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Application Note

Surfactant Analysis Using The 2420 Evaporative Light Scattering Detector

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Abstract

This application note demonstrates the capability of Waters 2420 ELS Detector in surfactant analysis.

Introduction

Surfactants, or surface-active agents, are one of the most widely used classes of chemicals. They usually consist of an apolar lipophilic alkyl chain linked to a polar hydrophilic moiety and are classified in four families depending on the charge of the polar moiety: anionic, nonionic, cationic, or amphoteric. They are used in all home care products such as detergents and fabric softeners and all body care products such as shower gels, shampoos, or creams.

A wide range of analysis methods are used for surfactant analysis. These analysis methods include liquid, gas, thin-layer chromatography, UV/Vis, IR, NMR, Mass spectrometries, and other methods, such as titration, extraction, and ion-exchange. High-performance liquid chromatography is one of the important methods.

The Evaporative Light Scattering Detector (ELSD) is relatively new, but it is becoming more popular as HPLC detector, especially for non-UV absorbing samples at gradient elution conditions. This is mainly because it responses to nearly all the analytes, as long as the analytes have lower vapor pressure than the mobile phase. UV chromophores are no longer required for the analytes. Since many surfactants do not have UV absorbing chemical group, ELSD is widely used in their analysis. This application note demonstrates the capability of Waters 2420 ELS Detector in surfactant analysis.

Experimental

Instruments

1525 Binary pumping system

717plus Autosampler

2420 ELS Detector

2996 Photodiode Array Detector

Column Heater

Waters Empower Software

Column

Waters Symmetry C_8, 3.9 x 150 mm, 5 µm particle size

Waters Sperisorb C_1, C_8, ODS2 (C_{18}), 4.6 x 150 mm, 3 µm particle size

Samples

Anionic surfactants: Fatty acid (chain length from C_{11} to C_{19}): Undecanoic acid, tridecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, nonadecanoic acid. Alkyl sulfate salts: Dodecyl sulfate sodium, tetradecyl sulfate sodium, and octadecyl sulfate sodium.

Nonionic surfactants: Ethoxylated alcohols. Tergitol (Spectrum Lab Products Inc., Gardena, CA) 15-s-3, 15-s-5, 15-

s-7, 15-s-9, 15-s-30, 15-s-40.

Cationic surfactants: Alkyl quaternary ammonium bromides: Dodecyl trimethyl ammonium bromide, cetyltrimethyl ammonium bromide, and octadecyltrimethyl ammonium bromide.

All samples are dissolved in THF at concentrations specified in the results.

Results and Discussion

Fatty acids (anionic surfactant)

A series of fatty acids were separated in reverse-phase HPLC condition and detected by 2420 ELSD (see Figure 1). Under these conditions, all the fatty acids were separated by their alkyl chain length. The longer the alkyl chain length, the longer the retention time. It is surprising to find that 2420 can detect fatty acid as small as undecanoic acid (molecular weight 186.3), although the signal is far lower than its analogues with higher molecular weights. Figure 1 also reveals that the response of ELSD varies from sample to sample. All these fatty acids are prepared in similar concentrations (from 2.3 to 2.6 mg/mL), but their peak height and peak areas varies considerably.

