method for the determination of surfactants is by HPLC separation with conductivity detection. Both suppressed and nonsuppressed methods have been reported [7,8]. Ion suppression method offers lower detection limits because the suppressor reduces the

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mobile phase conductivity while increasing the analyte signal. A reversed-phase separation along with suppressed conductivity detection using a membrane-based suppressor has been used [9]. The disadvantage of this suppressor is that it requires an additional pump and regenerant solution for the continuous regeneration of the suppressor. A self-regenerating membrane suppressor was recently invented, but due to its incompatibility with organic solvents, it cannot be used with organic-containing mobile phases [10].

Surfactants are hydrophobic in nature and it is necessary to add a certain percentage of organic solvents in the mobile phase for shorter retention time and better peak shape.

This paper describes the analysis of surfactants using HPLC separation with suppressed conductivity detection using two types of suppressor devices that are simpler to use. These suppressors were developed for the detection of anions and cations at low levels by ion chromatography [11,12]. Since these suppressors are compatible with organic solvents, they are ideal for surfactant analysis. The compatibility of these suppressors with organic solvents simplify the surfactant analysis by eliminating the need for a regenerant reagent and system. The separation of both anionic and cationic surfactants using both suppressors are discussed.

## 2. Experimental

The ion chromatography was performed using the Alltech Odyssey ion chromatography system (Alltech Associates, Deerfield, IL, USA). This system includes the Alltech Model 526 metal-free HPLC pump, the ERIS 1000HP Autosuppressor, the Model 530 column heater, and the Model 550 conductivity detector. An additional 526 metal-free pump was used for gradient application. All sample injections were done using the Alltech Model 570 autosampler. All data were recorded by PE Nelson Turbochrom EL datasystem (San Jose, CA, USA). The surfactants were separated on an Alltech Surfactant/R Column (150×4.6 mm), 7 μm (Alltech). An Anion Scavenger Column (30×4.6 mm) (Alltech) was used when anionic surfactants were analyzed to remove carbonate from the sodium hydroxide mobile phase.

### 2.1. Reagents and standards

The mobile phase and standards were prepared from analytical-reagent grade chemicals from Aldrich (Milwaukee, WI, USA) and Fischer Scientific (Itasca, IL, USA). Distilled deionized water was used to prepare the mobile phases and the standards.

## 3. Results and discussion

### 3.1. Anionic surfactants

Anionic surfactants are classified into three main groups. They are alkanesulfonates (ASO<sub>3</sub>), alkyl sulfates (AOSO<sub>3</sub>) and the linear alkyl benzenesulfonates (LASs). The retention behaviour of these compounds depends on the carbon chain length which contribute the hydrophobicity of these surfactants. An increase in chain length causes an increase in hydrophobicity and therefore retain longer on the column. A neutral polydivinylbenzene column was used for the separation of these surfactants. This column can tolerate pressures up to 6000 p.s.i.g. and pH from 0 to 14 (1 p.s.i.=6894.76 Pa). The column is also compatible with 100% organic solvents. Such a column is ideal for surfactant analysis because the conditions for this application require mobile phase gradient that cause changes in pressures, pH and organic concentrations.

It has been reported that the retention, selectivity, and peak shape for alkanesulfonates and alkyl sulfates by reversed-phase separation are improved significantly when a high ionic strength mobile phase is used [9]. An isocratic separation of some alkyl sulfates and alkanesulfonates are shown in Fig. 1a and b, respectively. In this application, we added 5 mM of lithium hydroxide to the mobile phase to increase its ionic strength. The mobile phase was made of 5 mM lithium hydroxide in 5% acetonitrile, 5% methanol and 90% water. Methanol and acetonitrile was added to improve the peak shape of surfactants.

Two types of suppressors can be used for surfactant analysis. The electrochemically regenerated ion suppressor (ERIS; patent pending) is ideal for continuous unattended operation [11]. The ERIS autosuppressor was developed for improving the de-

