

Quantitation of Surfactants in Samples by High Performance Liquid Chromatography and Corona Charged Aerosol Detection

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Overview

Purpose: To develop HPLC methods for the quantitation of surfactants in a variety of products and matrices.

Methods: Methods using reversed phase and the specialty Thermo Scientific™ Acclaim™ Surfactant Plus HPLC column, along with the Thermo Scientific™ Dionex™ Corona™ ultra RS™ charged aerosol detector and UltiMate™ 3000 LC systems are outlined.

Results: Surfactants in machine oils were determined qualitatively, while poloxamers in consumer products were determined quantitatively. Other consumer products were analyzed to show method specificity.

Introduction

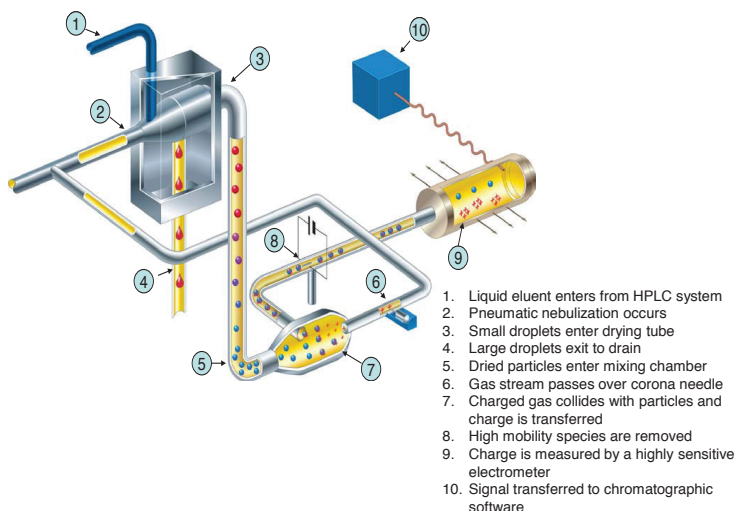
High performance liquid chromatography (HPLC) is the ideal tool for the analysis of surfactants in samples. However, since surfactants do not typically possess a chromophore, sensitive detection by ultraviolet or fluorescence is difficult. Universal detectors, such as refractive index (RI) and evaporative light scattering (ELS) exist, but each has significant limitations with sensitivity and capability. Mass spectrometry (MS) is a useful tool for these analytes but is more expensive to own and operate in a quality control environment than a simpler detector such as the Corona charged aerosol detector.

Sample preparation is simple and does not require derivatization since the detector responds to all non-volatile analytes. Samples can simply be diluted and analyzed. Different methods are presented that allow either characterization or quantification of surfactants. Examples include both aqueous and mineral oil-based matrices.

The charged aerosol detector is a sensitive, mass-based detector, especially well-suited for the determination of any nonvolatile and most semi-volatile analytes. The charged aerosol detector uses nebulization to create aerosol droplets (Figure 1). The mobile phase evaporates in the drying tube, leaving analyte particles, which become charged in the mixing chamber. The charge is then measured by a highly sensitive electrometer, providing reproducible, nanogram-level sensitivity. This technology has greater sensitivity and precision than ELSD and RI, is gradient compatible and is simpler to operate than a mass spectrometer. Compounds do not have to possess a chromophore (unlike UV detection) or be ionized (as with MS).

Analyte response for the charged aerosol detectors is largely independent of chemical structure). With little chemical dependence, clear relationships among different analytes in a sample can be inferred. These attributes when combined with the specificity of the new Acclaim Surfactant Plus column for reversed phase analysis, provide a unique analytical solution for sensitive, reproducible, and routine analysis of surfactant-containing samples.

FIGURE 1. Schematic and functioning of charged aerosol detection



Methods

Sample Preparations

Samples and standards were dissolved in methanol/tetrahydrofuran (1:1), isopropyl alcohol/water (1:1), or water. Centrifugation (10,000 g for 3 min) was used if insoluble materials were present.

