

The Strategy of Surfactant Analysis by HPLC

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INTRODUCTION

Surfactants are widely used in the consumer, industrial, agricultural, and pharmaceutical markets in products as diverse as pesticides, detergents, petroleum, and cosmetics. The separation and identification of surfactants can be difficult due to both their diversity and the complexity of sample matrices. Although high-performance liquid chromatography (HPLC) is the preferred and most commonly used approach for surfactant analysis, it is always challenging to choose suitable methods for specific applications. For example, the existing HPLC methods do not provide optimal separation for anionic, nonionic, cationic, and amphoteric surfactants in a single analysis. This poster provides an overview of solutions for surfactant analysis by HPLC, including separation columns, instrumentation, method development, and applications.

DETECTION METHOD CONSIDERATION

For surfactant analysis, detection methods such as ultraviolet/visible (UV), refractive index (RI), charged aerosol detection (CAD[®]), evaporative light scattering detection (ELSD), mass spectrometry (MS), or suppressed conductivity can be used. The preferred detection method for surfactants with chromophores is UV. However, many surfactants have no chromophore and thus cannot be detected by UV. MS is often used for trace analysis and in cases when peak identification is required. ELSD is a universal detection method and is compatible with gradient methods, making it suitable for surfactant analysis when pursuing exploratory work or performing routine analysis of high-concentration samples. Its limitations include poor reproducibility, low sensitivity, and nonlinear response. Compared to ELSD, CAD provides (1) excellent reproducibility, (2) 5 to 10 times better sensitivity than ELSD, and (3) more uniform peak response in addition to all the benefits of ELSD. Suppressed conductivity detection provides good sensitivity and excellent selectivity for ionic species, making it an economical method for ionic surfactant analysis requiring high sensitivity and selectivity.

EXPERIMENTAL

For UV and ELSD: Summit HPLC System (Dionex) equipped with a P680 gradient pump, ASI-100 autosampler, TCC-100 column oven, and UVD 340 detector. A Sedex 85 ELS detector (Sedere, Alfortville, France) was used for detecting surfactants with weak or no chromophore.

For suppressed conductivity detection: ICS-3000 ion chromatography system (Dionex) equipped with a DP Dual Pump module, AS autosampler, and DC Detector/Chromatography module with a conductivity detector. A CSRS® ULTRA II 4 mm suppressor was used in external water mode for detecting cationic surfactants and an AMMS® III 4 mm suppressor was used in chemical mode for detecting anionic surfactants.

Software: Chromeleon® 6.7 Chromatography Data System (Dionex).

HPLC-grade acetonitrile and methanol used were from Burdick and Jackson (Muskegon, MI, USA). Deionized water (>18 MΩ resistivity) was purified by a Milli-Q® water purification system (Millipore, Bedford, MA, USA). The boric acid was obtained from EM Science (Cherry Hill, NJ, USA). Ammonium acetate, acetic acid, and sulfuric acid were purchased from Sigma-Aldrich (Milwaukee, WI, USA). All surfactant standards were from ChemService (West Chester, PA, USA).

APPLICATIONS AND DISCUSSIONS

Simultaneous Analysis of a Mixture of Anionic, Cationic, Nonionic, and Amphoteric Surfactants

The Acclaim® Surfactant column is the most versatile column for surfactant analysis in the market. Its novel chemistry provides ideal selectivity for separating different types of surfactants as well as hydrotropes. Figure 1 shows the separation of a mixture of anionic, nonionic, cationic, and amphoteric surfactants as well as hydrotropes, with excellent resolution and peak asymmetry. The mobile phase is volatile, thus making it compatible with CAD, ELSD, MS, and UV (>230 nm) detection methods.