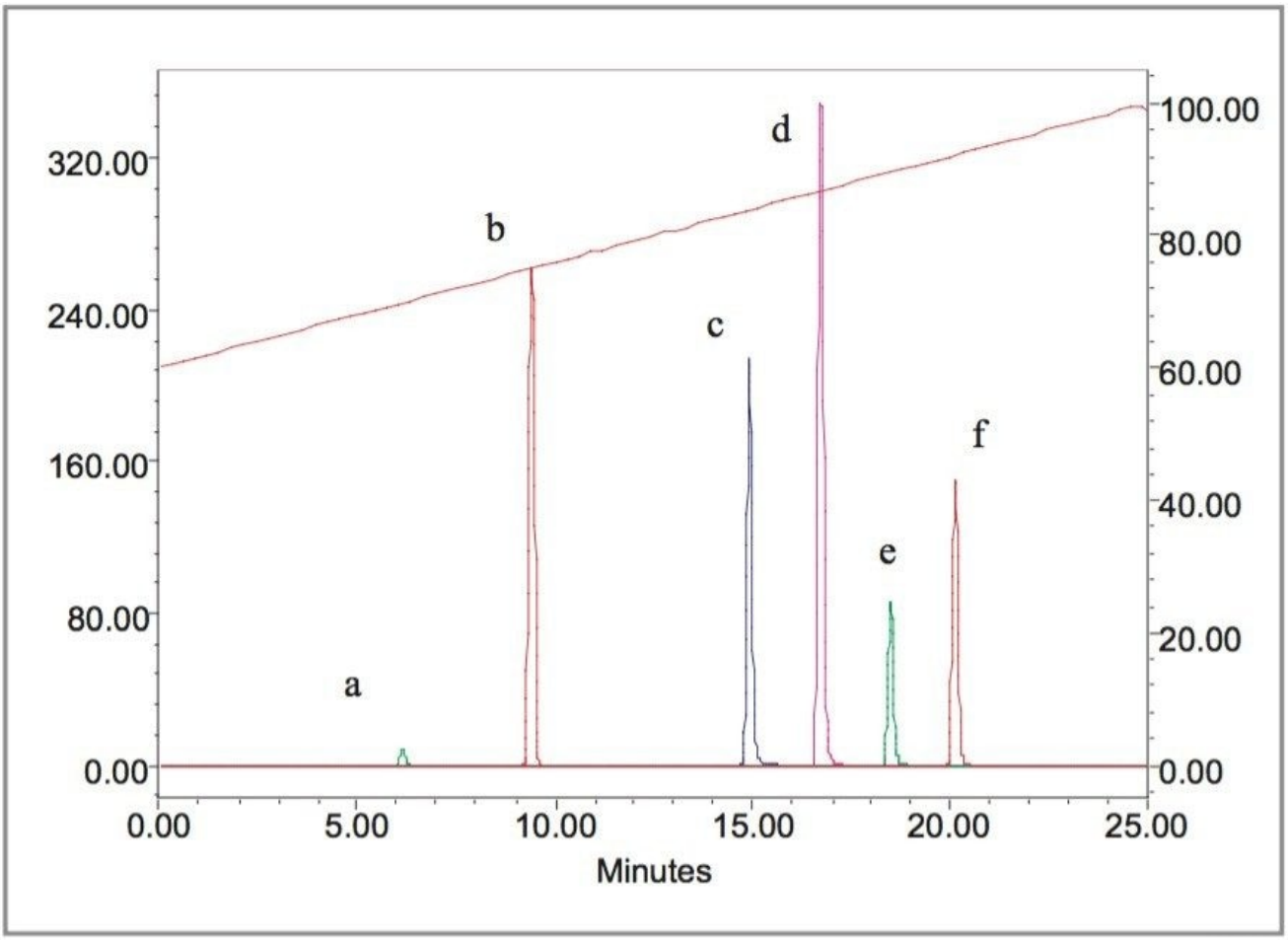

Figure 1. Chromatograms of fatty acids from 2420 ELSD. a: Undecanoic acid, b: Tridecanoic acid, c. Palmitic acid, d. Heptadecanoic acid, e. Stearic acid, f. Nonadecanoic acid (Concentrations: 2.3–2.6 mg/mL). Column: Waters Symmetry C_8, 3.9 x 150 mm, 5 µm particle size; Mobile phase: Acetonitrile/Water (60/40 v/v) to Acetonitrile/Water (100/0 v/v) in 25 min; Flow rate: 1.0 mL/min; Column temperature: 45 °C. ELSD conditions: Nebulizer heating rate: 60%; Drift-Tube temperature: 40 °C. Gas (Nitrogen) Pressure: 45 psi.

