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Dioctyl sulfosuccinate analysis in near-shore Gulf of Mexico water by direct-injection liquid chromatography–tandem mass spectrometry

Johnson Mathew[a], David L. Schroeder[b,*], Lawrence B. Zintek[b], Caitlin R. Schupp[b], Michael G. Kosempa[b], Adam M. Zachary[b], George C. Schupp[b], Dennis J. Wesolowski[b]

[a] United States Environmental Protection Agency, Houston Regional Laboratory, 10625 Fallstone Road, 6MD, Houston, TX 77099, USA
[b] United States Environmental Protection Agency, Chicago Regional Laboratory, 536 S Clark, ML-10C, Chicago, IL 60605, USA

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ABSTRACT

Dioctyl sulfosuccinate (DOSS) was a major component of the dispersants most used in the 2010 *Deepwater Horizon* Oil Spill incident response. This analytical method quantifies salt water DOSS concentrations to a reporting limit of 20 μg/L, which was below the United States Environmental Protection Agency's (U.S. EPA) 40 μg/L DOSS Aquatic Life Benchmark. DOSS in Gulf of Mexico water samples were analyzed by direct-injection reversed-phase liquid chromatography–tandem mass spectrometry (LC–MS/MS). Sample preparation with 50% acetonitrile (ACN) enabled quantitative transfer of DOSS and increased DOSS response 20-fold by reducing aggregation. This increased sensitivity enabled the detection of a confirmatory transition over the calibration range of 10–200 μg/L. U.S. EPA Region 5 and Region 6 laboratories analyzed hundreds of near-shore surface Gulf of Mexico water samples, none contained more than the 20 ppb reporting limit. The matrix spike DOSS/deuterated surrogate (DOSS-D34) correlation of determination varied with mobile phase modifier (ammonium formate $R^2 = 0.95$ and formic acid $R^2 = 0.27$). Using ammonium formate, DOSS-D34 accurately measured DOSS matrix effect. The near-shore sodium concentrations varied more than 10,000-fold, but were not strongly correlated with DOSS recovery. DOSS detection by LC–MS/MS enabled rapid analysis which was valuable in guiding incident response.

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1. Introduction

A deluge of Louisiana Sweet Crude (LSC) was released from the MC 252 Macondo well into the Gulf of Mexico as a result of the April 20, 2010 *Deepwater Horizon* explosion. The resulting oil spill was named "the greatest environmental disaster of its kind in our history" [1]. Dispersants listed on the United States Environmental Protection Agency (U.S. EPA) National Contingency Plan Product Schedule were used to mitigate the impact of floating oil on sensitive shoreline habitats [2]. Smaller volumes of dispersant were used in the past to emulsify spilled oil. In response to the *Deepwater Horizon* incident, 6.977 million liters of dispersant were applied to the sea surface and subsurface near the wellhead [3]. Although COREXIT® EC9527A was used, the majority of the dispersant applied was COREXIT® EC9500A (NALCO, Naperville, IL).

Dioctyl sulfosuccinate (DOSS, Fig. SD1) was a major component of COREXIT® EC9500A and EC9527A. The DOSS median lethal concentration (LC_{50}) for gulf coast mysid shrimp, *Americamysis bahia*, was lower than the LC_{50} for COREXIT® EC9500A formulation [4–6]. In the absence of any other available criterion the U.S. EPA's 40 μg/L DOSS Aquatic Life Benchmark was established [7].

DOSS was selected for rapid method development due to the low benchmark criteria and its high concentration in the dispersants. A rapid analytical method would enable results to be reported in a timely manner which could be used to direct incident response. Rapid seawater DOSS analysis methods were not available at the time of the *Deepwater Horizon* incident.

The hydrophobic region of the DOSS molecule allowed separation from aqueous samples by reversed phase liquid chromatography (LC). The negatively charged sulfonate moiety, which imparts DOSS emulsification functionality, enabled sensitive detection by electrospray ionization (ESI) mass spectrometry (MS). The amphiphile forms direct and reverse aggregates dependent on numerous factors including concentration, nonpolar solvent, and counterions [8,9] which complicate analysis. This article details DOSS sample collection, preparation, and analysis by direct-injection reversed-phase liquid chromatography–tandem mass spectrometry (LC–MS/MS).

2. Materials and methods

Note: DOSS is surface active and binds to both glass and plastic. Solutions of 50% acetonitrile (ACN) were found to increase DOSS

* Corresponding author. Tel.: +1 312 353 3100; fax: +1 312 697 2663.
E-mail addresses: Schroeder.David@epa.gov, davidschroeder@gmail.com (D.L. Schroeder).