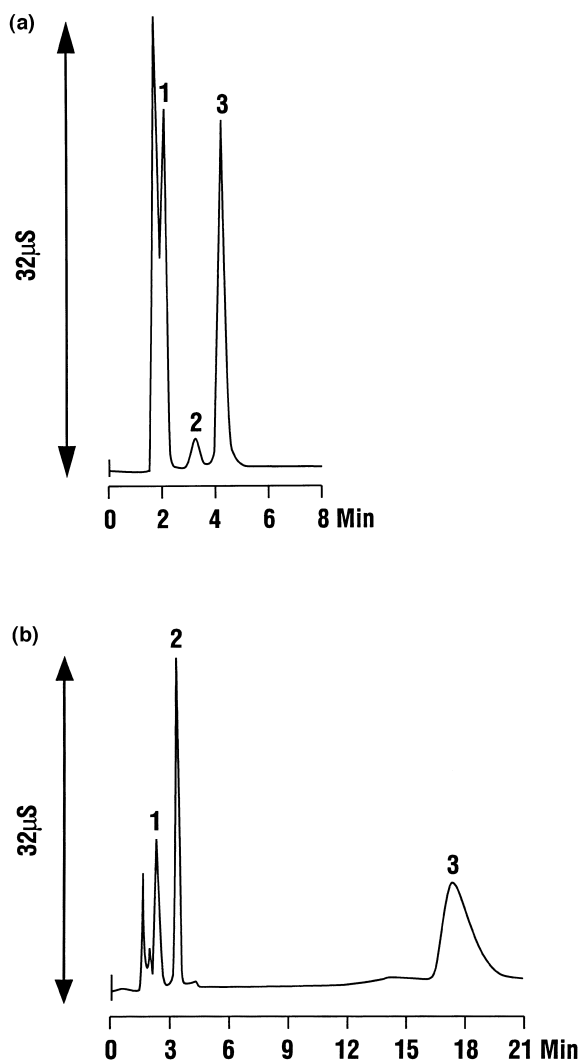
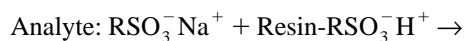
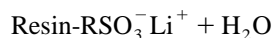
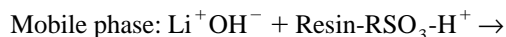


Fig. 1. (a) Alkyl sulfates. Column: Alltech surfactant/R, 150×4.6 mm; mobile phase: 5 mM lithium hydroxide in acetonitrile–methanol–water (5:5:90); flow-rate: 1.0 ml/min; detector: suppressed conductivity, peaks: 1=sulfate C<sub>7</sub> (5 ppm) 2=sulfate C<sub>8</sub> (2 ppm) 3=Sulfate C<sub>10</sub> (10 ppm). (b) Alkane sulfonates. Column: Surfactant/R, 150×4.6 mm; mobile phase: 5 mM lithium hydroxide in acetonitrile–methanol–water (5:5:90); flow-rate 1.0 ml/min; detector: suppressed conductivity, peaks: 1= sulfonate C<sub>7</sub> (10 ppm) 2=sulfonate C<sub>8</sub> (10 ppm) 3=C<sub>10</sub> (40 ppm).

tection sensitivity of anions and cations. The same device can be used for surfactant analysis. This suppressor uses an electrochemical process to self-regenerate the suppressor cells. No regenerant reagent or system is required and no chemical waste

(other than the detector effluent) is generated. This suppressor is compatible with up to 30% organic solvents in the mobile phase. A higher percentage of organic solvents can shrink the ERIS cell packing material, causing a high voltage and failure of cell regeneration. Research is in progress to develop better ERIS cells to use with higher organic concentration mobile phases. Another type of suppressor is the solid-phase chemical suppressor (SPCS) [12]. The SPCS uses disposable suppressor cartridges as the suppression device. The SPCS is also widely used for increasing the sensitivity of anions and cations. No regeneration or maintenance is needed with this suppressor since the cartridges are disposable. Depending on the ionic strength of the mobile phase, each cartridge will last between 4–10 h of continuous use. The SPCS cartridges are compatible with up to 80% organic solvents. The resin material in the SPCS cartridge can shrink if higher (higher than 80%) concentration organic mobile phases are used, causing poor peak shape.

The ERIS 1000HP Autosuppressor was used in experiments resulted in Fig. 1a and b. The ERIS cells were packed with cation-exchange resin in the hydrogen form. The following ion-exchange reactions take place when the mobile phase and the analyte passes through the suppressor.



The ERIS Autosuppressor cell converts the high conductivity lithium hydroxide to water, improving the detection sensitivity for the surfactants. The SPCS suppressor may also be used for this application. Since the packing material for both suppressors is coated with an inert dye, a colour change can be monitored easily through the transparent cell and cartridge housing as the hydrogen ions are being replaced by the lithium ion from the mobile phase. In this analysis, the colour changes from beige to magenta. This provides fast verification of the suppressor operation.

