

# New Development in Surfactant Analysis by HPLC

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## ABSTRACT

This presentation provides the state-of-the-art for surfactant analysis in various sample matrices using the most reliable and most advanced HPLC technology.

## INTRODUCTION

Surfactants are widely used in the consumer product, industrial, agricultural, and pharmaceutical markets, in products as diverse as pesticides, detergents, petroleum products, cosmetics, and pharmaceuticals. Their separation and identification can be difficult due to both the diversity of surfactants and the complexity of sample matrices. Although HPLC is the preferred and commonly used approach for analyzing surfactants, and a variety of methods have been developed, it is challenging to choose proper methods for specific applications. None of the existing analytical solutions provide optimal separation for anionic, nonionic, cationic, and amphoteric surfactants in a single analysis. This presentation gives an overview on the total solution for surfactant analysis by HPLC including separation columns, instrumentation, method development, and applications.

## SEPARATION COLUMN SELECTION

The Acclaim® Surfactant column is the most versatile column and the first choice for surfactant analysis. Its advanced column technology provides ideal selectivity for anionic, nonionic, cationic, and amphoteric surfactants as well as hydrotropes (Figure 1). In addition, it is the column of choice for separating cationic surfactants (Figure 2).

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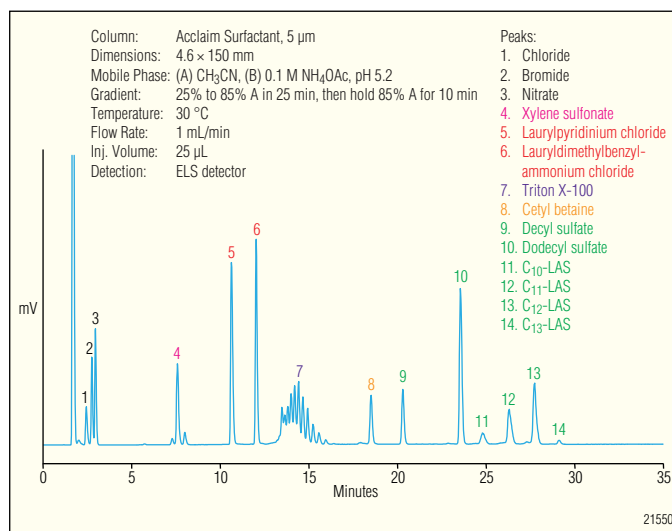


Figure 1. Simultaneous separation of *hydrotrope, cationic, nonionic, amphoteric, and anionic* surfactants using the Acclaim Surfactant column.

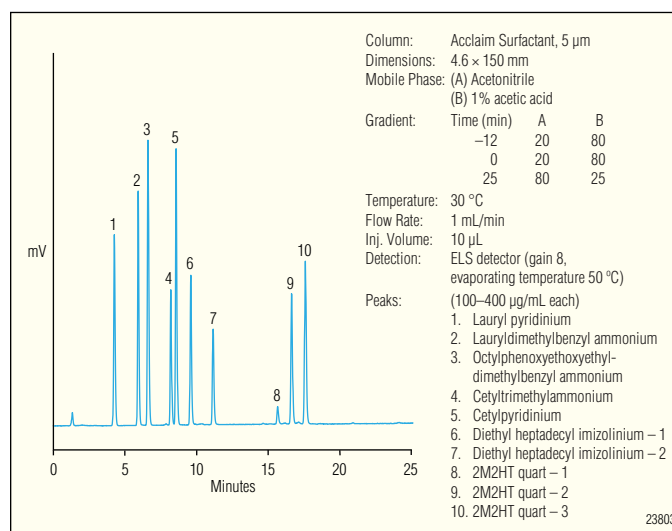


Figure 2. Separation of cationic surfactants using the Acclaim Surfactant column.

The Acclaim Mixed-Mode HILIC-1 column complements the Acclaim Surfactant column, and is suitable for analyzing ethoxylated surfactants. In HILIC mode, the degree of ethoxylation (EO) can be determined. In RPLC mode, the separation of ethoxylated oligomers is suppressed, and the alkyl chain distribution can be characterized (Figures 3 and 4).

