

Application News

SSI-LCMS-006

Liquid Chromatography Mass Spectrometry

Oil Dispersants

Diocetylsulfosuccinate, 2-Butoxyethanol, and Dipropylene Glycol t-Butyl Ether



LCMS-8030



Summary

A rapid LC-MS-MS method for detection of oil dispersants in water was developed.

Background

Oil dispersants are used to reduce the impact of oil spills in an aquatic environment. Dispersants break up and promote natural breakdown of oil slicks from the ecosystem. Conflicting information regarding the safety of oil dispersants has been reported, but whatever their effect on the environment, rapid and sensitive methods for determination of the components are needed.

Method

The individual components in a common oil dispersant formulation were purchased from Sigma Aldrich (St. Louis, Mo.). The components were: Diocetylsulfosuccinate (DOSS), 2-Butoxyethanol (2-BE) and Dipropyleneglycol t-butyl ether (DPGBE), shown in **Figure 1**. Natural sea-

water purchased from a local aquarium supply store was used as a matrix.

Electrospray ionization with continuous polarity switching was used, and multiple MRM transitions for each compound were monitored. Optimized parameters are shown in **Table 2**. The observed protonated molecules, ammonium adducts, or deprotonated molecules were selected for each compound as appropriate.

The ionization parameters were: Spray voltage, 4.5 kV (pos) and -3.5 kV (neg); Nebulizing gas, 2 L/min; Drying gas, 15 L/min; DL temperature, 250 °C; and Heat Block temperature, 200 °C.

A Restek Pinnacle DB PFP Propyl UHPLC column (1.9 μm, 2.1 × 50 mm) was used at a flow rate of 0.5 mL/min and a column temperature of 30 °C. A binary gradient of 5 mM ammonium acetate

(Pump A) and acetonitrile containing 5 mM ammonium acetate (Pump B) was used. The gradient started at 5% B and increased to 90% B over 2.75 min, followed by an isocratic hold to 3.8 min, then returning to initial conditions for equilibration for the remainder of the 5 min run. Injection volumes were 10 μ L.

The standard needle wash program using methanol was used, as it was found sufficient to minimize carryover when using the Pinnacle DB PFP Propyl column. A divert valve switched salts to waste to avoid contaminating the ESI source

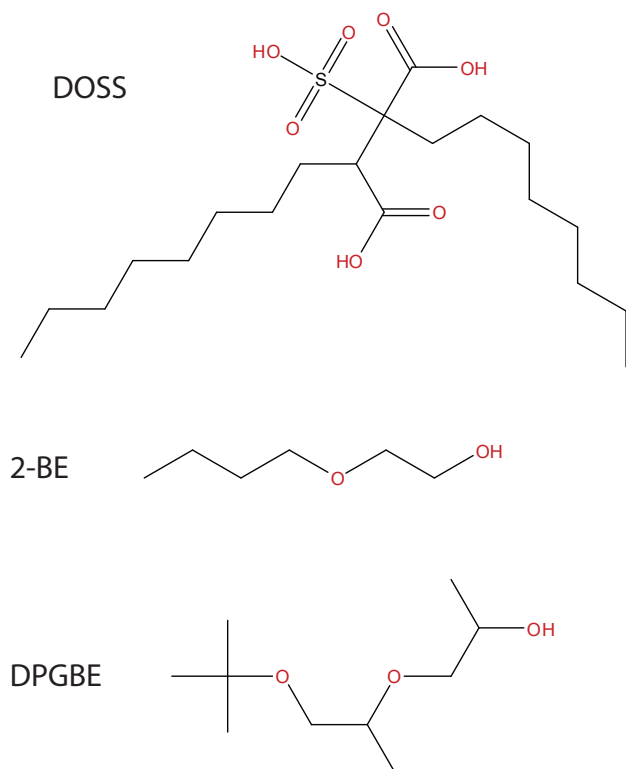
Results and Discussion

A rapid LC-MS-MS method for determination of oil dispersants was developed. Representative

mass chromatograms are shown in **Figures 2 and 3**.

Calibration curves were constructed over the range shown in **Table 1**. The curves for 2-BE and DPGBE were linear in the tested range and the curve for DOSS followed a quadratic response. This behavior for DOSS has been reported previously and may be due to the fact that, as concentrations increase, DOSS changes the physical or chemical properties of the charged ESI droplets.