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recovery and sensitivity. Samples and standards were prepared with 50% ACN to reduce bias induced by DOSS surface binding.

2.1. Reagents and supplies

Aqueous solutions were prepared using ASTM Type 1 water (reagent water). Millex 33 mm 0.22 μm polyvinylidene fluoride (PVDF, SLGV033NS) and 0.20 μm polytetrafluoroethylene (PTFE, SLLGC25NS) filters were purchased from Millipore Corp. (Billerica, MA). Optima Grade ACN was purchased from Fisher Scientific (Pittsburgh, PA). HPLC grade methanol was purchased from Burdick & Jackson (Morristown, NJ). Ninety-eight percent pure DOSS (CAS #577-11-7) sodium salt, sodium chloride, and ammonium formate (NH_4CO_2H) were purchased from Sigma–Aldrich (St. Louis, MO). Bis(2-ethylhexyl-D17)sulfosuccinate (DOSS-D34) sodium salt was purchased from Isotec, Inc. (Miamisburg, OH). New pre-cleaned glass collection vials (20 mL and 40 mL) were used for sample collection and preparation. Glassware was cleaned with detergent that did not contain DOSS such as Alconox (Alconox, White Plains, NY). Clean glassware was rinsed with reagent water followed by methanol.

2.2. Method development

Initial findings indicated DOSS bound to many surfaces. Multiple stationary phases (C18, C8, hydrophilic interaction liquid chromatography, pentafluorphenyl, and mixed modes) were tested. Additionally, LC gradients were compared with various wash solvents to maximize sensitivity and reduce DOSS carryover. ACN was evaluated for sample and standard preparation. Solutions with 0, 5, 10, 15, 20, 25 and 50% ACN were prepared with 10 and 200 μg/L DOSS and analyzed with the LC–MS/MS conditions described below. Since seawater samples with addition of greater than 50% ACN resulted in biphasic solutions, ACN addition was limited to 50%.

Field samples commonly contain particulates and organisms that negatively impact LC–MS/MS system performance and operation. Samples are commonly filtered prior to LC to prevent blockages that increase system backpressure. DOSS recovery was evaluated by filtering seawater spiked to contain 100 μg/L DOSS using 0.22 μm PVDF and 0.20 μm PTFE filters with and without ACN addition. Samples were prepared to contain 50% ACN.

2.3. Sodium chloride addition

Triplicate 500 μL 0, 1, 2, 3, and 4% sodium chloride reagent water solutions were prepared and combined with 500 μL 200 μg/L DOSS in ACN. Solutions were thoroughly mixed prior to analysis. Neither NH_4CO_2H nor formic acid were added to the sodium chloride samples.

2.4. Storage

Gulf of Mexico surface water was spiked to contain 100 μg/L DOSS and stored up to 2 weeks. The samples were prepared in triplicate using separate 20 mL glass collection vials for each storage time and temperature. The samples were stored at 4 °C or 21 °C for 0, 2, 4, 7 and 14 days. Samples were analyzed following the laboratory sample preparation LC–MS/MS procedure (Section 2.7) for each storage time.

2.5. Partitioning

Crude oil recovered 22–23 May 2010, by the *Enterprise* from the MC 252 Macondo Well was used to test DOSS partitioning. Duplicate samples were prepared with 0.4 mL oil and 3.6 mL Gulf of Mexico water and were spiked to contain 20 μg/L DOSS-D34. They were mixed and allowed to settle 16 h. Whole oil/water samples and water subsamples were analyzed by the Laboratory Sample Preparation LC–MS/MS procedure.

2.6. Subsurface sample collection

Polypropylene tubing was used for subsurface water sample collection. In order to determine DOSS binding to polypropylene tubing, a 2.2-m polypropylene tube used to collect a sample (3.2 mm inner diameter, 6.4 mm outer diameter) was rinsed with 50% ACN/50% water. The rinsate was analyzed. Tubing was dried with compressed air. In order to examine DOSS association with sample tubing, 100 mL of Gulf of Mexico water was spiked to contain 100 μg/L DOSS. Twenty mL of the solution was decanted into a 20 mL glass collection vial and was analyzed. The remaining solution was siphoned through the tubing. Three 20 mL samples of the siphoned Gulf of Mexico water were collected consecutively from the tubing in 20 mL glass collection vials. The three siphoned samples were analyzed.

2.7. Sampling and laboratory sample preparation

Gulf of Mexico surface water samples were collected in precleaned 20 mL glass vials with Teflon-lined septa caps. The samples were shipped on ice and received at or below 6 °C. Separate co-located samples were sent directly to Accutest Laboratory (Houston, TX) for metals quantification by EPA method SW846 6010B [10].