The Acclaim PolarAdvantage II (PA2) column provides excellent hydrolytic stability at both acidic and alkaline conditions, and is ideal for highly selective and sensitive analysis for anionic surfactants using RPLC and suppressed conductivity detection (Figure 5).

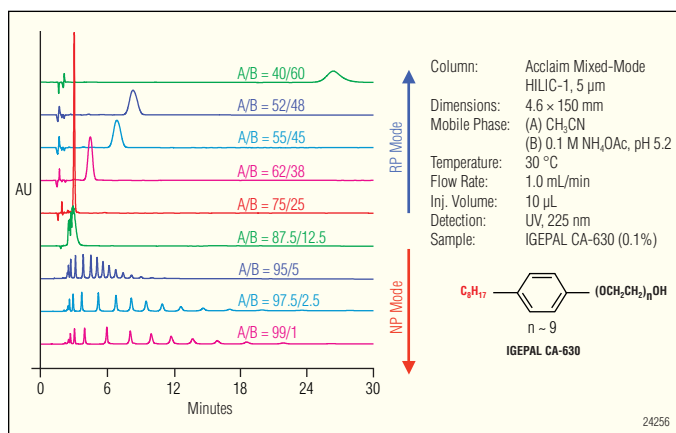


Figure 3. Dependency of separation mode on mobile phase organic content using the Acclaim Mixed-Mode HILIC-1 column.

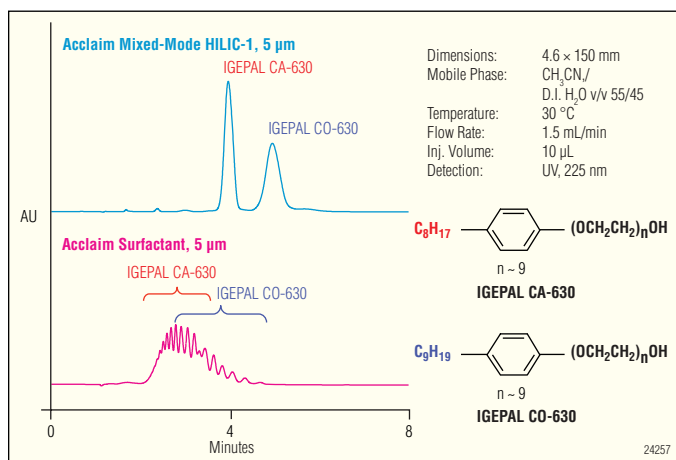


Figure 4. Separation of alkylphenol ethoxylates by hydrophobe using the Acclaim Mixed-Mode HILIC-1 column.

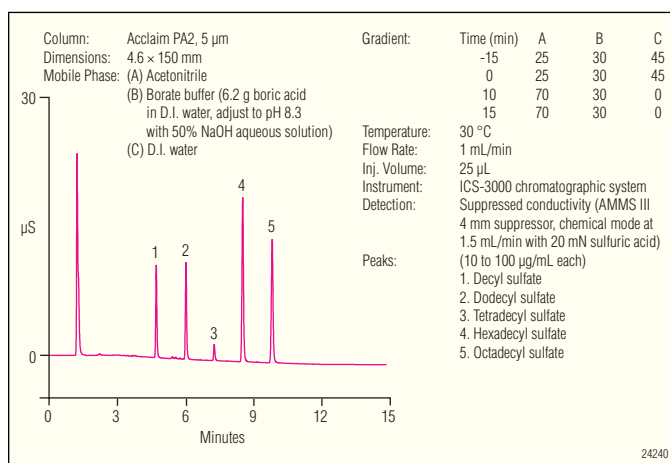


Figure 5. Separation of alkyl sulfates using the Acclaim PA2 column and conductivity detection.

## INSTRUMENTATION CONFIGURATION

For UV and ELSD: Summit<sup>®</sup> 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) or equivalent was used for evaporative light scattering detection.

For suppressed conductivity detection: ICS-3000 Chromatography System (Dionex) equipped with a DP Dual Pump module, AS autosampler with 15  $\mu L$  injection loop, and DC Detector/Chromatography module with a conductivity detector. A CSRS<sup>®</sup> ULTRA II 4 mm suppressor was used in external water mode for detecting cationic surfactants and an AMMS<sup>®</sup> III 4 mm suppressor was used in chemical mode for detecting anionic surfactants.