Alkyl sulfate salt (anionic surfactant)

Three alkyl sulfate salts were also detected by 2420 ELSD in reverse-phase HPLC conditions (see Figure 2).

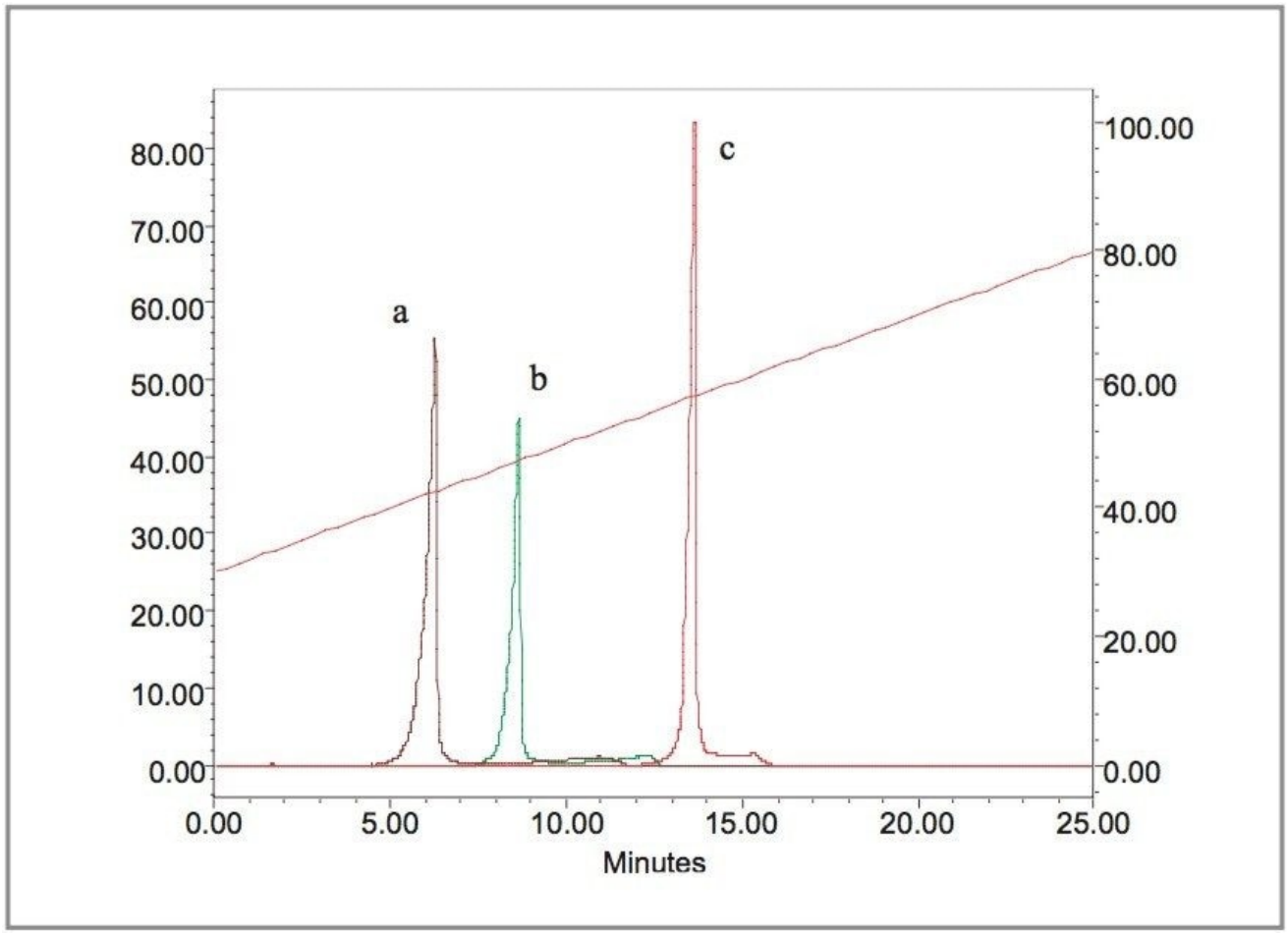

Figure 2. Chromatograms of Alkyl sulfate sodium from 2420 ELSD. Samples: a. Dodecyl sulfate sodium, b. Tetradecyl sulfate sodium, c. Octadecyl sulfate sodium. (1.8–2.2 mg/mL) Column: Waters Spheresorb C_{18}; 3 µm; 4.6 x 150 mm; Mobile phase: Acetonitrile/Water (30/70 v/v) to ACN/Water (90/10 v/v) in 30 min; Flow Rate: 1.0 mL/min; Column Temperature: 45 ˚C.

Tergitol 15-S-7 (nonionic surfactant)

Tergitol 15-S-7 is a nonionic surfactant. It contains mainly secondary alcohol ethoxylates with labled formula as C_{12}-$14H_{25}$-$29O(C_2H_{4O})xH$. It actually is the products of the reaction between fatty alcohols (with alkyl chain length between C_{12} to C_{14}) and excess amount of ethylene oxide. Such product usually contains small amount of unethoxylated alcohols and polyethylene glycols.

Chromatograms of an overlay of two injections of Tergitol 15-S-7 detected by 2420 ELSD is shown in Figure 3.

The oligomer resolution of this material is achieved.