All samples were spiked with 200 μL of 20 mg/L DOSS-D34 50% ACN/50% water solution in the 20 mL sample. The total sample was then transferred to a graduated cylinder, and the initial volume recorded. One molar NH_4CO_2H was added to each sample to make 5 mM NH_4CO_2H solutions. The sample was quantitatively transferred by rinsing the sample container with 3 aliquots of ACN. Sufficient ACN was added to the sample to prepare a 50% ACN solution. After mixing each sample, the final volume was recorded. Then each sample was filtered through a new 0.22 μm PVDF filter.

2.8. Quality control

Method blank, laboratory control spike and laboratory control spike duplicates were prepared with reagent water for every sampling date. For each sample collection day and field location a set of co-located samples were analyzed as duplicate, matrix spike and matrix spike duplicate. USEPA Chicago Regional Laboratory (CRL) matrix spike, matrix spike duplicate, laboratory control spike and laboratory control spike duplicate samples were spiked in the original container with 200 μL of 20 mg/L DOSS and DOSS-D34. Houston Regional Laboratory (HRL) varied the surrogate (20 and 80 mg/L) and DOSS (10 mg/L) spike concentrations between batches.

2.9. Instrumental analysis and quantification

2.9.1. Calibration

DOSS and DOSS-D34 are hygroscopic; neat compounds were sealed and stored in a desiccator. The DOSS concentrations were calculated to account for purity and cation mass. Stock standards were prepared in 50% ACN/50% water from neat DOSS and DOSS-D34. Intermediate 20 mg/L DOSS and DOSS-D34 stocks were made weekly. The calibration standard contained 200 μg/L DOSS and DOSS-D34 made from intermediate stocks. The 200 μg/L calibration standard was used to prepare calibration concentrations of 3 (detection verification), 10 (reporting limit), 20, 40, 60, 100, 150 and 200 μg/L DOSS and DOSS-D34. Calibration standards were prepared within 24 h of analysis. Samples were all analyzed within 24 h

Table 1
United States Environmental Protection Agency Chicago Regional Laboratory dioctyl sulfosuccinate liquid chromatography gradient conditions.

Time (min)	Flow (mL/min)	Percent 95% water/5% CH_3CN, 5 mM NH_4CO_2H	Percent 95% CH_3CN/5% water, 5 mM NH_4CO_2H
0.0	0.3	100	0
2.0	0.3	100	0
5.0	0.3	0	100
8.0	0.3	0	100
8.3	0.3	100	0
10.0	0.3	100	0

CH_3CN: acetonitrile; NH_4CO_2H: ammonium formate.

of calibration. Calibration checks of 100 μg/L were analyzed after every 20 samples or less and at the end of each sample set. All calibration standards contained 50% ACN and 5 mM NH_4CO_2H.

2.9.2. LC–MS/MS

CRL prepared samples were analyzed using a Waters ACQUITY UPLC® and Quattro Premier™ XE tandem quadrupole mass spectrometer (MS/MS). Fifty μL injections were loaded onto a Waters Atlantis® dC18 analytical column (2.1 mm × 150 mm, 3 μm particle size, 35 °C). The CRL LC gradient conditions are shown in Table 1. The column flow was diverted away from the ESI source for 5 min following injection. Following each injection, the needle was rinsed with 2.0 mL strong wash (60% ACN/40% 2-propanol) followed by 4.0 mL weak wash (50% ACN/50% water).

The negative ESI-MS conditions were optimized to maximize the DOSS quantitation transition (421 > 81, 24 eV), DOSS confirmation transition (421 > 183, 15 eV) and DOSS-D34 (455 > 81, 24 eV). The optimized conditions for the Quattro Premier™ XE included: capillary voltage 3.5 kV, cone voltage 36 V, source temperature 120 °C, desolvation temperature 350 °C, desolvation gas flow 800 L/h, and cone gas flow 25 L/h. HRL modified conditions are described in Section SD2. As DOSS was an approved food additive and laxative [11,12], transitions for glycol ethers in COREXIT® EC9500A (Section SD3) were also collected for qualitative analysis.

2.10. Statistical analysis

Analysis of variance (ANOVA) was done using the PROC GLM procedure of SAS 9.1.3 (SAS, Cary, NC) including Tukey–Kramer multiple means comparison and Anderson-Darling tests. When the treatment factor effect was significant, indicated by a significant *F*-test ($P \leq 0.05$), differences between the respective means were determined using the Tukey–Kramer multiple means comparison test. Normality of variance was tested using the Anderson-Darling test. DOSS-D34 and DOSS spike correlation were tested using the PROC REG procedure of SAS 9.1.3 (SAS, Cary, NC).

