

Analysis of Anionic Surfactants Using RPLC and Suppressed Conductivity Detection

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ABSTRACT

Anionic surfactants are widely used in a variety of applications, such as formulations for laundry detergents, shampoos, hand soaps, and pesticides. HPLC is the preferred technique to determine anionic surfactants in mixtures. Very often, analysis of anionic surfactants is performed by reversed-phase (RP) chromatography using a C18 or C8 column. In this mode, all compounds are separated according to increasing hydrophobicity. Depending on the surfactant of interest, detection is by ultraviolet-visible (UV), refractive index (RI), evaporative light scattering detection (ELSD), mass spectrometry (MS), or suppressed conductivity. UV detection is most useful for compounds with phenyl rings, while ELSD can be used to determine most non-volatile compounds. However, many anionic surfactants lack a chromophore. Moreover, analysis can be complicated as a result of interferences from complex matrices, so that the use of UV and ELSD is limited. Conductivity detection in suppressed mode provides excellent selectivity and sensitivity for ionic species, making it suitable for trace level analysis and sample detection in complex matrices.

We report herein a methodology for HPLC analysis of anionic surfactants using a new RP silica column and suppressed conductivity detection on a newly developed liquid chromatography system. The new column features unique selectivity, enhanced hydrolytic stability, compatibility with IC mobile phases, and superior efficiency compared to its polymeric counterparts, facilitating separation of a broad variety of anionic surfactants. In this paper, we will discuss various aspects in method development, including stationary phase, instrumentation, mobile phase selection, linearity, and limit of detection. In addition, analyses of several formulated commercial products will be presented using the new method.

INSTRUMENTATION AND MATERIALS

• HPLC Column

Acclaim® PolarAdvantage II (PA2), dp = 5 µm, 4.6 × 150 mm (Dionex, Sunnyvale, CA, USA)

• Instrumentation

ICS-3000 Chromatographic System (Dionex) equipped with an ICS-3000 DP Dual Pump module, ICS-3000

AS Autosampler with a 25 µL injection loop, ICS-3000 DC Detector/Chromatography module, and AMMS® III 4 mm suppressor used in chemical mode

• Software

Chromeleon® 6.7 Chromatography Management Software (Dionex)

• Chemicals

HPLC grade acetonitrile (Burdick and Jackson, Muskegon, MI, USA)

Deionized water (>18 M resistivity) purified by a Milli-Q water purification system (Millipore, Bedford, MA, USA)

Boric acid (EM Science, Cherry Hill, NJ, USA)

Sulfuric acid (Sigma-Aldrich, Milwaukee, WI, USA)

Surfactant standards (ChemService, West Chester, PA, USA)

RESULTS AND DISCUSSION

Considerations for method development

Although UV is the preferred detection method because of its ease of use and high sensitivity, it is unsuitable for detecting surfactants that are UV-inactive (no or very weak chromophores). ELSD is a universal detection method, compatible with gradients. It is inexpensive compared to MS, making it useful for detecting a variety of compounds with high-concentration samples, for either exploratory work or routine analysis. However, its poor reproducibility, low sensitivity, and lack of selectivity impede its use for quantitative analysis, trace level analysis, or detection in complex matrices. Compared to other detection methods, cation-suppressed conductivity detection provides good sensitivity and excellent selectivity for anionic surfactants in a wide range of matrices.

Mobile phases containing acetonitrile and borate buffer were used in the present work. The borate buffer was chosen because of its low conductance and rather mild alkaline condition (pH 8.5) required for sufficient borate buffering. Acetonitrile was used as the organic modifier in the mobile phase.

Silica-based RP columns are used in determining a broad variety of small molecules, including anionic surfactants. However, most RP columns have a limited pH range (2–8). In fact, most conventional RP silica columns suffer decreased lifetime when used extensively above pH 8, due to the dissolution of silica substrate in alkaline conditions. This work used the Acclaim PA2 column because of its wide pH range (1.5 to 10) and high efficiency. Compared to other alkaline stable RP columns, the Acclaim PA2 exhibits superior peak shape and loadability.