Since the retention of alkanesulfonates and alkyl sulfates on reversed-phase stationary phases in-

creases as surfactant hydrophobicity increases, the separation of multicomponent mixtures requires mobile phase gradients. A gradient separation of nine alkyl sulfate and alkanesulfonate mixture within 18 min is shown in Fig. 2. By increasing the acetonitrile/methanol concentration, the hydrophobic characteristic of the long chain surfactants is suppressed, thus, reducing the retention time. Gradient separation with a mobile phase containing lithium hydroxide is possible only when used with suppressed conductivity detection. In this application, we used the SPCS device to suppress the mobile phase conductivity. The SPCS is more suitable for this application since it requires higher organic solvents in the mobile phase. A noticeable drift in baseline occurs during gradient run. This is due to the lower background conductance of solvent B versus solvent A.

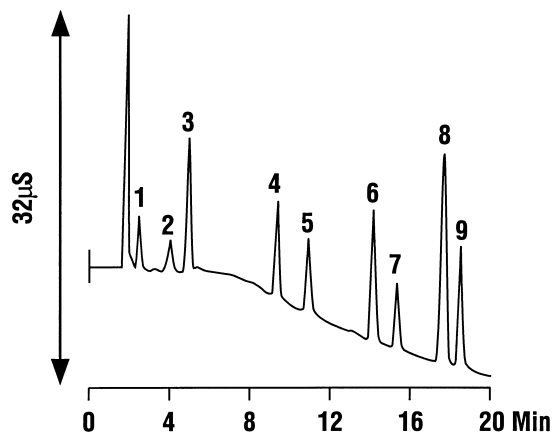


Fig. 2. Column: Alltech Surfactant/R, 150×4.6 mm, mobile phase: A: 10 mM lithium hydroxide, B: acetonitrile–water–methanol (60:20:20)

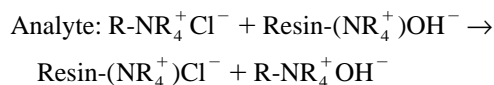
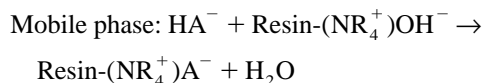
Gradient:	Time	0	3	10	20
	%A	97	97	80	50
	%B	3	3	20	50

Flow-rate: 1.0 ml/min; detector: suppressed conductivity, peaks: 1=sulfate C<sub>6</sub> (5 ppm) 2=sulfonate C<sub>6</sub> (5 ppm) 3=sulfonate C<sub>7</sub> (10 ppm), 4=sulfonate C<sub>8</sub> (10 ppm), 5=sulfate C<sub>8</sub> (20 ppm), 6=sulfonate C<sub>10</sub> (20 ppm), 7=sulfate C<sub>10</sub> (30 ppm), 8=sulfonate C<sub>12</sub> (30 ppm), 9=sulfate C<sub>12</sub> (40 ppm).

### 3.2. Cationic surfactants

Cationic surfactants are quaternary ammonium compounds (QAs) and they are used in variety of industrial applications such as disinfectants, foam depressants, cosmetics and textile softeners. These compounds are separated commonly by ion-pair chromatography with nonpolar stationary phases and chloride, chlorate as ion-pair reagents [13]. We have developed a method for analysing cationic surfactants using the same stationary phase used for the anionic surfactants. Since this polymeric stationary phase is very durable, switching from one mobile phase to another did not cause any problem. An acidic mobile phase along with suppressed conductivity detection was used for cationic surfactant analysis. Adding acetonitrile to the mobile phase improved the peak shape and reduced the retention time for more hydrophobic surfactants. Either isocratic or gradient elution can be used depending on the number of surfactants in the sample.

An isocratic separation of short chain cationic surfactants is shown in Fig. 3a. Since the mobile phase contained less than 30% acetonitrile, we used the ERIS Autosuppressor as the suppression device. For long chain cationic surfactants, as shown in Fig. 3b, 45% acetonitrile was used in the mobile phase and the SPCS suppressor was used. The suppressor is an anion exchanger in the hydroxide form. The following reactions take place in the suppressor when the mobile phase and the cationic surfactants pass through the suppressor.



Where A=The counter anion in the mobile phase.