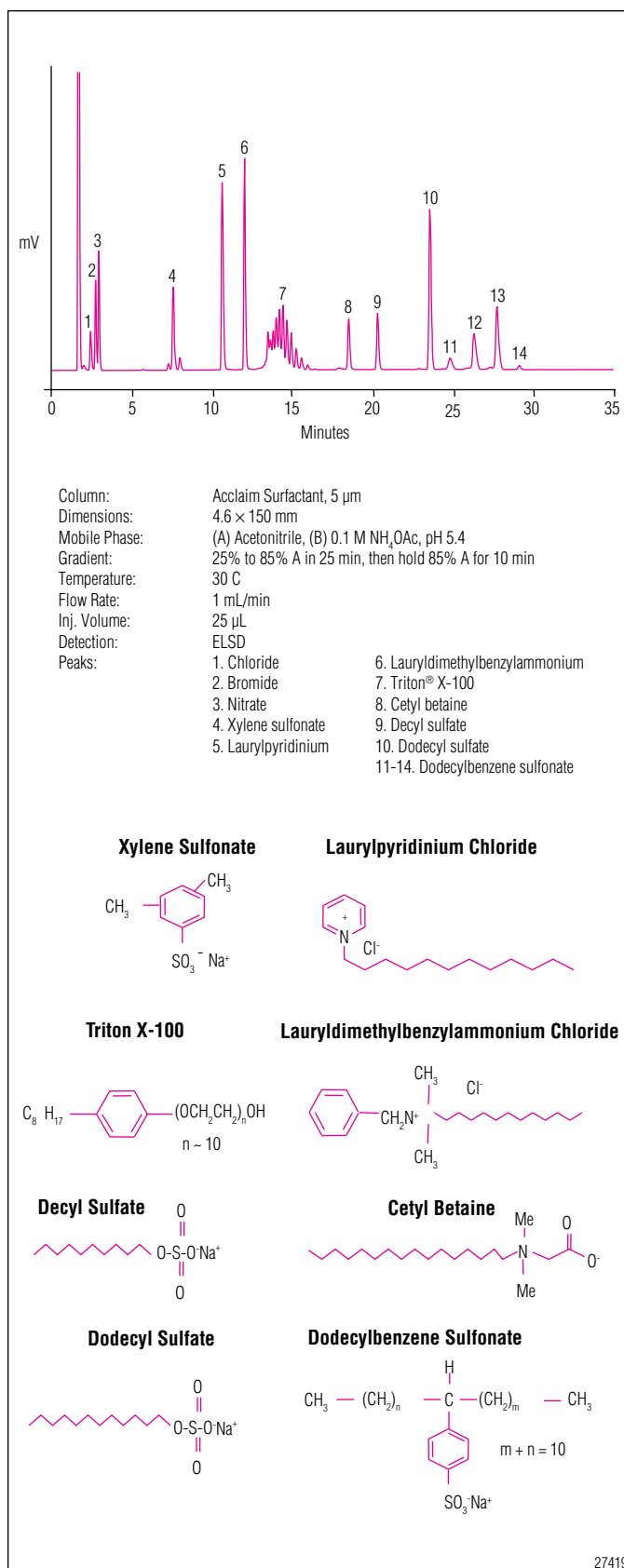


Figure 1. Simultaneous separation of inorganic anions, hydrotropes, cationic, nonionic, amphoteric, and anion surfactants.

Analysis of Cationic Surfactants

The Acclaim Surfactant column is the column of choice for separating cationic surfactants. Cationic surfactants are used in many formulated products, such as fabric softeners, corrosion inhibitors, and antimicrobial agents. Commonly used cationic surfactants include alkyl quaternary ammonium, benzylalkylammonium, alkylpyridinium, and imidazolium salts. Silica-based, reversed-phase (RP) columns often exhibit peak tailing and excessive retention because of the undesirable ion-exchange interactions between residual silanols on the silica surface and the analytes, accompanied by high hydrophobicity of cationic surfactants. The novel column chemistry of the Acclaim Surfactant column effectively deactivates these interactions, resulting in excellent selectivity, high efficiency, and good peak shape (Figure 2).