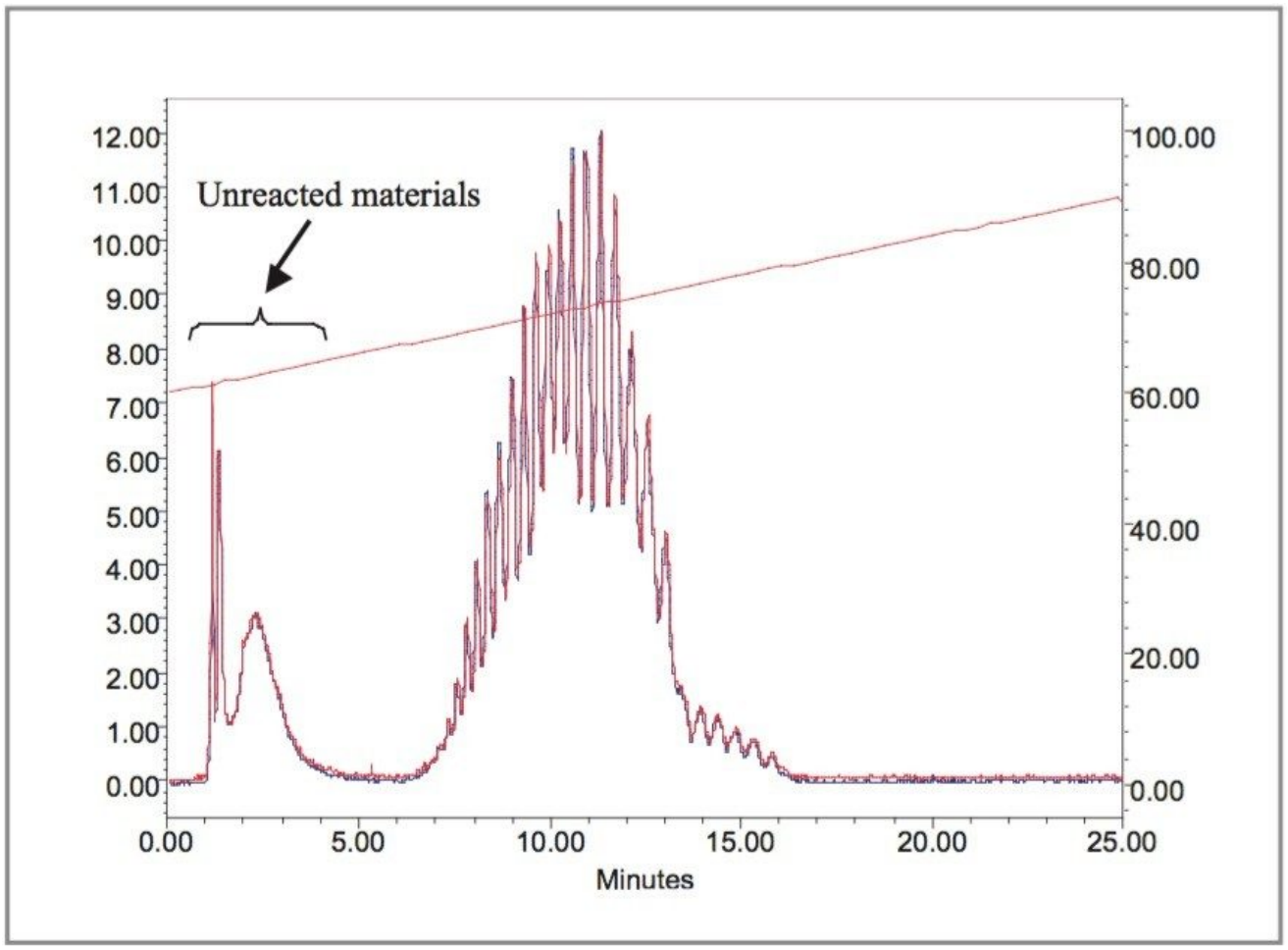

Figure 3. Chromatograms of Secondary alcohol ethoxylate (Two injections. Tergitol 15-S-7, 6.01 mg/mL) from 2420 ELSD. Column: Waters Symmetry C_8; 5 µm, 3.9 mm x 150 mm; Mobile phase: Acetonitrile/Water (60/40 v/v) to ACN/Water (90/10 v/v) in 25 min. Flow Rate: 1.0 mL/min; Column Temperature: 22 ˚C; Nebulizer heating rate: 60%; Drift Tube temperature: 40 ˚C; Gas (N_2) Pressure: 45 psi.

Alkyl ammonium bromide (cationic surfactant)

Three alkyl quaternary ammonium salts were separated under reverse-phase HPLC conditions as shown in Figure 4. These samples are separated based on their alkyl chain length. The longer the alkyl chain length, the longer the elution time (peak identifications are shown in Figure 4).