These reactions convert the low conductivity quaternary ammonium compounds to high conductivity bases while the background conductivity of the mobile phase is reduced to near zero, resulting in better sensitivity for cationic surfactants. Both ERIS Autosuppressor cell and the SPCS cartridge packing is coated with an inert dye so when the exchange sites are taken up by the counter anions from the

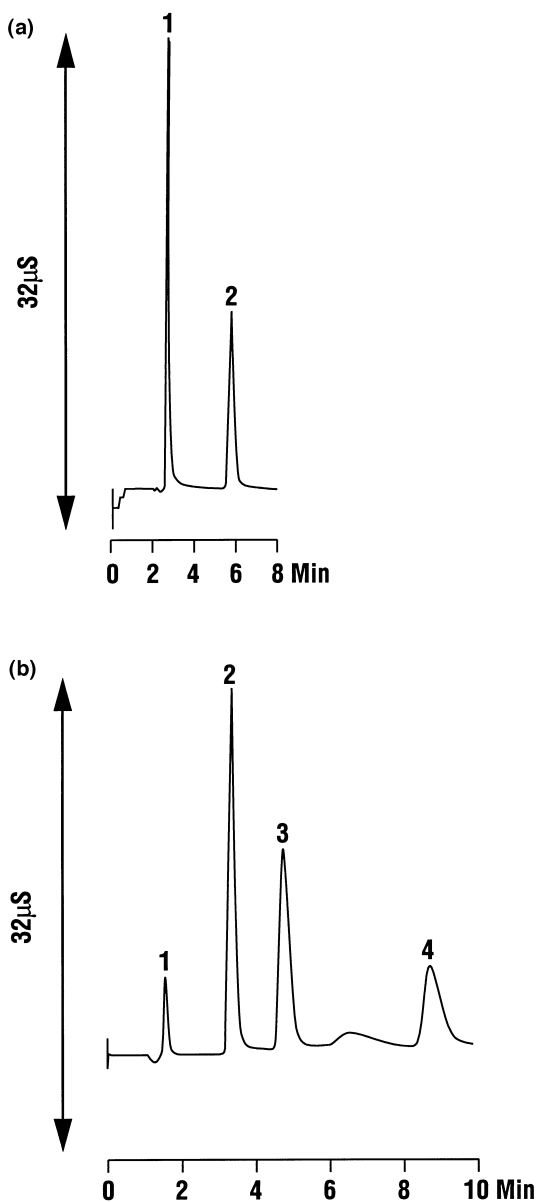


Fig. 3. (a) Isocratic separation of short chain cationic surfactants. Column: Alltech Surfactant/R, 150×4.6 mm (P/N 25101), mobile phase: 2 mM nonafluoropentanoic acid in 30% acetonitrile, flow-rate: 1.0 ml/min, detector: suppressed conductivity, peaks: 1=tetramethyl ammonium, 20 ppm, 2=tetrapropyl ammonium, 20 ppm. (b) isocratic separation of long chain cationic surfactants. Column: Alltech Surfactant/R, 150×4.6 mm (P/N 25101), mobile phase: 2 mM nonafluoropentanoic acid in 45% acetonitrile, flow-rate: 1.5 ml/min, detector: suppressed conductivity, peaks: 1=tetrabutyl ammonium, 10 ppm, 2=dodecyltrimethyl ammonium, 20 ppm, 3=cetyltrimethyl ammonium, 20 ppm, 4=myristyltrimethyl ammonium, 20 ppm.

mobile phase and the samples, a colour change occurs. The colour changes from blue to beige as the suppressor is being exhausted that is visible through the cell or cartridge housing. This is an easy way to check the suppressor condition.

A gradient separation of a multicomponent mixture of cationic surfactants is shown in Fig. 4. A mixture of short and long chain surfactants can only be separated in one run by gradient elution. A slight

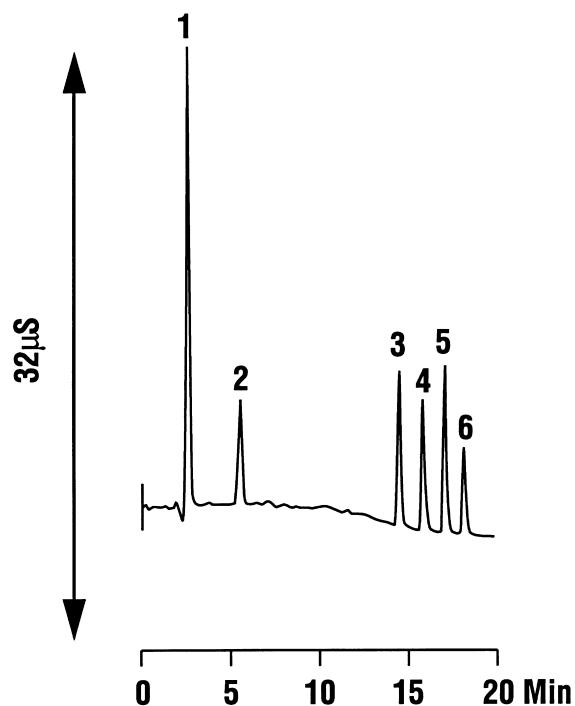


Fig. 4. Gradient separation of short and long chain cationic surfactants. Column: Surfactant/R Column, 150×4.6 mm (P/N 25100), mobile phase: A: 2 mM nonafluoropentanoic acid, B: 100 % acetonitrile.