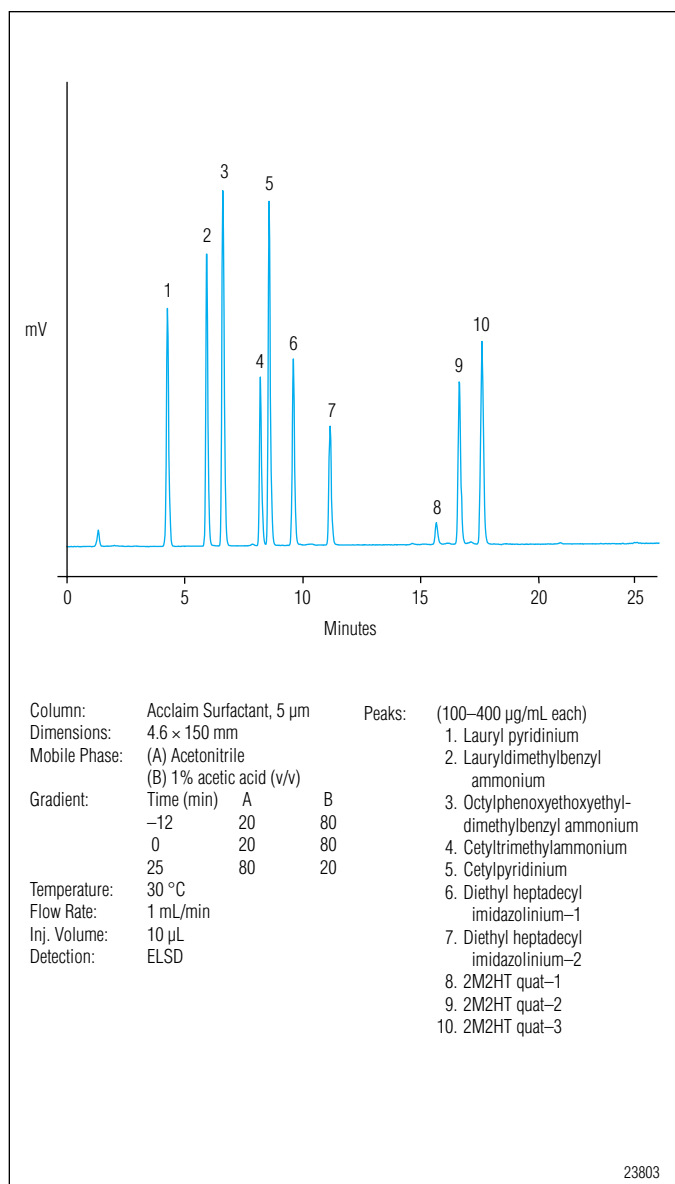


Figure 2. Separation of cationic surfactants using the Acclaim Surfactant column.

Determination of the Degree of Ethoxylation and Alkyl Chain Distribution for Nonionic Ethoxylated Surfactants

The Acclaim Mixed-Mode HILIC-1 column is suitable for analyzing nonionic ethoxylated surfactants. In HILIC mode, the degree of ethoxylation (EO) can be determined. In RP mode, the separation of ethoxylated oligomers is suppressed and the alkyl chain distribution can be characterized. Figure 3 illustrates an example of analyzing Brij[®] 35 [lauryl alcohol condensed with 23 moles ethylene oxide; molecular formula: $C_{12}H_{26}O(C_2H_4)_nH$]. In RP mode, the surfactant is separated into four single peaks, corresponding to free PEGs (early-eluting peak) and three ethoxylates corresponding to different alkyl chain lengths. Under this condition, all EO oligomers with the same hydrophobe collapse into a single peak. Alternately, in HILIC mode, all EO oligomers are separated in addition to the hydrophobe-based separation. In this way, the degree of ethoxylation can be determined.

