High-Resolution and High-Throughput Surfactant Analysis by HPLC

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Overview

Purpose: Methodology for high-resolution, high-throughput, and routine analysis of surfactant-containing samples using HPLC with charged aerosol detection.

Methods: HPLC methods, including an application-specific column (Thermo Scientific Acclaim Surfactant Plus), HPLC system (Thermo Scientific Dionex UltiMate 3000 RS), charged aerosol detector (Thermo Scientific Dionex Corona ultra RS), mobile phase system, and elution conditions are outlined.

Results: Generic method for simultaneous determination of different surfactant types was developed. Determinations of various surfactant-containing samples, including laundry detergents, shampoo, hand soap, and nasal spray are demonstrated.

Introduction

Surfactants are a diverse group of chemicals whose structures vary widely but typically contain an oil-soluble hydrocarbon "tail" group and a water-soluble "head" group. Surfactants can be categorized based upon the structure of their water-soluble group, and include nonionic, anionic, cationic, and amphoteric classes. Surfactants are widely used in industrial, agricultural, pharmaceutical, as well as consumer products (e.g. cleaning agents, pesticides, pharmaceutical formulations, laundry detergents, cosmetics, etc.). Their separation and identification can be challenging due both to the diversity of surfactants and complexity of the sample matrix. The commonly used methods for surfactant characterization include titration, spectroscopy, and chromatography. HPLC is the preferred technique for surfactant analysis, and typically is performed in different separation modes: reversed-phase (RP), normal-phase (NP), ion-exchange (IEX), and size-exclusion chromatography (SEC). However, depending on the type of surfactant, different chromatographic conditions need to be developed. Moreover, when analyzing cationic surfactants, silica based columns often give severe peak tailing. The charged aerosol detector (CAD) is a universal detector for all classes of surfactants. This work describes a complete, simple, and versatile methodology for surfactant analysis, consisting of an application-specific column (Acclaim™ Surfactant Plus), HPLC system (UltiMate™ 3000 RSLC system), charged aerosol detector (Corona ™ ultra RS™), mobile phase system, and elution conditions. Determinations of surfactants in laundry detergents, shampoo, and nasal spray are demonstrated using this system.

FIGURE 1. Simultaneous separation of different types of surfactants.

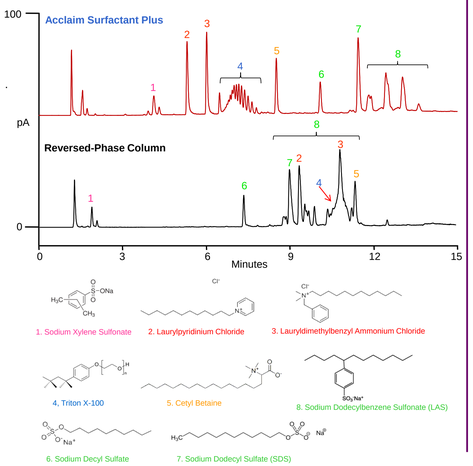
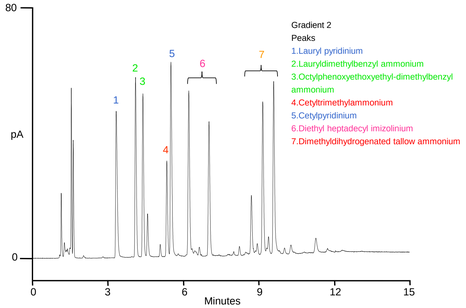


FIGURE 2. Separation of cationic surfactants.



Methods

Separation Column

All separations were performed on an Acclaim Surfactant Plus column (3 µm, 3 × 150 mm).

Samples

All surfactant standards were purchased from ChemService (West Chester, PA, USA). All consumer products were purchases from local stores. Samples were dissolved in a isopropanol, isopropanol/water (1:1), or acetonitrile/water (1:1) to a concentration of 1 to 20 mg/mL, and filtered before injection.