Software: Chromeleon<sup>®</sup> 6.7 Chromatography Management Software (Dionex)

## METHOD DEVELOPMENT CONSIDERATION

ELS detection is a universal detection method, compatible with gradient methods and inexpensive compared to MS. Therefore, it is widely used for surfactant analysis when pursuing exploratory work or performing routine analysis of high-concentration samples. The limitations include poor reproducibility, low sensitivity, and nonlinear response.

UV is the preferred detection method for surfactants with chromophores and is complementary to ELSD. However, many surfactants cannot be detected by UV.

Suppressed conductivity detection (SCD) provides good sensitivity and excellent selectivity for ionic species, making it the preferred means of detection for ionic surfactants in a wide range of sample matrices.

Table 1 shows a comparison of the three aforementioned detection methods.

**Table 1. Comparison of ELSD, UV, and Suppressed Conductivity Detection (SCD) for Surfactant Analysis**

	ELSD	UV	SCD
Versatility	Universal	Limited	Limited
Sensitivity	Poor to fair	Fair to good	Good
Signal Response	Quadratic	Linear	Linear
Selectivity	Nonselective	For surfactants with chromophores	For ionic surfactants
Resistance to Matrix Interference	Poor to good	Poor to good	Good
Reproducibility	Poor to fair	Good	Good
Mobile Phase	Volatile	Non-UV absorbance	Conductivity suppressible
Suitability for Surfactant Analysis	Suitable for most applications	Limited use	Suitable for anionic and cationic surfactants
Recommended Applications	<ol style="list-style-type: none"> <li>High concentration samples</li> <li>Pre-MS application development</li> <li>Applications that need universal detection</li> </ol>	<ol style="list-style-type: none"> <li>Surfactants with chromophores</li> <li>Complement to ELSD</li> </ol>	<ol style="list-style-type: none"> <li>Trace level analysis (ppb)</li> <li>Complex sample matrices</li> <li>Selective analysis</li> </ol>

An ammonium acetate/acetonitrile system is the preferred mobile phase because of its compatibility with ELSD, MS, and UV detections.

An acetic or formic acid/acetonitrile mobile phase is recommended for analyzing cationic surfactants using suppressed conductivity detection on the Acclaim Surfactant column.

A borate buffer/acetonitrile mobile phase is required for analyzing anionic surfactants using suppressed conductivity detection on the Acclaim PA2 column.

## APPLICATIONS

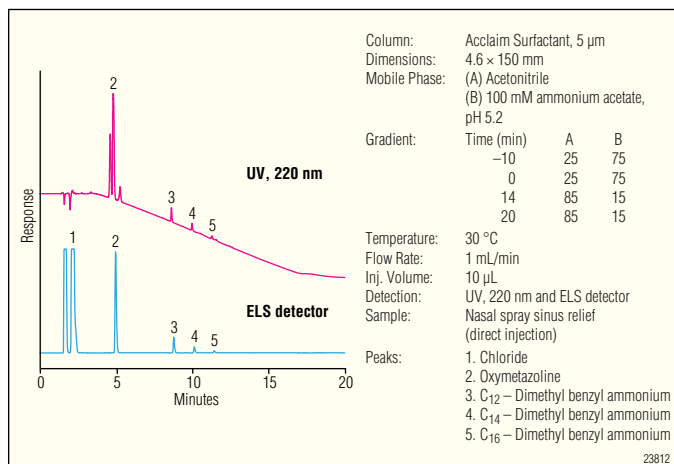


Figure 6. Ingredients in nasal spray using the Acclaim Surfactant column and ELSD and UV detections.