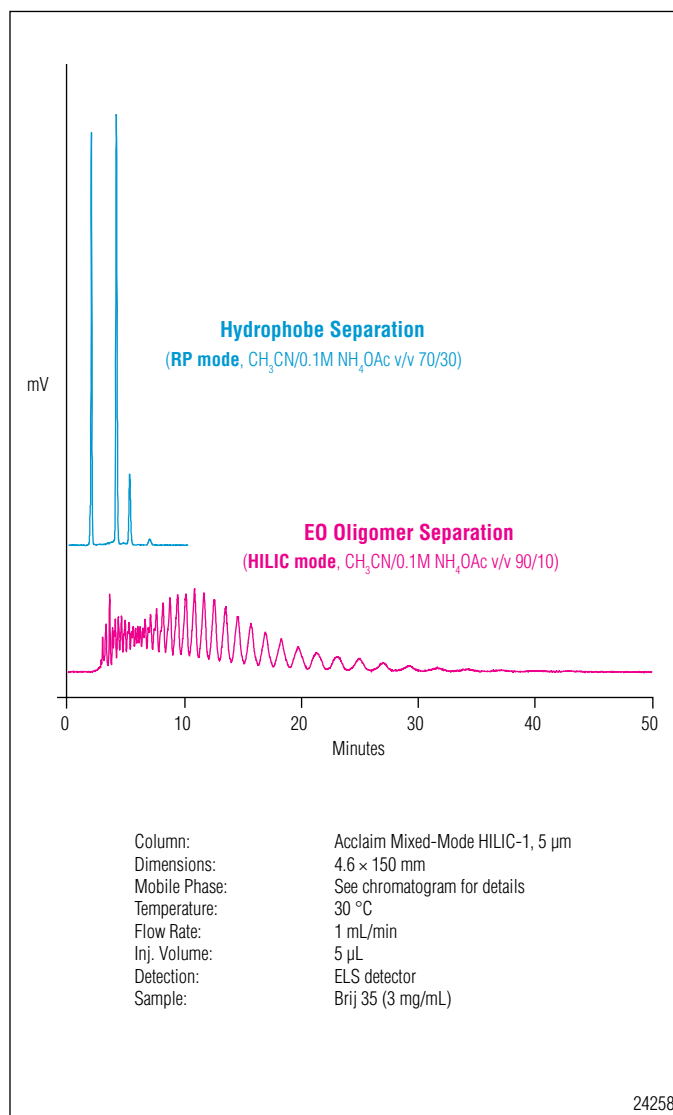


Figure 3. Analysis of ethoxylated fatty alcohols in both RP and HILIC modes.

Highly Sensitive and Selective Method for the Determination of Anionic Surfactants Using Suppressed Conductivity Detection

The Acclaim PolarAdvantage II (PA2) column provides excellent hydrolytic stability in both acidic and alkaline conditions, and is ideal for highly selective and sensitive analysis for anionic surfactants using RPLC and suppressed conductivity detection. 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. Figure 4 demonstrates the separation of a series of alkyl sulfates on the Acclaim PA2 column. The developed method has good linear responses 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 the LOQ is estimated to be approximately 50 ppb ($S/N = 10$).