Both isocratic and gradient methods were studied for separating anionic surfactants. The isocratic method is used mainly to determine certain surfactants in well-defined samples (Figures 1 and 5). For the analysis of an unknown sample, sample in a complex matrix, or simultaneous determination of several anionic surfactants with different hydrophobicity, a gradient method (from high aqueous to high organic) is recommended, as shown in Figures 2–4 and 6.

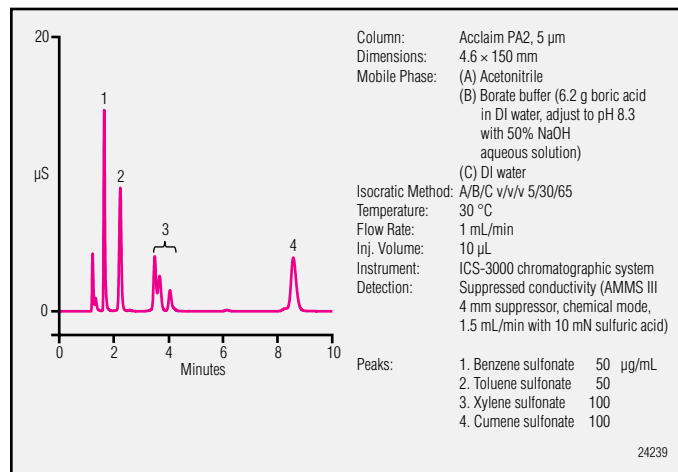


Figure 1. Separation of hydrotropes with Acclaim PA2 and conductivity detection.

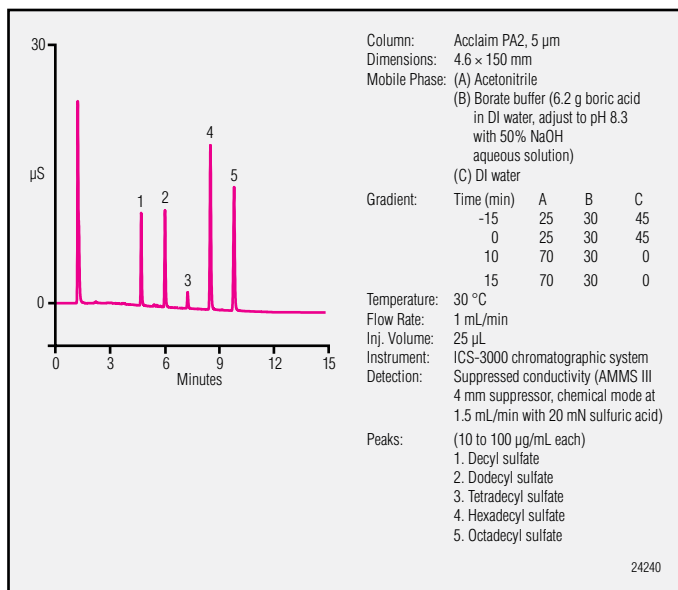


Figure 2. Separation of alkyl sulfates with Acclaim PA2 and conductivity detection.

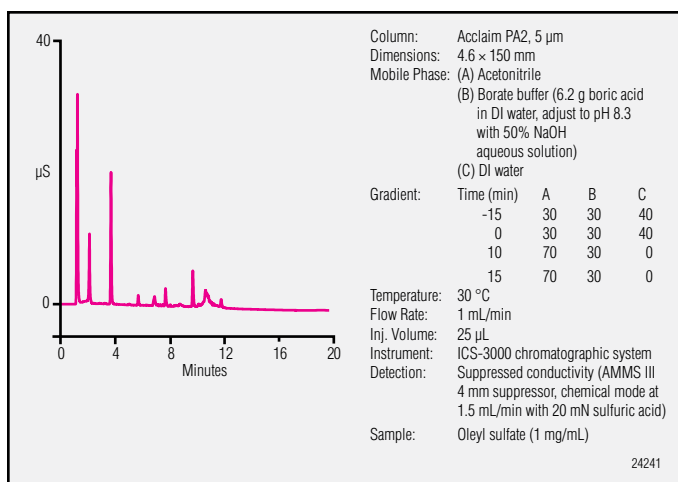


Figure 3. Analysis of oleyl sulfate with Acclaim PA2 and conductivity detection.