Mobile Phase System

The mobile phase contained acetonitile and 0.1 M ammonium acetate (pH5) buffer. HPLC grade acetonitrile was obtained from Burdick and Jackson (Muskegon, MI, USA). Deionized water (>18MΩ-cm) was purified by a Milli-Q® water purification system (Millipore, Bedford, MA, USA). Ammonium acetate salt (99.99+% pure) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Glacial acetic acid was purchased from Thermo Fisher Scientific. The buffer consists of 7.78 g/L ammonium acetate and 2.05 g/L glacial acetic acid in water.

Gradient Methods

Gradient 1 (Figures 1, 4 to 6)

Time (min)	Flow Rate (mL/min)	MeCN (%)	0.1 M NH_4OAc,pH5 (%)
-8	0.6	25	75
0	0.6	25	75
10	0.6	80	20
15	0.6	80	20

Gradient 2 (Figure 2)

Time (min)	Flow Rate (mL/min)	MeCN (%)	0.1 M NH_4OAc,pH5 (%)
-8	0.6	35	65
0	0.6	35	65
8	0.6	85	15
15	0.6	85	15

HPLC Instrument

Separations were performed on a modular UltiMate 3000 HPLC system equipped with an LPG 3600 gradient pump, WPS-3000 Autosampler, TCC-3200 column oven, and PDA-3000 detector. A Corona ultra charged aerosol detector or an evaporative light scattering detector was used to detect analytes with no or weak chromophore.

Data Analysis

Thermo Scientific Dionex Chromeleon 6.80 Chromatography Management software was used for system control and data processing.

Discussion and Results

Separation Column

The Acclaim Surfactant Plus is the most versatile high-performance HPLC column designed for the determination of surfactants, including anionics, nonionics, cationics, and amphoterics, in a wide range of samples, such as consumer products, pharmaceuticals, food & beverages, environmental samples, etc. This column, based on novel mixed-mode chromatography technology and advanced surface chemistry, provides both reversed-phase and anion-exchange retention mechanisms. The column chemistry is designed in such way that it elutes in the order of cationic, nonionic, amphoteric, and anionic surfactants. Figure 1 shows that the Acclaim Surfactant Plus column provides ideal selectivity for the simultaneous separation of anionic, nonionic, cationic and amphoteric surfactants, whereas the C18 column fails to resolve them under the same conditions. In addition, the surface chemistry of the Acclaim Surfactant Plus effectively deactivates the surface silanol activity so that cationic surfactants elute as symmetrical and efficient peaks (Figure 2).

Detection Method

The Corona ultra RS charged aerosol detector is a sensitive, mass-based detector, especially well-suited for the determination of non-volatile and many semi-volatile analytes. This technology has greater sensitivity and precision than evaporative light scattering detectors (ELSD), and it is simpler to operate than a mass spectrometer (MS). Its benefits include high sensitivity (sub to single digit nanogram), excellent injection-to-injection reproducibility, wide dynamic range, and gradient compatibility. Therefore, the Corona ultra RS detector is the preferred detector to accompany Acclaim Surfactant Plus columns for determinations of various types of surfactants. Figure 3 demonstrates the superior sensitivity of the Corona ultra RS compared to an ELSD. In addition, methods developed with charged aerosol detection can be easily transferred to LC-ESI-MS methods with little or no modifications, because both detectors share the same mobile phase requirements.

Method Development

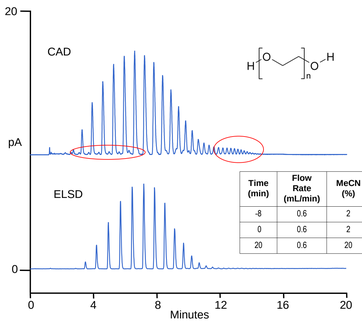
The Acclaim Surfactant Plus column is fully compatible with isocratic and gradient conditions. Because surfactants are much different in hydrophobicity and/or charge, a gradient method is usually advantageous for determining different types of surfactants within the same analysis. For the analysis of known surfactants, it is sometimes easier to develop an isocratic method for higher throughput and simpler operation.

This column is designed for applications using volatile buffers, such as ammonium acetate, which is compatible with CAD, ELSD, MS, and UV (> 225 nm). It can be also used with phosphate buffers (pH ≤ 7) when required by applications.

