

Characterization of Dispersants by Reversed-Phase High-Pressure Liquid Chromatography and Charged Aerosol Detection



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ABSTRACT

An HPLC method for quantification of dispersants used to treat oil in the recent Gulf of Mexico drilling incident is an analytical challenge. These dispersants lack a chromophore, which limits the sensitivity of ultraviolet detection for these analytes. They are also nonvolatile, limiting the use of highly sensitive gas chromatography (GC) analysis.

A reversed-phase HPLC/charged aerosol detection method is presented that can be used to characterize nine different dispersants: Aerosol® OT*, Span® 20, Span 60*, Span 80*, Span 83, Span 85, Tween® 80*, and Tween 85* (*used in COREXIT® 9500).

INTRODUCTION

Surfactants are a crucially important class of compounds found in products that are used every day, including cleaning agents, personal care products, cosmetics, foods, paints, and pharmaceuticals. The purpose of these compounds is to maintain a homogenous mixture of materials that normally do not mix, like oils and water. To function, these molecules are amphipathic and contain two different ends, one that is hydrophilic/polar and the other that is hydrophobic/nonpolar. This structure allows the surfactant to interact with the immiscible/nonsoluble material while maintaining interaction with the bulk solvent. This is normally achieved through micelle formation, shown in Figure 1. The hydrophobic terminal surrounds a droplet of oil, and the hydrophilic terminal interacts with the aqueous, bulk solvent forming a stable emulsion.

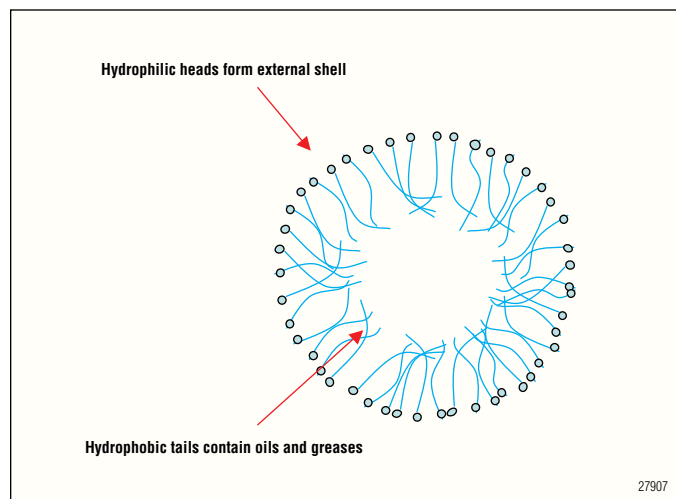


Figure 1. Structure of a micelle in aqueous solvent.

Recently, a large quantity of surfactants was used to treat the oil released into the Gulf of Mexico in an attempt to disperse the bulk oil into smaller droplets, facilitate biological decomposition, and minimize the amount of oil that would contaminate the ecologically sensitive marshlands of the Gulf Coast region.

Surfactants have a variety of forms: nonionic, cationic, anionic, organic, and inorganic. Two commercial products were used to treat the oil in the Gulf of Mexico, Nalco's Corexit EC9500A and EC9575A, both of which contain organic, nonionic, and anionic surfactants. A concern about the effects of these surfactants in the ecosystem has arisen because these products may enter the food chain thereby contaminating larger organisms. To trace where these compounds migrate, analytical methods are necessary to help characterize and quantify these dispersants.

Surfactants pose several analytical challenges: they are nonvolatile, eliminating the use of highly sensitive gas chromatography. They lack a good chromophore for fluorescence or ultraviolet detection by HPLC. Other possible HPLC detectors include mass spectrometry (MS), evaporative light scattering (ELS), refractive index (RI), suppressed conductivity (SC), and charged aerosol detection (CAD). ELS lacks sensitivity and reproducibility. RI cannot be used with gradient chromatography, which is required with these complex analytes. SC is limited only to ionic surfactants. LC-MS is suitable for trace analysis and when identification is necessary, but it is an expensive approach and can be technically challenging. CAD overcomes many of these limitations. It offers a sensitive means of mass-based detection with high reproducibility and response independent of chemical structure.

Two separate, reversed-phase HPLC methods using the Corona® *ultra*™ Charged Aerosol Detector (CAD®) were developed to either characterize the components in a surfactant or determine total concentration.

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EXPERIMENTAL—CHARACTERIZATION

Corona *ultra* Parameters

Gas: 35 psi by nitrogen generator
Filter: High
Nebulizer Heater: 25 °C

HPLC Parameters

HPLC System: Dionex UltiMate® 3000 RSLC
HPLC Column: Dionex RSLC C8, 100 × 2.1 mm, 2.2 μm
Mobile Phase A: DI water
Mobile Phase B: Acetone
Flow Rate: 0.6 mL/min
Injection Volume: 10 μL
Gradient: 25–100% B in 240 min, curve 3
Run Time: 240 min
Column Temp.: 45 °C
Sample Temp.: Ambient

Sample Preparation

Dissolve samples in isopropanol at a concentration of 20 mg/mL using either a vortex mixer or sonication, as needed.