Liquid Chromatography – Metal Working Oils

HPLC System: Thermo Scientific™ Dionex™ UltiMate™ 3000 LPG-3400SD pump (normal phase), WPS-3000RS autosampler, and TCC-3000RS column oven
 HPLC Column: Thermo Scientific™ Acclaim™ C8, 4.6 × 150 mm, 5 μm
 Column Temperature: 40 °C
 Mobile Phase A: 50 mM ammonium acetate, pH 5
 Mobile Phase B: 500 mM ammonium acetate, pH 5/methanol (100:900)
 Mobile Phase C: tetrahydrofuran (unstabilized)
 Injection Volume: 10–50 μL
 Sample: Mineral oils in methanol/tetrahydrofuran (1:1)
 Detector: Corona ultra RS
 Nebulizer Temperature: 15°C
 Filter: 5
 Data rate: 10 Hz
 PowerFunction: 1.00
 Flow Gradient:

Time (min)	Flow Rate (mL/min)	%A	%B	%C
0	0.5	67	33	0
3	0.5	67	33	0
10	0.9	0	96	2
12	0.9	0	96	2
15	0.9	0	15	85
20	0.9	0	10	90
20	0.9	67	33	0
25	0.5	67	33	0

Liquid Chromatography – Poloxamer Quantitation, Surfactants in Products

HPLC System: Thermo Scientific™ Dionex™ UltiMate™ 3000 DGP-3600RS pump, WPS-3000RS autosampler, and TCC-3000RS column oven
 HPLC Columns: Acclaim Surfactant Plus, 3 μm, 3.0 × 150 mm and Acclaim Phenyl-1, 3 μm, 2.1 × 150 mm (2nd column for poloxamer in product)
 Column Temperature: 50 °C
 Mobile Phase A1: 100 mM ammonium formate, pH 4
 Mobile Phase A2: 50 mM ammonium acetate, pH 5 in acetonitrile/water (1:1)
 Mobile Phase B1: n-propanol/acetone (1:1)
 Mobile Phase B2: 50 mM ammonium acetate, pH 5 in acetonitrile/methanol/water (5:4:1)
 Flow Rate: 0.4 mL/min (poloxamer), 0.6 mL/min (surfactants)
 Injection Volume: 20 μL (poloxamer), 5 μL (surfactant products)
 Samples: Fluoride mouth wash, containing Polaxamer 407, undiluted
 Other surfactant products were made into solutions of 50 μL or 50 mg in 1 mL of isopropyl alcohol/water (1:1)
 Detector: Corona ultra RS
 Nebulizer Temperature: ambient
 Filter: 5
 Data Rate: 10 Hz
 PowerFunction: 1.75 (Poloxamer), 1.00 (Surfactants)
 Flow Gradient: Poloxamers

Time (min)	%A1	%B1	Curve
-5	95	5	5
0	95	5	5
1	95	5	5
7	50	50	2
10	10	90	5
10	10	90	5
19	10	90	5
19	95	5	5

Surfactants		
Time (min)	%A2	%B2
-5	95	5
0	95	5
1	95	5
7	50	50
10	10	90
10	10	90
14	10	90

Data Analysis

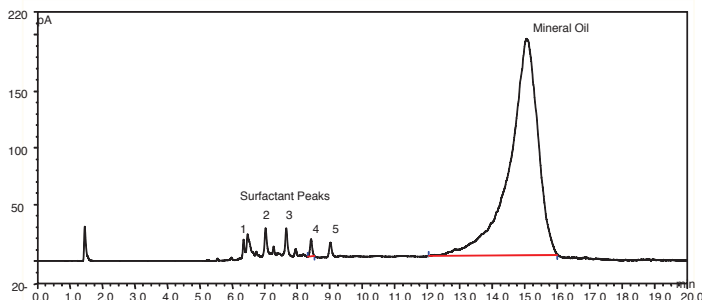
All HPLC chromatograms were obtained and compiled using Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data Station, 7.1 SR 1 software.

Results

Analysis of Machine Oils

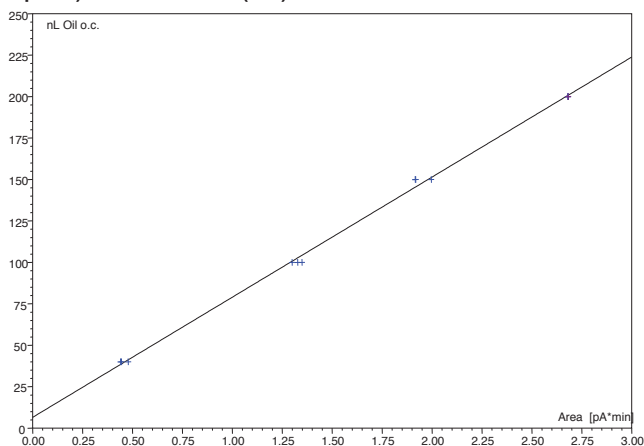
No standards were available for these surfactants, so calibration curves were generated based on varying injection volumes. This provided a means of determining calibration fit, accuracy, and precision, with each injection volume analyzed in triplicate. A chromatogram of a metal working oil generated on a C8 column is shown in Figure 2, as well as a peak for unretained ions, the surfactants, and the mineral oil.