The detection limit (LOD, signal-to-noise ratio of 3:1) for 2-BE was approximately 1 ppm and the limit of quantitation (LOQ, signal-to-noise ratio of 10:1) was approximately 3 ppm. For DOSS the



Level	DOSS (ppb)	2-BE (ppm)	DPGBE (ppb)
L1	5000	100	10000
L2	2500	50	5000
L3	1250	25	2500
L4	625	12.5	1250
L5	313	6.25	625
L6	156	3.13	313
L7	78		156
L8	39		78
L9	19.5		39
L10			19.5

Table 1: Calibration levels spiked into natural seawater matrix

Figure 1: Structures of oil dispersants

Type	Event#	+/-	Compound Name (m/z)	Dwell (msec)	Q1 Pre Bias(V)	CE	Q3 Pre Bias(V)	Measurement Time
MRM	1-1	+	2-BE+NH4 136.1>63.1	20	-26	-15	-27	0-5
MRM	1-2	+	2-BE+NH4 136.1>45.05	20	-26	-20	-23	0-5
MRM	2-1	+	DPGBE+H 191.1>59.1	20	-13	-15	-26	0-5
MRM	3-1	+	DPGBE+NH4 208.2>59.1	20	-25	-20	-23	0-5
MRM	3-2	+	DPGBE+NH4 208.2>135.0	20	-25	-10	-20	0-5
MRM	4-1	+	DOSS+NH4 440.25>113.1	20	-21	-15	-11	0-5
MRM	4-2	+	DOSS+NH4 440.25>199.1	20	-21	-15	-21	0-5
MRM	5-1	-	DOSS-H 421.2>80.9	20	21	25	18	0-5