RESULTS

Three different surfactants, Span 80 (Figure 2) and Tweens 80 and 85 (Figures 3 and 4), were analyzed with the method describe above. The chromatogram for Span 80 (Figure 2) illustrates more resolved species, compared to the chromatograms for Tween 80 (Figure 3) or Tween 85 (Figure 4).

This method can be used to provide qualitative characterization of the surfactants that may be present in a water sample, through identification of the unique peak profiles that are present in many of the different surfactants. A method for the quantitation of single surfactants is provided, using the conditions outlined below.

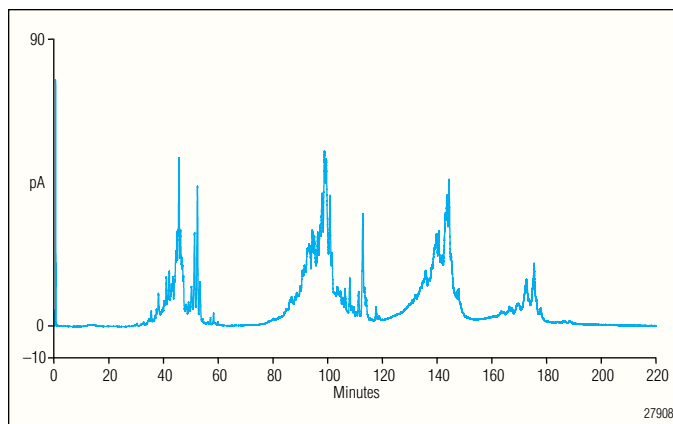


Figure 2. Characterization of Span 80, (20 mg/mL in isopropanol).

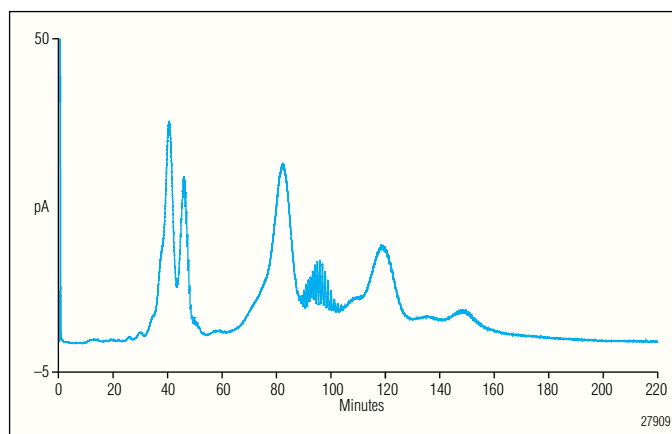


Figure 3. Characterization of Tween 80, (20 mg/mL in isopropanol).

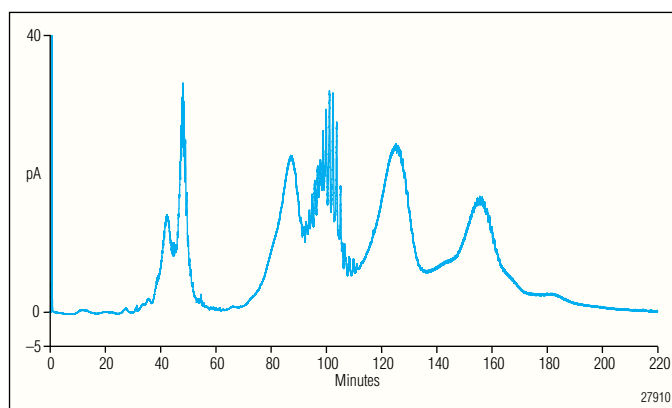


Figure 4. Characterization of Tween 85, (20 mg/mL in isopropanol).

EXPERIMENTAL—QUANTIFICATION

Corona *ultra* Parameters

Gas: 35 psi by nitrogen generator
Filter: High
Nebulizer Heater: 25 °C

HPLC Parameters

HPLC System: Dionex UltiMate 3000 RSLC
HPLC Column: Shiseido (#12207) C8 guard column,
4.6 × 10 mm, 5 μm
Column Temp.: Ambient
Mobile Phase A: DI water
Mobile Phase B: Acetone/n-propanol (1:1)
Flow Rate: 1.0 mL/min
Injection Volume: 5 μL
Sample Solvent : 4 mg/mL in ethanol
Gradient: 20% B from 0 to 2 min; 100% B from 2 to 5 min;
20% B from 5 to 7 min
Run Time: 7 min

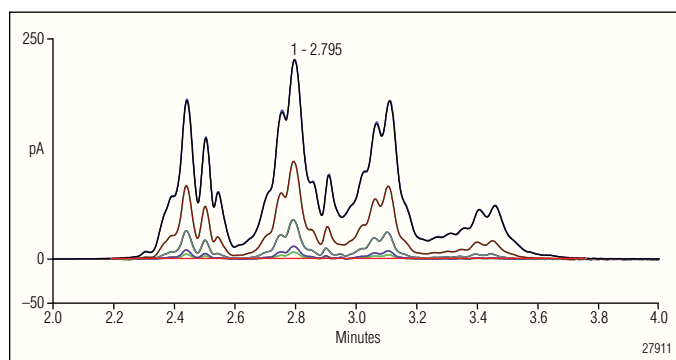


Figure 5. Analysis of Span 80, (156–20,000 ng o.c. in ethanol, in triplicate).