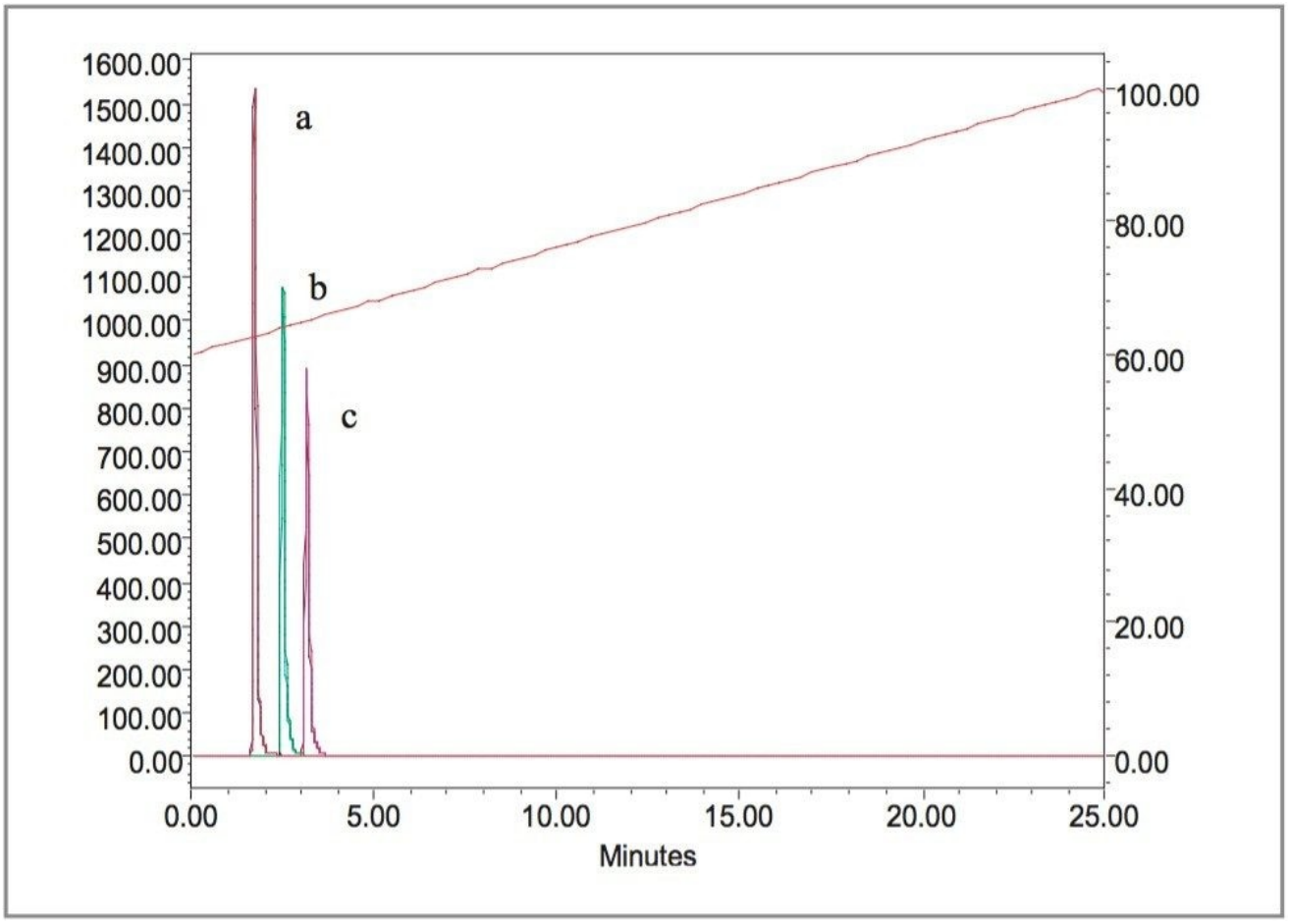

Figure 4. Chromatograms of Alkyl ammonium bromide from 2420 ELSD under reverse-phase HPLC conditions. (Overlay of two injections for each sample) Samples: a. Dodecyltrimethyl ammonium bromide, b. Cetyltrimethyl ammonium bromide, c. Octadecyl trimethyl ammonium bromide. (4.4-4.9 mg/mL). Column: Waters Symmetry C_8; 5 µm, 3.9 mm x 150 mm; Mobile phase: Acetonitrile/Water (60/40 v/v) to ACN/ Water (100/0 v/v) in 25 min. Flow Rate: 1.0 mL/min. Column Temperature: 45 ˚C. ELSD conditions: Nebulizer heating rate: 60%, Drift Tube temperature: 40 ˚C, Gas (N_2) Pressure: 45 psi.

Comparison of ELSD with UV detections

All the samples measured in this application note do not have UV absorption in the suitable light wavelength range. A typical comparison between UV and ELS detection is shown in Figure 5, which is obtained from reverse-phase separation of anionic surfactant (Octadecyl sulfate sodium) and nonionic surfactants (Tergitol 15-S-5). In ELSD chromatogram, there is one well distinct peak, while from UV detection at 230 nm and 190 nm, the

chromatogram barely shows a peak at corresponding elution times. Also, at the scaling level in the UV chromatogram, the baseline drifting caused by the change in the composition in mobile phase is obvious.