FIGURE 2. HPLC-Corona detector chromatogram of a mineral oil (200 nL oil o.c.) containing surfactants



A calibration curve, using analyte peak area (surfactant peak #4 vs. volume of mineral oil injected, as nanoliters of oil per injection) was generated with good precision results, and this fit is shown in Figure 3. The correlation coefficient, r^2 , of a second-order polynomial fit on inverted axes was 0.998, and the replicate injections has peak area percent residual standard deviations (%RSD) of 0.2 to 5% over the range of 40 to 200 nL of oil (as prepared). The method was specific, with a number of oils exhibiting different peaks in the surfactant region of the chromatogram.

FIGURE 3. Calibration curve of peak 4 (in Figure 2) in mineral oil from 50 to 200 nL (as prepared) of oil on column (n=3)



Based on the calibration results above and with the appropriate standard references, the method can be used for the determination of surfactant materials in oil-based products.

Analysis of Poloxamers in an over-the-counter product

Poloxamers are a special class of non-ionic surfactants, consisting of a triblock copolymer of one polypropylene oxide connected to two polyethylene blocks. They are used in many detergents, consumer, and pharmaceutical products. They typically lack a chromophore so cannot be measured using ultraviolet absorption detectors. Furthermore, their polymeric nature often produces broad peaks which make the use of evaporative light scattering detectors challenging (poor sensitivity and reproducibility). However, such issues are not problematic for the Corona ultra RS detector when used with the specificity of the Acclaim Surfactant Plus column. Other matrix components can contribute to interference problems, as was encountered with a fluoride mouth rinse containing the Poloxamer 407 surfactant.

A small shoulder was found on the front of the Poloxamer 407 peak in a chromatogram using the Acclaim Surfactant Plus column, and mobile phase changes were not sufficient to resolve the two analytes. The use of a second HPLC column was required to separate the Poloxamer 407 (Pluronic® 407) surfactant from the matrix peak. Based upon the high number of double bonds in the poloxamer compounds, an Acclaim Phenyl-1 column was chosen and placed after the Acclaim Surfactant Plus column. Consequently, the poloxamer moved from the central peak to the last peak in the chromatogram. A linear calibration curve was then fit to data generated from triplicate injections from 156 to 20,000 ng o.c. The fit exhibited high correlation ($r^2 = 0.9993$) and precision (calibration %RSD= 2.30). Replicate precision of peak area varied from 0.28 to 2.09 % RSD, and the limit of quantitation was determined at 156 ng o.c., based on a signal-to-noise ratio of 10.0.

A fluoride mouth rinse was then analyzed without dilution. Three samples were prepared for spike recovery determinations: a sample comprised of 980 μL of fluoride mouth wash with 20 μL each of water, a 1 mg/mL solution (+200 ng o.c., 10 ppm) of Pluronic F127, and a 0.5 mg/mL (+400 ng o.c., 20 ppm) solution of Pluronic F127. The overlaid chromatograms are shown in Figure 4.

The results of the analysis of the fluoride mouth wash are presented in Table 1. Spike recovery values were calculated by dividing the found-spiked amount by the theoretical-spiked amount, and these values were within 15% of theoretical values. This demonstrates good sensitivity and accuracy, considering that the spike levels were less than 7% of the product's poloxamer concentration.

FIGURE 4. HPLC chromatogram overlay of over-the-counter fluoride mouth rinse product, spiked and unspiked, and the Poloxamer 407 standard at 10,000 ng o.c.

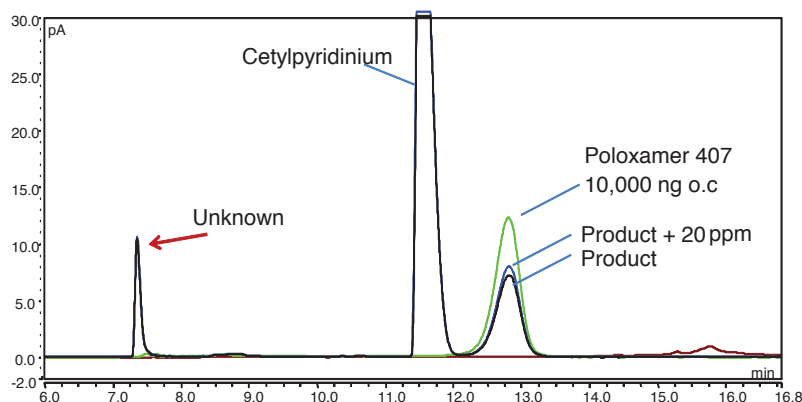


TABLE 1. Spike recovery results for Poloxamer 407 in fluoride mouth rinse at two spike values.