Gradient:	Time	0	5	8	20
%A		70	70	65	20
%B		30	30	35	80

Flow-rate: 1.0 ml/min, detector: suppressed conductivity, peaks: 1=tetramethyl ammonium, 20 ppm and tetraethyl ammonium, 20 ppm, 2=tetrapropyl ammonium, 20 ppm, 3=tetrabutyl ammonium, 30 ppm, 4=dodecyltrimethyl ammonium, 30 ppm, 5=cetyltrimethyl ammonium, 40 ppm, 6=myristyltrimethyl ammonium, 50 ppm.

drift in baseline occurs during the gradient run due to the increase in the nonconductive acetonitrile concentration in the mobile phase.

### 3.3. Detection limits

Method detection limits for both anionic and cationic surfactants are shown in Table 1. The conditions for the anionic and cationic surfactants are identical to those used in Figs. 2 and 4 respectively. The detection limits are calculated based on  $3 \times$  signal-to-noise ratio. The detection limits for the anionic surfactants are in the parts per billion range and the detection limits for the cationic surfactants are in the low parts per million range. These detection limits are better than the reported detection limits [9].

### 3.4. Applications

Fig. 5 shows a chromatogram of sodium dodecyl sulfate in a toothpaste sample. The following sample preparation was necessary before injection. A gram of the sample was added to 100 ml deionized water and sonicated for 10 min. The sample was then filtered through an Alltech HPLC-grade nylon syringe filter ( $0.45 \mu\text{m}$ ) and injected. Fig. 6a and b are chromatograms of cationic surfactants in household cleanser and mouth wash. Only simple dilution with

Table 1  
Detection limits for surfactants

Surfactants	MDL <sup>a</sup> (ppm)
Hexyl sodium sulfate	0.023
Hexanesulfonate	0.06
Heptane sulfonate	0.08
Octanesulfonate	0.08
Sodium octane sulfate	0.85
Decyl sodium sulfate	0.04
Decane sulfonic acid	0.90
Dodecane sulfonate	0.66
Dodecyl sodium sulfate	0.80
Tetramethyl ammonium	1.30
Tetrapropyl ammonium	2.00
Tetrabutyl ammonium	2.00
Dodecyl ammonium	2.00
Cetyltrimethylammonium	2.60
Myristyltrimethyl ammonium	3.30

<sup>a</sup> Detection limits at  $3 \times$  signal-to-noise level for 100  $\mu\text{l}$  injection volume.

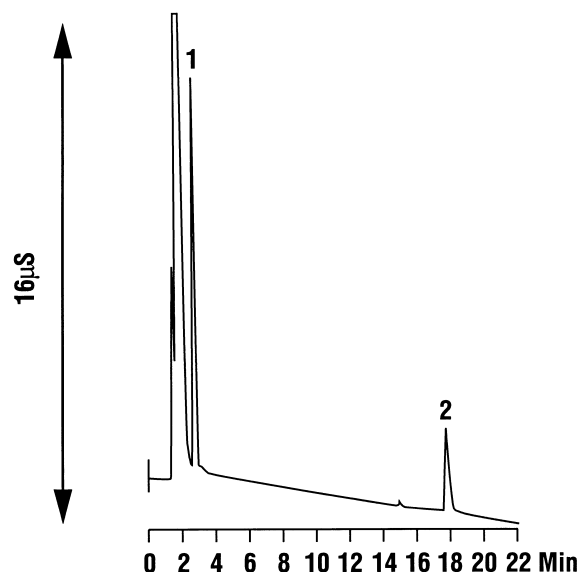


Fig. 5. Toothpaste. Column: Surfactant/R Column,  $150 \times 4.6$  mm, mobile phase: A: 10 mM lithium hydroxide, B: acetonitrile–water–methanol (60:20:20).