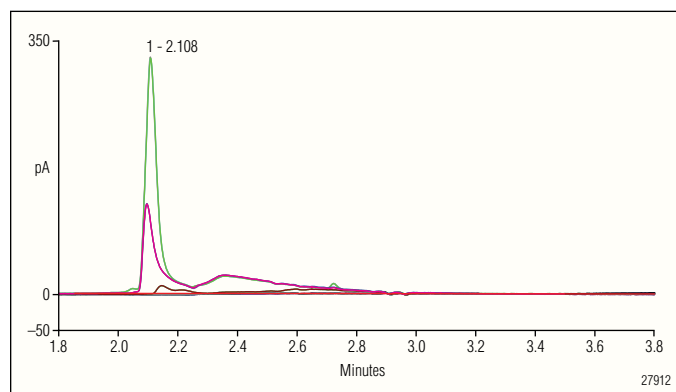


Figure 6. Analysis of Aerosol OT, (156–20,000 ng o.c. in ethanol, in triplicate).

CALIBRATION CURVES

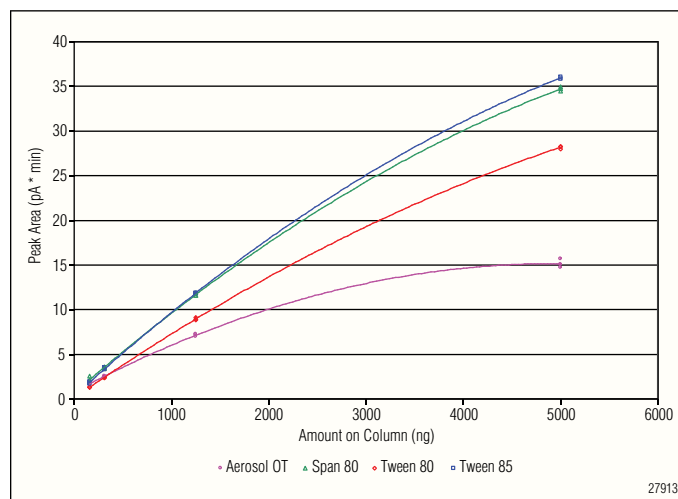


Figure 7. Calibration curves for Aerosol OT, Span 80, Tween 80, and Tween 85. (Samples were dissolved in ethanol, from 156–5000 ng o.c.).

DISCUSSION AND CONCLUSIONS

Two separate HPLC methods are presented. The first method uses a longer HPLC column to help characterize these compounds and provides a suitable technique to characterize many different surfactants. This method clearly illustrates sufficient resolution of these highly complex surfactant materials to help profile the type of surfactants used in a dispersant mixture.

The second, shorter method was used to quantify these surfactants. The HPLC–CAD chromatograms for Span 80 and Aerosol OT are shown in Figure 5 and Figure 6, respectively, using this method. High reproducibility was observed for Tween 80 and 85 (0.2–5% RSD) but a slightly lower reproducibility was seen for Span 80 (0.5–13% RSD). Calibration curves were highly correlated, with coefficients (R^2) > 0.999 for all four surfactants. All surfactants were fit to second-order polynomials, as shown in Figure 7.

The difference between the response curves of the Aerosol OT and the other three surfactants is attributed to the differences in chromatographic separation: the bulk of the Aerosol OT analyte lies in a high-response peak, which yields a relatively lower ratio of peak area to amount on column.

When using the second method, the response factors for the nonionic surfactants, Span 80 and Tween 80 and 85, were quite similar, varying between 75 and 93 pA*min, with an average of 84 ± 9 pA*min ($\pm 11\%$). Excellent sensitivity was found with LOD values of approximately 50 ng on column for these nonionic surfactants, based on a signal-to-noise ratio of 3. This LOD is sufficient for detection of surfactants using minimal sample preparation of water from the Mississippi River. It is currently reported that these waters contain dispersants at a level of 50 ppm.¹ Thus, the Corona *ultra* CAD has sufficient sensitivity to determine concentrations of surfactants in environmental water samples down to levels that currently exist in some U.S. waters. This method overcomes the limitation of other methods due to the sensitivity of the charged aerosol detector for compounds that do not contain a suitable chromophore.

Future studies will evaluate the use of columns with shorter alkyl chain lengths (C4 and C1) and solid-phase extraction techniques of samples to provide additional sensitivity improvements. Further efforts to enhance these analytical techniques so that they may be applied to the analysis of biological and environmental samples will be evaluated.

REFERENCES

1. http://www.nola.com/news/gulf-oil-spill/index.ssf/2010/08/mississippi_river_pours_as_muc.html, last accessed 13 Sep 2010.



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