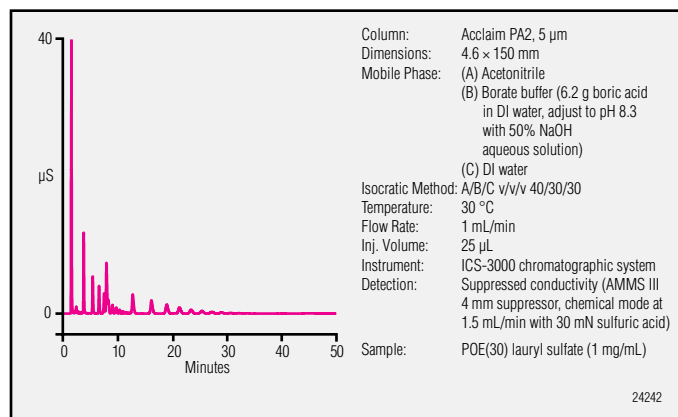


Figure 4. Analysis of POE(30) lauryl sulfate with Acclaim PA2 and conductivity detection.

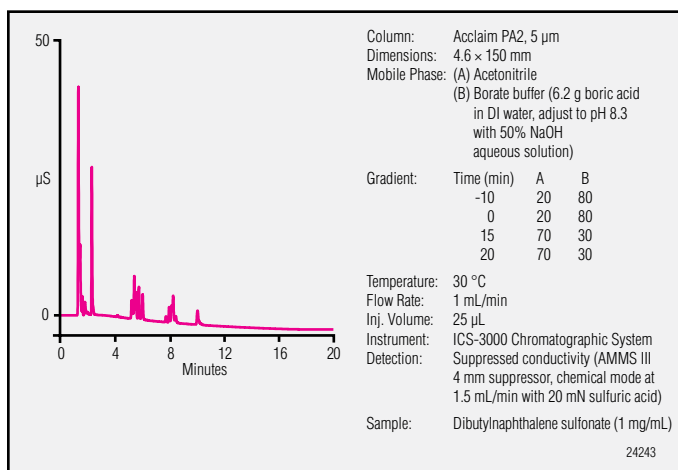


Figure 5. Analysis of dibutyl naphthalene sulfonate with Acclaim PA2 and conductivity detection.

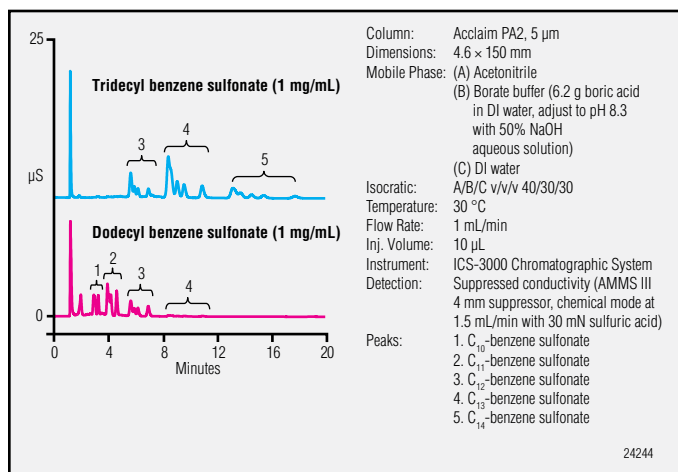


Figure 6. Analysis of alkyl benzene sulfonates with Acclaim PA2 and conductivity detection.

Linearity, LOD, and LOQ

The developed methods provide good linear responses (for sodium dodecyl sulfate or SDS) in a wide dynamic range (0.1 to 1000 ppm), under both isocratic and gradient conditions. With the injection volume of 25 µL, the LOD is estimated to be approximately 20 ppb (S/N = 3), and LOQ is estimated to be approximately 50 ppb (S/N = 10).

Recovery is affected by the sample matrices, possibly due to the presence of Ca₂⁺ and Mg₂⁺. The recoveries of SDS in tap water at spiked levels of 1 ppm, 20 ppm, and 200 ppm were ~70%, ~87%, and 98%, respectively.