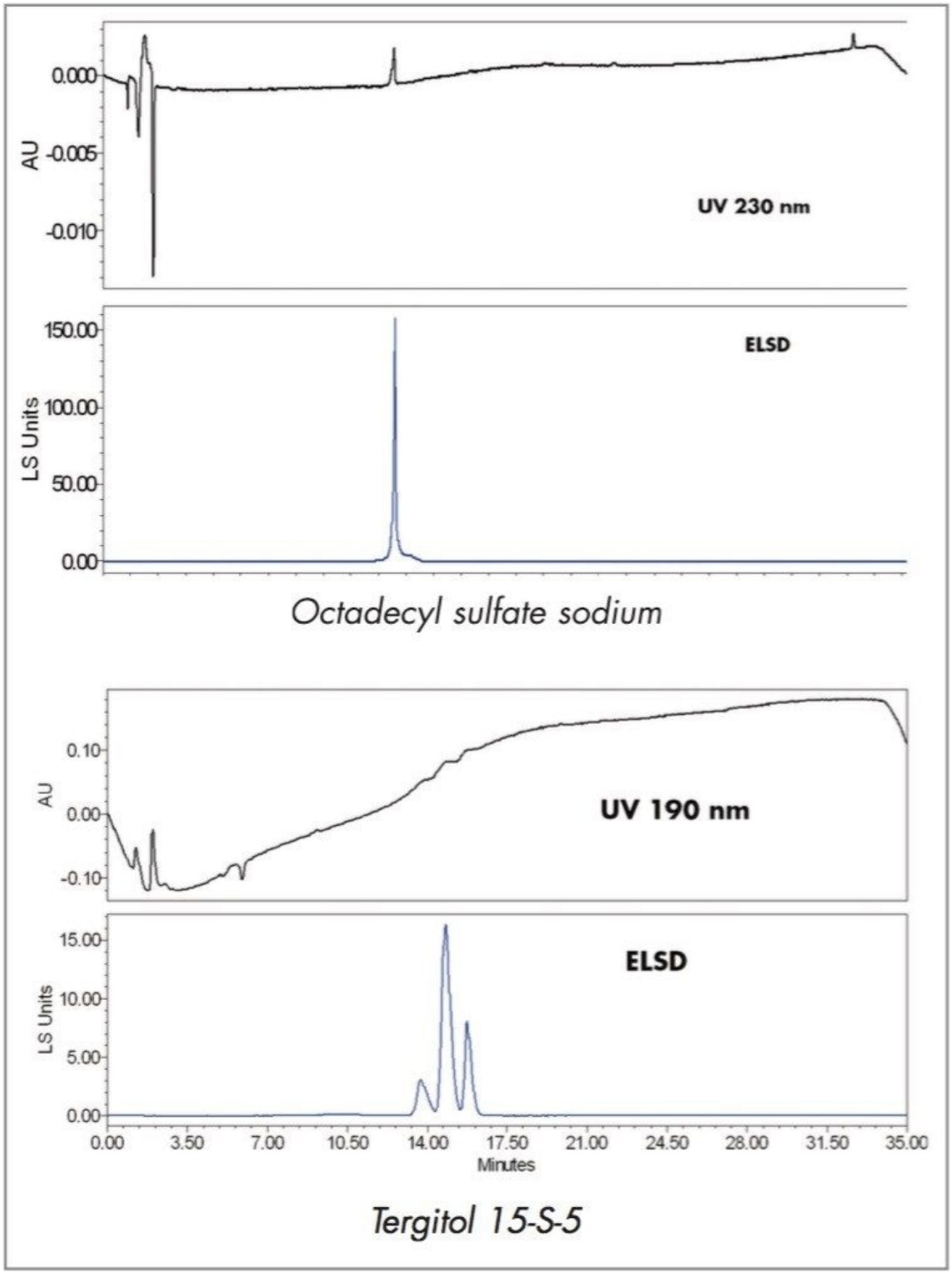

Figure 5. Comparison of chromatograms obtained from Photodiode Array Detector (UV 230 nm) and 2420 ELSD

for sample Octadecyl sulfate sodium and Tergitol 15-S-5 from the same measurement.

Conclusion

A series of surfactants (fatty acids, alkyl sulfate salts, alcohol ethoxylates, and alkyl quaternary ammonium bromides) are separated by reverse-phase HPLC and detected by ELSD. ELSD is a suitable method to detect these surfactants at gradient elution condition.

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