Sample	Theoretical Amount (ng o.c., ppm)	Experimental Amount Found (ng o.c., ppm)	Spike Recovery (%)
Fluoride mouth rinse product	--	5894, 294.7	--
Spiked + 10 ppm	6094, 304.7	6123, 306.2	114.5
Spiked + 20 ppm	6294, 314.7	6342, 317.1	112.0

Other examples of surfactants in consumer products

Additional examples of consumer products that contain a variety of surfactants were prepared and analyzed using the single column Acclaim Surfactant Plus method. Samples were dissolved in either water or a sample solvent that was compatible with reversed phase mobile phases. Concentrations of 50 mg/mL or 50 $\mu\text{L}/\text{mL}$ were prepared and centrifuged.

Figure 5 shows an HPLC chromatogram of a hair conditioning product containing five surfactants. Good resolution was achieved and the five surfactants were well resolved. Figure 6 shows the separation of two types of surfactants (alcohol ethoxylates and alkylsulfonates) in a sample of a laundry detergent. As can be seen, this approach clearly separates the different classes of surfactants as well as the different surfactants within each surfactant class and congeners.

FIGURE 5. HPLC chromatogram of a hair conditioner containing five different surfactants. 50 mg/mL in tetrahydrofuran/methanol/water/chloroform (12:40:5:40)

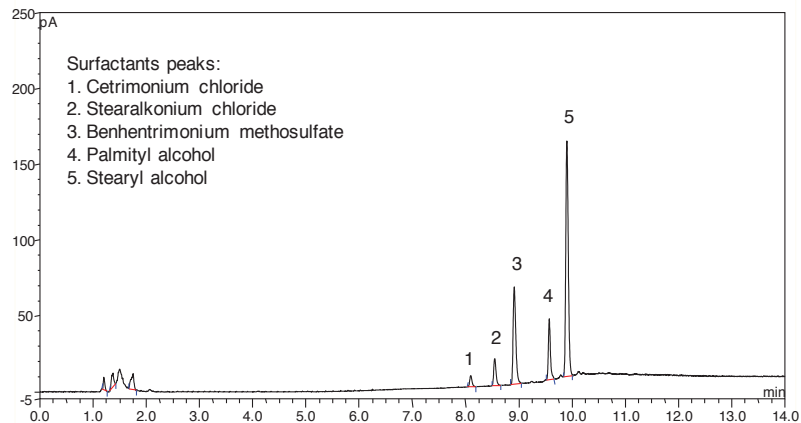
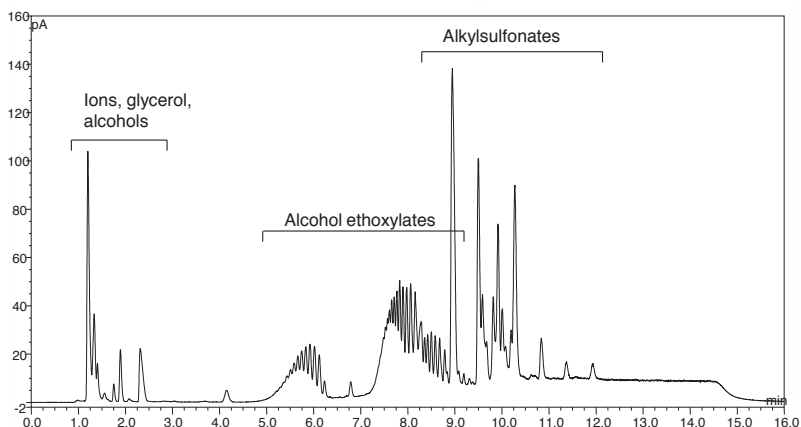


FIGURE 6. HPLC chromatogram of sustainable laundry detergent containing two different classes of surfactants. Sample is 50 mg/mL in water.



Conclusions

- Three different methods were used to characterize surfactants in a wide variety of different products.
- Analytes were detected using a charged aerosol detector which offers the best sensitivity and the most homogenous response factors of universal HPLC detectors.
- Surfactants in machine oil were separated on a C8 column and surfactants in a hair conditioner and a laundry detergent were resolved using the Acclaim Surfactant Plus column.
- A quantitative analysis was performed on a poloxomer contained in an over-the-counter fluoride mouth wash product: spiked recovery values were 112.0–114.5 % at two levels.
- Methods using the Acclaim Surfactant Plus column require use of a buffered mobile phase and a volatile, reversed-phase organic eluent. The design of the solid phase enables high specificity for the different surfactant classes, with high resolution between all analytes.

Acknowledgement

We thank BASF Corporation for the gift of the Pluronic polymers used in this evaluation.

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