Introduction
Anionic surfactants are widely used in commercial detergents, cleansing agents, cosmetics, and hygienic products. They are classified as alkanesulfonates, alkyl sulfates, and alkylbenzenesulfonates. Detection of these surfactants in trace levels is of growing concern due to their effect on the environment. Different analytical methods have been reported for surfactant analysis. One common method for analyzing surfactants is reversed-phase HPLC using conductivity detection. Both ion suppression and ion-pair methods have been used. Determination of surfactants by the ion suppression method gives lower detection limits, because the suppressor reduces the mobile phase conductivity while increasing the analyte signal. Reversed-phase separations using suppressed conductivity detection with a membrane-based suppressor have been reported. The disadvantage of this suppressor is that it requires additional pumping of sulfuric acid reagent for the continuous regeneration of the suppressor. A self-regenerating membrane suppressor was recently invented, but due to incompatibility with organic solvents it cannot be used with organic mobile phases.

This application note describes the analysis of anionic surfactants using a self-regenerating suppressor that is compatible with organic solvents. The Electrochemically Regenerated Ion Suppressor (ERIS) uses an electrochemical process to self-regenerate solid-phase suppressor cells for continuous, reagent-free operation. Surfactant analysis with the ERIS Autosuppressor is simple, sensitive, and economical.

Experimental
The Alltech (Deerfield, IL) Odyssey Ion Chromatography System includes the Alltech Model 526 Metal-Free 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 this gradient application. All sample injections were made with the Alltech Model 570 Autosampler. All data was recorded by the PE Nelson (San Jose, CA) Turbochrom EL datasystem. The surfactants were separated on an Alltech Surfactant/R Column (150 x 4.6mm), 7µm. Two anion scavenger columns (50 x 4.6mm) were used to trap anions from the mobile phase.

The mobile phase and standards were prepared from analytical-reagent grade chemicals from Aldrich (Milwaukee, WI) and Fisher Scientific (Itasca, IL).

Results and Discussion
Reports show that the retention, selectivity, and peak shape for alkanesulfonates and alkyl sulfates by reversed-phase HPLC improve significantly if high ionic strength mobile phases are used. Figures 1 and 2 show isocratic separations of some alkyl sulfates and alkanesulfonates. In this application, 5mM lithium hydroxide was added to the mobile phase to increase ionic strength. The mobile phase was made of 5mM lithium hydroxide, 5% acetonitrile, 5% methanol, and 90% water. Methanol was added to improve the peak shape of surfactants. The ERIS 1000 Autosuppressor converts the high conductivity lithium hydroxide to water, improving the detection sensitivity for the surfactants.

Since retention of alkanesulfonates and alkyl sulfates on reversed-phase stationary phases increases as surfactant hydrophobicity increases, the separation of multicomponent mixtures requires mobile phase gradients. Figure 3 shows a gradient separation of nine alkyl sulfate and alkanesulfonate mixture within 18 minutes. By increasing the organic concentration, retention times for the hydrophobic long chain surfactants are reduced. Gradient separation with a mobile phase containing lithium hydroxide is possible only when using suppressed conductivity detection. Since the ERIS converts the lithium hydroxide to water, the changes in the lithium hydroxide concentration during the gradient does not affect the background conductivity.

Figure 4 shows a chromatogram of a toothpaste sample. The following sample preparation was necessary before injection. One gram of the sample was added to 100mL deionized water and sonicated for 10 minutes. The sample was then filtered through an Alltech HPLC grade nylon syringe filter (0.45µm) and injected. A small quantity of dodecyl sulfate was found in the toothpaste.

Only the ERIS 1000 Autosuppressor provides a simple method for the separation of alkyl sulfates and alkanesulfonates analysis. Since the cell regenerates electrochemically, no regenerant reagents or pumps are required and no chemical waste (other than the detector effluent generated on any IC system) is generated. Since this suppressor uses no fragile membranes, it tolerates organic solvents.

Conclusion
The Alltech Odyssey IC system in combination with the ERIS 1000HP Autosuppressor provides a simple, sensitive and economical method for anionic surfactant analysis. Reversed-phase separation with isocratic or gradient elution can be used depending on the number of surfactants to be analyzed. Since the ERIS Autosuppressor self-regenerates the suppressor cells electrochemically, no regenerant reagents or pumps are required. The organic compatibility of the ERIS Autosuppressor simplifies surfactant analysis.

References

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Figure 1

Alkyl Sulfates

1. C7 (5ppm)
2. C8 (2ppm)
3. C10 (10ppm)

Column: Alltech Surfactant/R, 150 x 4.6mm
Mobile Phase: 5mM Lithium Hydroxide in Acetonitrile:Methanol:Water (5:5:90)
Flowrate: 1.0mL/min
Detector: Suppressed Conductivity

Figure 2

Alkanesulfonates

1. C7 (10ppm)
2. C8 (10ppm)
3. C10 (40ppm)

Column: Alltech Surfactant/R, 150 x 4.6mm
Mobile Phase: 5mM Lithium Hydroxide in Acetonitrile:Water (5:5:90)
Flowrate: 1.0mL/min
Detector: Suppressed Conductivity

Figure 3

Alkyl Sulfates and Alkanesulfonates

1. Sulfate C6 (5ppm)
2. Sulfonate C6 (5ppm)
3. Sulfonate C7 (10ppm)
4. Sulfonate C8 (10ppm)
5. Sulfate C8 (20ppm)
6. Sulfonate C10 (20ppm)
7. Sulfate C10 (30ppm)
8. Sulfonate C12 (30ppm)
9. Sulfate C12 (40ppm)

Column: Alltech Surfactant/R, 150 x 4.6mm
Mobile Phase: A: 10mM Lithium Hydroxide
B: Acetonitrile:Water:Methanol (60:20:20)
Gradient: Time:
%A: 97 97 80 50
%B: 100 97 80 50
Flowrate: 1.0mL/min
Detector: Suppressed Conductivity

Figure 4

Toothpaste Sample

1. Unidentified
2. Sodium Dodecyl Sulfate (C12)

Column: Alltech Surfactant/R, 150 x 4.6mm
Mobile Phase: A: 10mM Lithium Hydroxide
B: Acetonitrile:Water:Methanol (60:20:20)
Gradient: Time:
%A: 100 97 80 50
%B: 100 97 80 50
Flowrate: 1.0mL/min
Detector: Suppressed Conductivity

Description Part No.

INDIVIDUAL COMPONENTS

550 Conductivity Detector
120V | 550100
240V | 550101

ERIS 1000HP Autosuppressor
110V | 533101
220V | 533102

Anion Suppressor Cell (1500psig Pressure Limit)
14 x 7.5mm, 2pkg | 5330020

HP Anion Suppressor Cell (3000psig Pressure Limit)
14 x 7.5mm, 2pkg | 533011

530 Column Heater
110V | 530100
220V | 530101

526 HPLC Pump
110V | 526100
220V | 526101

Alltech Surfactant/R Column
150 x 4.6mm, SS | 25100
150 x 4.5mm, PEEK | 25101

Anion Scavenger Column
50 x 4.6mm, SS | 382161

** System includes: 550 Conductivity Detector, ERIS 1000HP Autosuppressor, 530 Column Heater, 526 HPLC Pump, Rheodyne Model 9725I Injection Valve, and an IC Accessories Starter Kit.

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