When analyzing a mixture of analytes, some of which lack a chromophore, it is beneficial to put UV and CAD detectors in series following the analytical column.

When analyzing real life samples, a guard cartridge must be used with the analytical column, and replaced periodically depending on the nature of the sample.

FIGURE 3. PEG monoethyl ether (MW ~ 550): Charged aerosol detection vs. ELSD



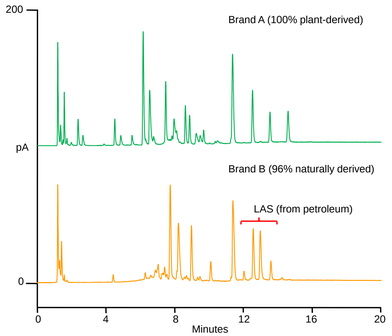
Time (min)	Flow Rate (mL/min)	MeCN (%)	0.1 M NH_4OAc,pH5 (%)
-8	0.6	2	98
0	0.6	2	98
20	0.6	20	80

Applications

Laundry Detergent

Laundry detergents contain many components, including biodegradable surfactants. While dodecyl benzene sulfonate (LAS), a petroleum-derived biodegradable anionic surfactant, has been widely used in laundry detergents, modern formulations tend to use plant-derived surfactants for their environmental and consumer safety benefits. Figure 4 shows the profiles of two laundry detergents – one is 100% plant-derived and the other contains LAS.

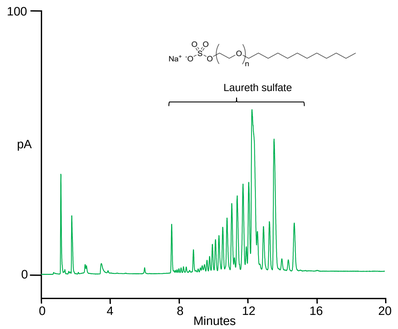
FIGURE 4. Laundry detergents (20 x dilution, Gradient 1)



Shampoo

Shampoos contain various combinations of anionic, cationic, nonionic, and amphoteric surfactants, designed to influence the essential characteristics of the shampoo: cleansing, foam, conditioning, and viscosity. Laureth sulfates are commonly used in shampoos to provide lather and cleansing. As shown in Figure 5, the individual oligomers in laureth sulfate are well resolved using the Acclaim Surfactant Plus column.

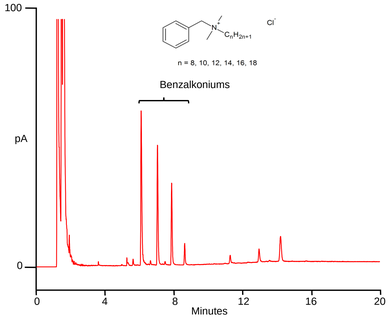
FIGURE 5. Shampoo (40 x dilution, Gradient 1)



Personal Care Products

Benzalkonium salts are a widely used preservative in nasal sprays and ophthalmic formulations because of their antimicrobial effects. Figure 6 shows the chromatographic separation of the major homologs of benzalkonium salts in nasal spray with excellent separation and symmetrical peaks.

FIGURE 6. Nasal spray (filter and inject, Gradient 1)



Conclusion

Combining the use of the Acclaim Surfactant Plus column with the Corona ultra RS charged aerosol detector enables a versatile, sensitive, and simplified approach for routine surfactant analysis.

- Highly versatile and simple: different types of surfactants can be determined using one column and one gradient method with one injection
- Well suited to cationic surfactant analysis
- Excellent resolution for ethoxylated surfactants
- Compatible with various detection methods, including charged aerosol, mass spectrometry, evaporative light scattering, suppressed conductivity, and UV-Vis
- A broad range of applications on consumer products have been demonstrated

References

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4. Acclaim Surfactant Plus Product Specifications: http://www.dionex.com/en-us/webdocs/111747-PS-Acclaim-SurfactantPlus-30Mar2012-PS20477.pdf (accessed June 1, 2012)
5. Acclaim Surfactant Plus Product Manual: http://www.dionex.com/en-us/webdocs/111745-065460-01_MANUALCOLACCLAIMSURFACTANTPLUS_FINAL.pdf (accessed June 1, 2012)

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