Table 2: Optimized MRM Parameters

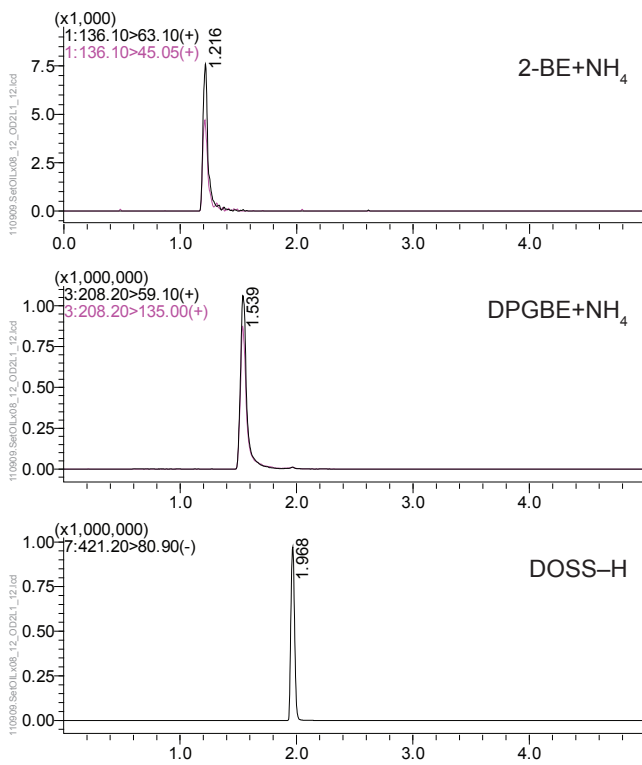


Figure 2: Mass Chromatograms of Std Level 1 in seawater matrix

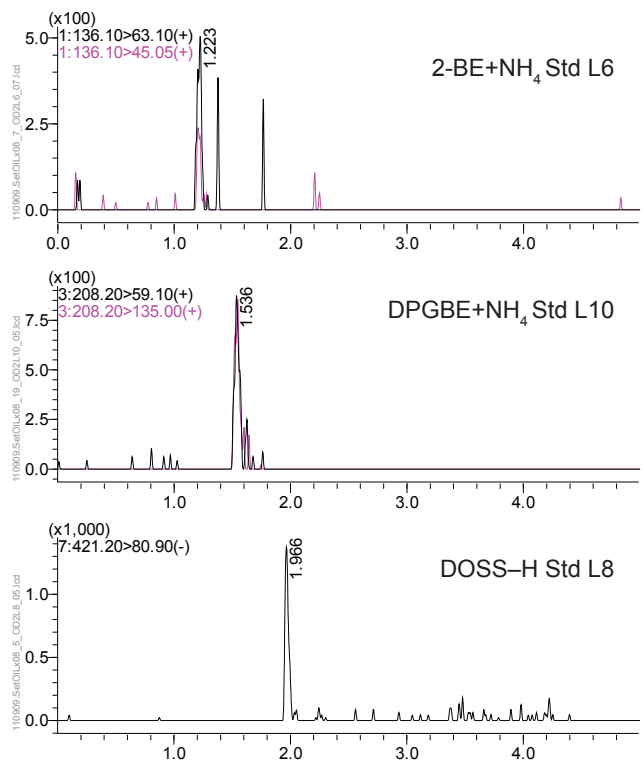


Figure 3: Mass Chromatograms of LOQ Samples in seawater matrix

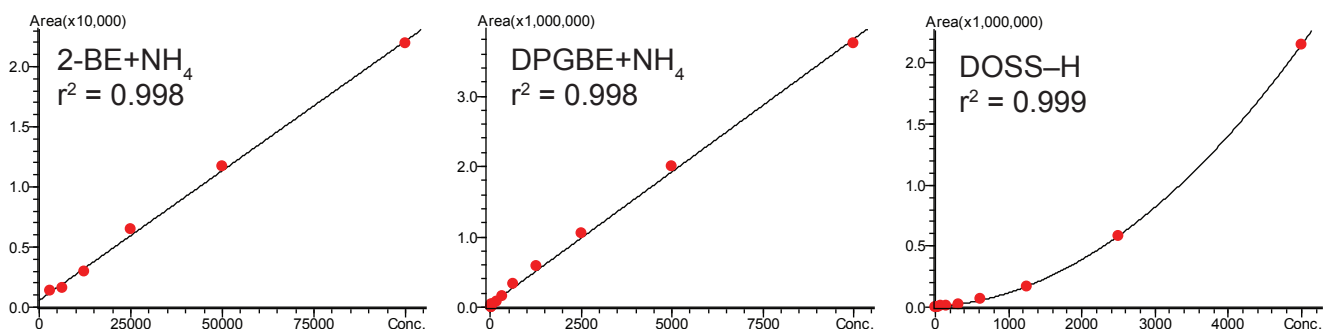


Figure 4: Calibration curves for the oil dispersants in seawater matrix

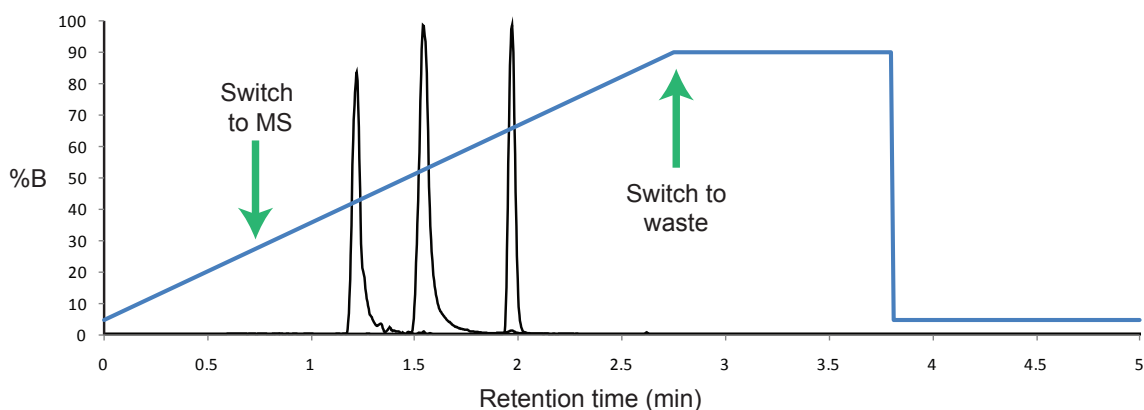


Figure 5: Gradient time program and divert valve sequence

LOD was below 10 ppb and the LOQ was about 20 ppb. The LOD for DPGBE was about 5 ppb and the LOQ was slightly below 20 ppb. Reproducibility was below 20% RSD at the LOQ and less than 5% RSD at the highest concentration.

Oil dispersants have both hydrophobic and hydrophilic properties and therefore may pose unpredictable challenges in LC-MS analysis. In particular, the compounds may adsorb onto LC columns or other surfaces in the sample flow-path. Various LC columns and needle washing parameters were evaluated, and the final choice of mobile phase, LC column, and standard needle

wash with methanol was found sufficient to minimize carryover.