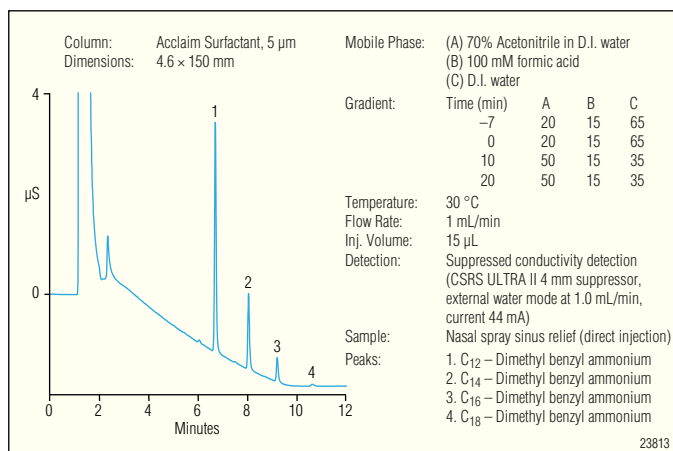


Figure 7. Cationic surfactants in nasal spray using the Acclaim Surfactant column and suppressed conductivity detection.

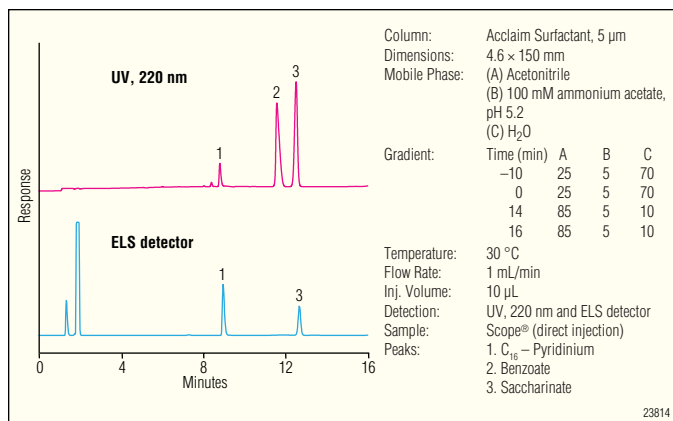


Figure 8. Ingredients in mouthwash liquid using the Acclaim Surfactant column and ELSD and UV detections.

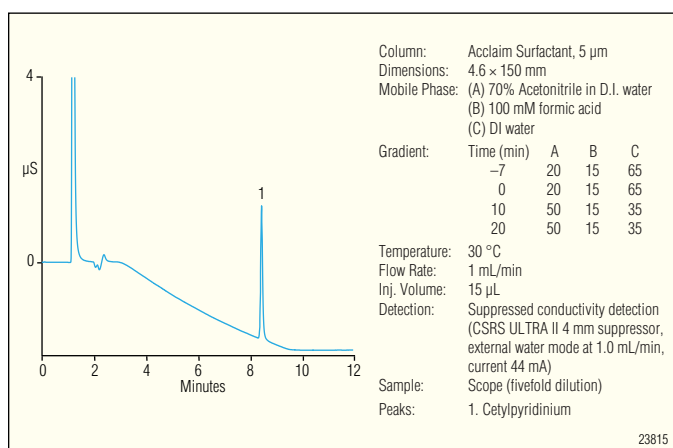


Figure 9. Cationic surfactants in mouthwash liquid using the Acclaim Surfactant column and suppressed conductivity detection.

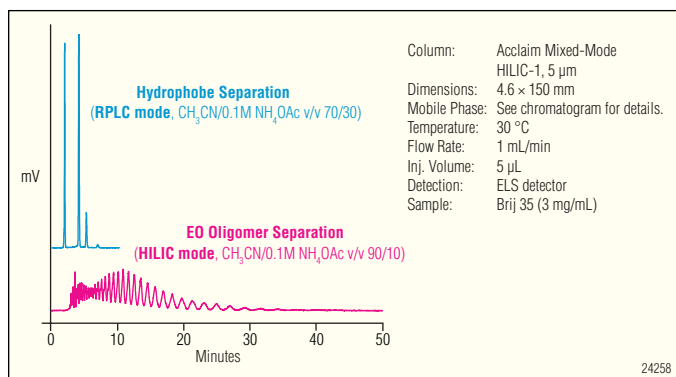


Figure 10. Analysis of ethoxylated fatty alcohols Brij 35 [lauryl alcohol condensed with 23 moles ethylene oxide, molecular formula: (C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>C<sub>12</sub>H<sub>26</sub>O] in both RPLC and HILIC modes with the Acclaim Mixed-Mode HILIC-1 column. In RPLC mode, the surfactant is separated into four single peaks, corresponding to the alkyl chain distribution. Under this condition, all EO oligomers with the same hydrophobe collapse into a single peak. In HILIC mode, on the other hand, all EO oligomers are separated in addition to the hydrophobe-based separation. Thus, the degree of ethoxylation can be determined.