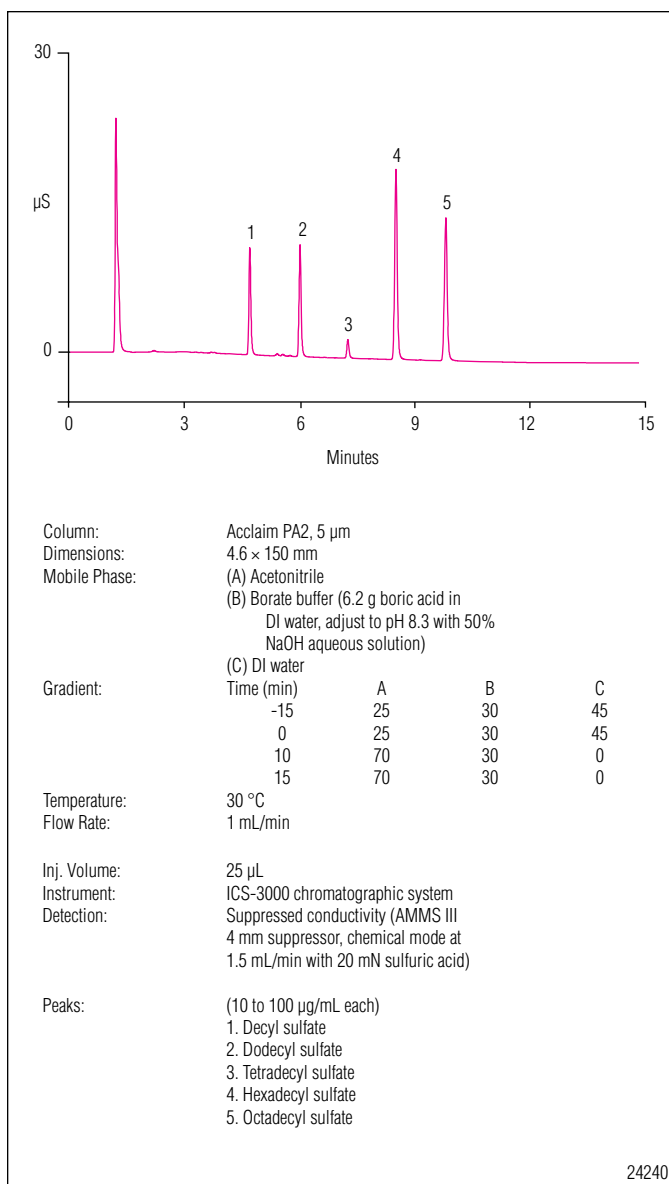


Figure 4. Separation of alkyl sulfates with the Acclaim PA2 column and conductivity detection.

Table 1. Summary of Methods for Surfactant Analysis

Application	Separation Column	Detection	Mobile Phase*	Instrument
Anionic Surfactants	Acclaim Surfactant	UV, ELSD, CAD, MS	Acetonitrile/ammonium acetate (or formate) buffer	HPLC
	Acclaim PolarAdvantage II	Suppressed conductivity	Acetonitrile/borate buffer	IC
Cationic Surfactants	Acclaim Surfactant	UV, ELSD, CAD, MS	Acetonitrile/ammonium acetate (or formate) buffer	HPLC
		Suppressed conductivity	Acetonitrile/acetic (formic) acid	IC
Nonionic Surfactants	Acclaim Mixed-Mode HILIC-1	UV, ELSD, CAD, MS	Acetonitrile (or methanol)/water or ammonium acetate (or formate) buffer	HPLC
	Acclaim Surfactant	UV, ELSD, CAD, MS	Acetonitrile (or methanol)/water or ammonium acetate (or formate) buffer	HPLC
Amphoteric Surfactants	Acclaim PolarAdvantage II	UV, ELSD, CAD, MS	Acetonitrile (or methanol)/water or ammonium acetate (or formate) buffer	HPLC
	Acclaim Surfactant	UV, ELSD, CAD, MS	Acetonitrile (or methanol)/ammonium acetate (or formate) buffer	HPLC
Hydrotropes	Acclaim Surfactant	UV, ELSD, CAD, MS	Acetonitrile/ammonium acetate (or formate) buffer	HPLC
	Acclaim PolarAdvantage II	Suppressed conductivity	Acetonitrile/borate buffer	IC
Mixture of Surfactants (anionic, cationic, nonionic, amphoteric, etc.)	Acclaim Surfactant	UV, ELSD, CAD, MS	Acetonitrile (or methanol)/ammonium acetate (or formate) buffer	HPLC

**When UV is used to detect surfactants that have a chromophore, phosphate buffer can also be used.*

CONCLUSION

The proven chromatographic methods, including separation column, detection method, mobile phase selection, and instrumentation platform (summarized in Table 1), provide a general guideline for surfactant analysis using HPLC.

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