Analysis of Anionic Surfactant-Containing Commercial Products

The chromatographic method developed in this work can be applied to the analysis of anionic surfactants in a variety of consumer products, such as liquid hand soap (Figures 8 and 9), laundry detergent (Figure 10), shampoo (Figure 11), and tooth paste (Figure 12). A gradient method, from 100% borate buffer to 70% acetonitrile, was used to determine the highly hydrophilic components such as a hydrotrope (xylene sulfonate) and an artificial sweetener (saccharin), as well as more hydrophobic surfactants such as LAS and lauryl sulfate, within a single run. In addition, highly retained species in the sample can be cleaned off the column at the end of the gradient.

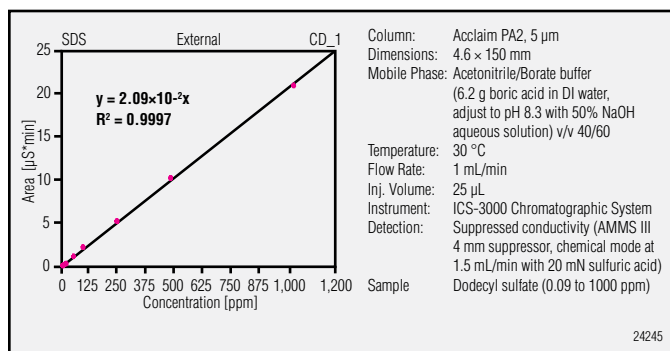


Figure 7. Linearity under isocratic conditions. Dynamic range — 0.1 to 1000 ppm.

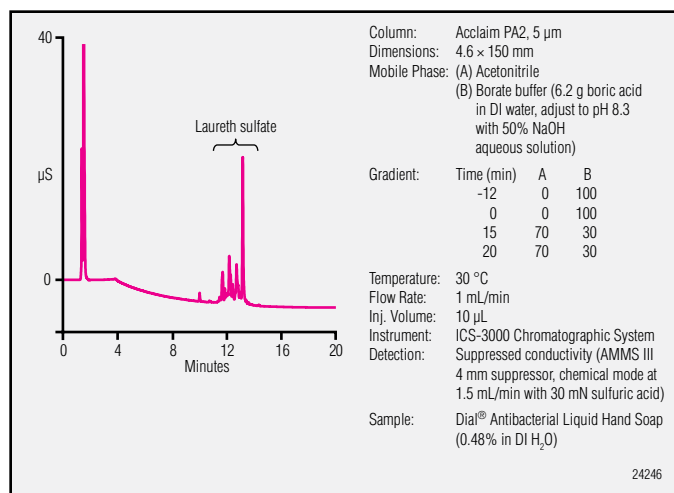


Figure 8. Anionic surfactants in antibacterial liquid hand soap.

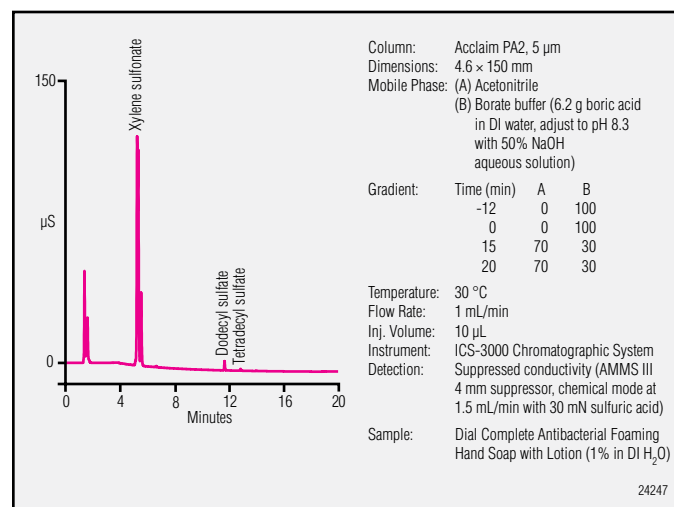


Figure 9. Anionic surfactants in antibacterial foaming hand soap.