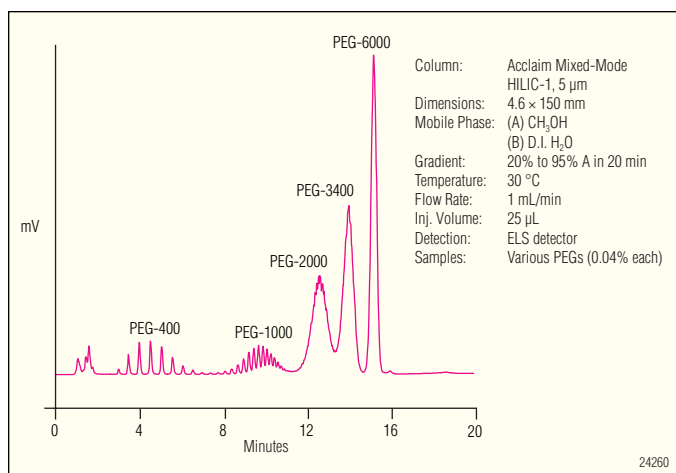


Figure 11. Separation of polyethylene glycols (PEGs) using the Acclaim Mixed-Mode HILIC-1 column.

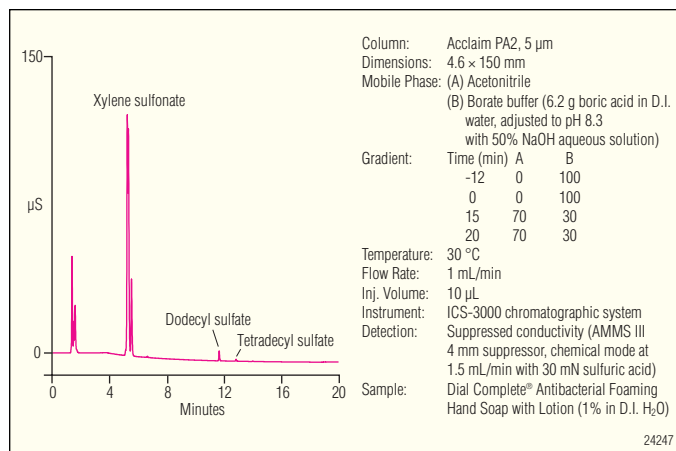


Figure 12. Anionic surfactants in antibacterial foaming hand soap using RPLC and suppressed conductivity detection with the Acclaim PA2 column.

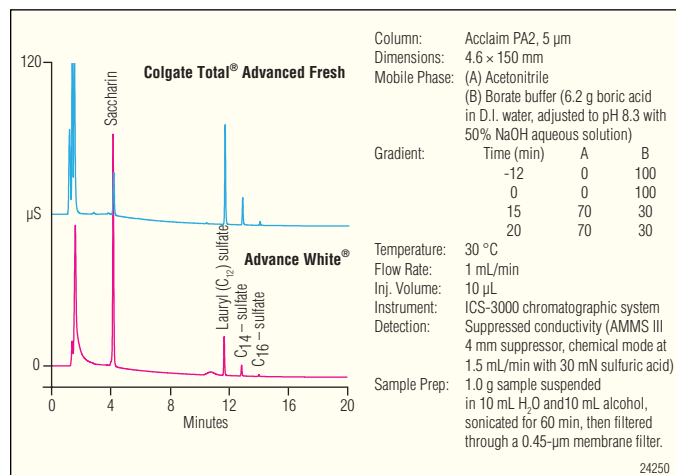


Figure 13. Anionic surfactants in toothpaste using RPLC and suppressed conductivity detection with the Acclaim PA2 column.

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