Some slight carryover of DOSS was observed in some blank samples after the highest concentration standards were injected (**Figure 6**). This carryover was determined to be from the LC column as carryover was still observed when no needle injection was made but not during flow injection analysis. It should be noted that other LC columns were found to have higher carryover despite more aggressive needle rinsing conditions.

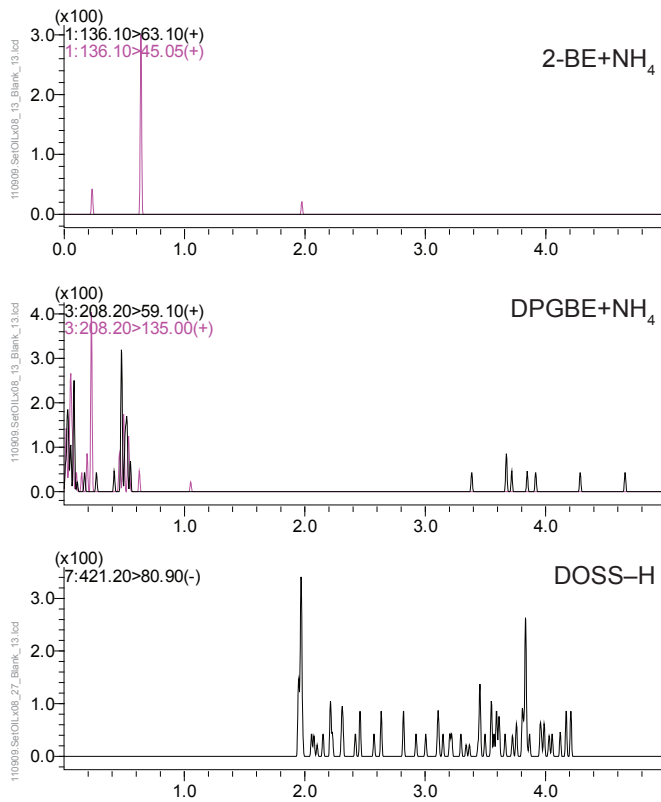


Figure 6: Mass Chromatograms of Blank run after highest concentration standard

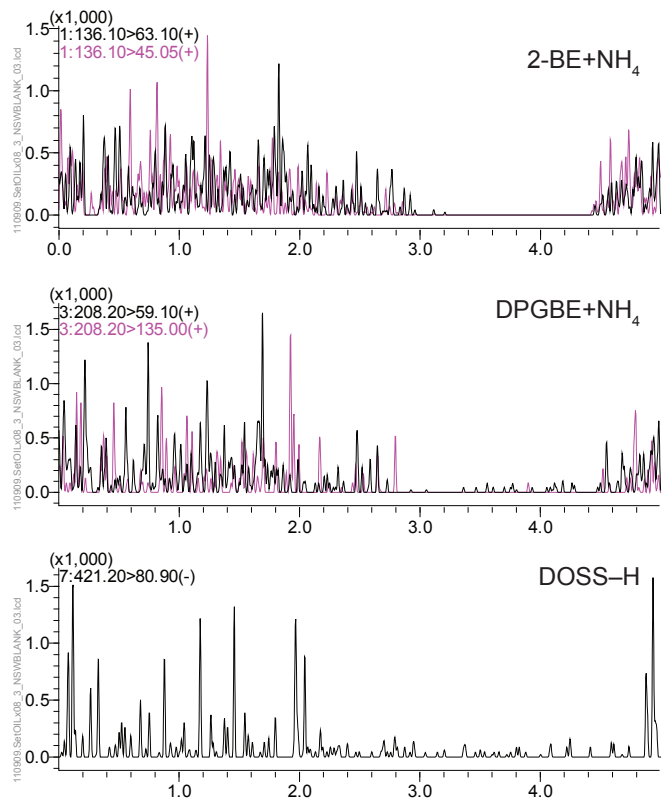


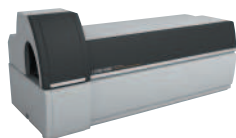
Figure 7: Mass Chromatograms of unspiked natural seawater blank

Conclusion

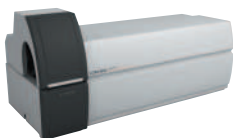
A rapid LC-MS-MS method for the determination of three common oil dispersants in seawater was developed. The fast polarity switch time, data acquisition rate, and UHPLC column and conditions allowed very fast run times while maintaining sensitivity and reproducibility.

UFMS

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First Edition: October, 2012