Gradient:	Time	0	3	10	20
%A		97	97	80	50
%B		3	3	20	50

Flow-rate: 1.0 ml/min, detector: suppressed conductivity, peaks: 1 = unidentified, 2. sodium dodecyl sulfate  $\text{C}_{12}$ .

deionized water ( $10 \times$ ) was necessary for the sample preparation.

## 4. Conclusion

Suppressed conductivity detection and ion-pair separation is a sensitive method for analysing anionic and cationic surfactants. Both ERIS 1000HP Autosuppressor and SPCS provide simple methods for analysing anionic and cationic surfactants. The ERIS cells are electrochemically regenerated, therefore, no regenerant reagents or pumps are required, and no chemical waste is generated. Since this suppressor uses no fragile membranes, it tolerates up to 30% organic solvents. Work is in progress in our laboratory to develop a better polymer packing for the ERIS cells so they will be compatible with higher percentage organic solvents. For high concentration

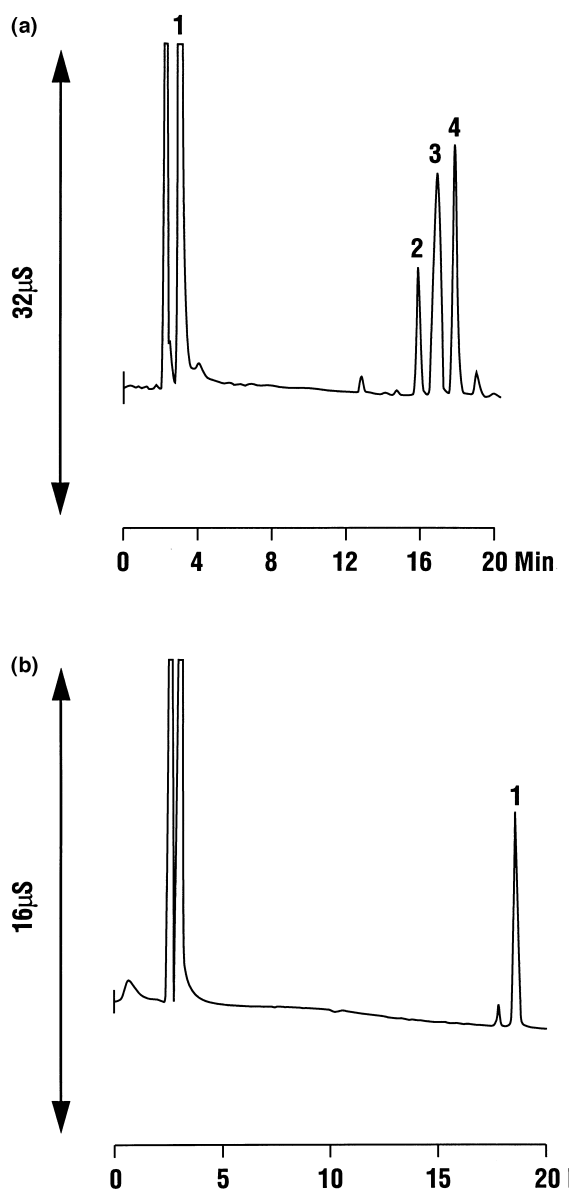


Fig. 6. (a) Household cleanser. Column: Surfactant/R Column, 150 $\times$ 4.6 mm, mobile phase: A: 2 mM nonafluoropentanoic acid, B: 100% acetonitrile:

Gradient:	Time	0	5	8	20
%A		70	70	65	20
%B		30	30	35	80

Flow-rate: 1.0 ml/min, detector: suppressed conductivity, peaks: 1 = dimethylbenzylammonium chloride, 2 = dioctyldimethylammonium chloride, 3 = octyldecylammonium chloride, 4 = didecyldimethylammonium chloride. (b) Mouth Wash. Column: Surfactant/R Column, 150 $\times$ 4.6 mm, mobile phase: A: 2 mM nonafluoropentanoic acid, B: 100% acetonitrile.

Gradient:	Time	0	5	8	20
%A		70	70	65	20
%B		30	30	35	80

Flow-rate: 1.0 ml/min, detector: suppressed conductivity, 1. Peak: 1 = cetylpyridinium chloride.

organic mobile phases, the SPCS can be used. The SPCS is compatible with up to 80% organic. Since the SPCS cartridges are disposable, no regeneration or maintenance is required. The colour indication of the ERIS cells and SPCS cartridges provide a quick and easy way to check suppressor operation and condition during analysis. The detection limits for the surfactants are in the parts-per billion and low parts-per million range.

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