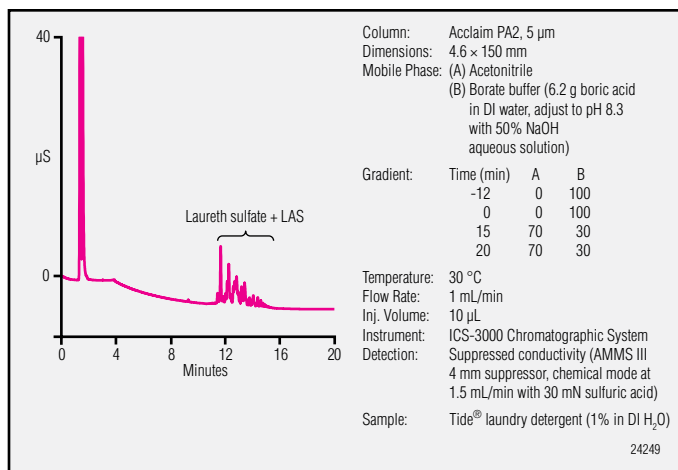


Figure 10. Anionic surfactants in laundry detergent.

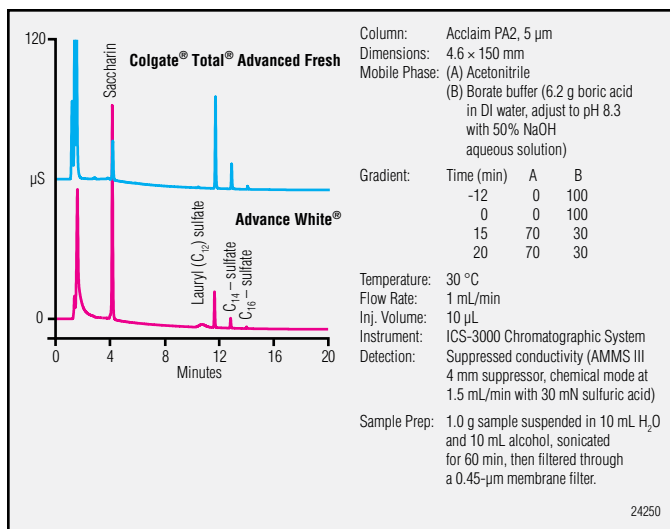


Figure 12. Anionic surfactants in tooth paste.

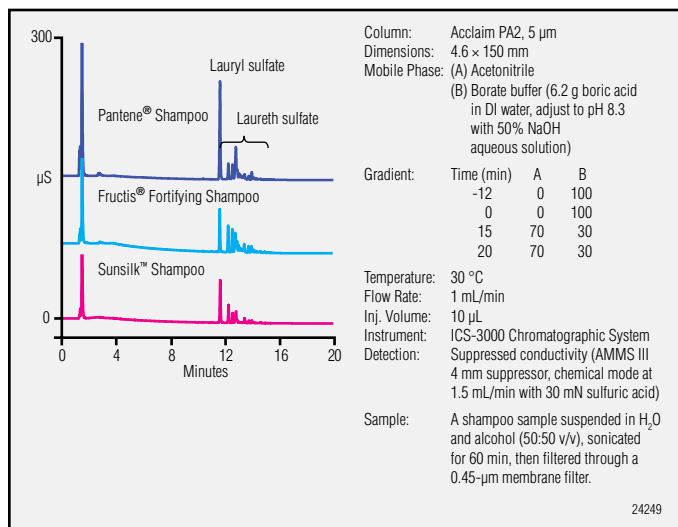


Figure 11. Anionic surfactants in shampoo.

CONCLUSION

1. RP-HPLC combined with suppressed conductivity detection provides simple, sensitive, and selective methods for determining anionic surfactants in a broad range of sample matrices.
2. The Acclaim PolarAdvantage II (PA2) column is the column of choice for RP-HPLC/suppressed conductivity detection because of its wide operating pH range, superior loadability, and high column efficiency.
3. The ICS-3000 chromatographic system is a versatile, metal-free instrument platform for ionic surfactant analysis.
4. It has been demonstrated that anionic surfactants in a collection of consumer products, such as liquid hand soap, laundry detergent, shampoo, and tooth paste, can be determined with the presented method.

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