2.11. Safety considerations

Normal laboratory safety practices applied to this method. Analysts should wear safety glasses, gloves, and lab coats when working in the lab. Analysts should review the Material Safety Data Sheets (MSDS) for all reagents used in this method.

3. Results and discussion

3.1. Method development

Reversed-phase columns allowed DOSS to elute after the majority of the salts were diverted to waste. The Waters Atlantis® dC18 and Agilent ZORBAX Eclipse XDB-C18 resulted in narrow reproducible DOSS peaks (Fig. SD2). The column stationary phase

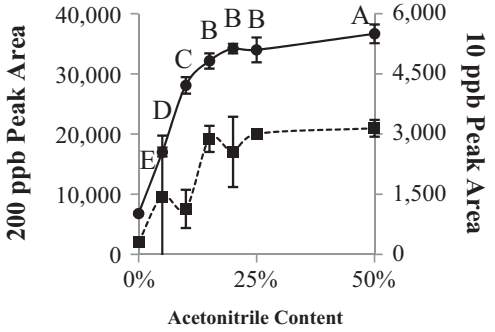

Fig. 1. Dioctyl sulfosuccinate (200 and 10 μg/L DOSS, 5 mM NH_4CO_2H) liquid chromatography–tandem mass spectrometry response in aqueous solution with 0, 5, 10, 15, 20, 25, and 50% acetonitrile: (●) 200 μg/L DOSS; (■) 10 μg/L DOSS. Mean value displayed for each treatment (triplicate) with standard deviations represented for each with vertical lines. Numberous treatment standard deviations were low, and the marker covers the standards deviation. Treatments with the same letter are not significantly different. Note 200 μg/L dioctyl sulfosuccinate peak area correspond to the left *y*-axis and 10 μg/L dioctyl sulfosuccinate correspond to the right horizontal axis.

appreciably affected the DOSS separation and quantification. Among the many columns tested, the Atlantis® and Eclipse columns enabled DOSS separation from the sample matrix with the best sensitivity.

A multiport switching valve was used to divert the flow from the mass spectrometer probe for 5 min after injection. Data collection began 5 min after injection. Solid phase extraction (SPE) was also evaluated as an alternative technique to reduce matrix interference. SPE effectively concentrated DOSS and removed sea salts, but was time intensive. The SPE sample preparation time would have delayed results needed for emergency response. The direct-injection technique using diversion allowed DOSS detection at the 40 μg/L Aquatic Life Benchmark with minimal sample preparation.

Reagent water, spiked to contain 50 μg/L DOSS, was analyzed without ACN addition and was biased 30% low. A series of water rinses collected the DOSS associated with the sample containers, but one rinse of 100% ACN extracted the surface associated DOSS completely. In an effort to recover DOSS in samples, ACN was added to samples to make 50% ACN solutions. DOSS spiked seawater with 50% ACN addition and PVDF filtration averaged 96% DOSS recovery. PTFE filtration resulted in 6% DOSS mean recovery. Addition of 50% ACN and PVDF filtration gave complete DOSS recovery from reagent water and seawater DOSS spiked samples. A polyethersulfone filter erroneously increased the 421 > 81 *m*/*z* response at the same retention time as DOSS. Polyethersulfone filters should be avoided in reagent and sample handling. Addition of 50% ACN followed by PVDF filtration resulted in accurate DOSS quantification by direct injection LC–MS/MS.

Acetonitrile addition to samples not only increased DOSS recovery, but increased the DOSS response. Ten and 200 μg/L DOSS standard responses increased as ACN content increased (Fig. 1). The average peak area of 200 μg/L DOSS standards increased more than 20-fold from 0 to 50% ACN. The mean response of 10 μg/L DOSS in 50% ACN was greater than the 0% ACN 200 μg/L DOSS response. The significant increase in response with ACN addition increased DOSS sensitivity despite dilution of samples. The significant increase in DOSS response with 50% ACN addition enabled detection of a confirmatory transition 421 < 183 over the calibration range (Figs. SD2, SD3, and Table SD1). The detection of the presumptive ethylhexyl partial succinate product increased confidence in DOSS identification. The confirmatory transition was not detected from DOSS-D34, DOSS-$^{13}C_4$ or polyetherssulfone.

CRL determined that ACN addition to water samples greatly reduced the aggregates detected at low DOSS concentrations. DOSS

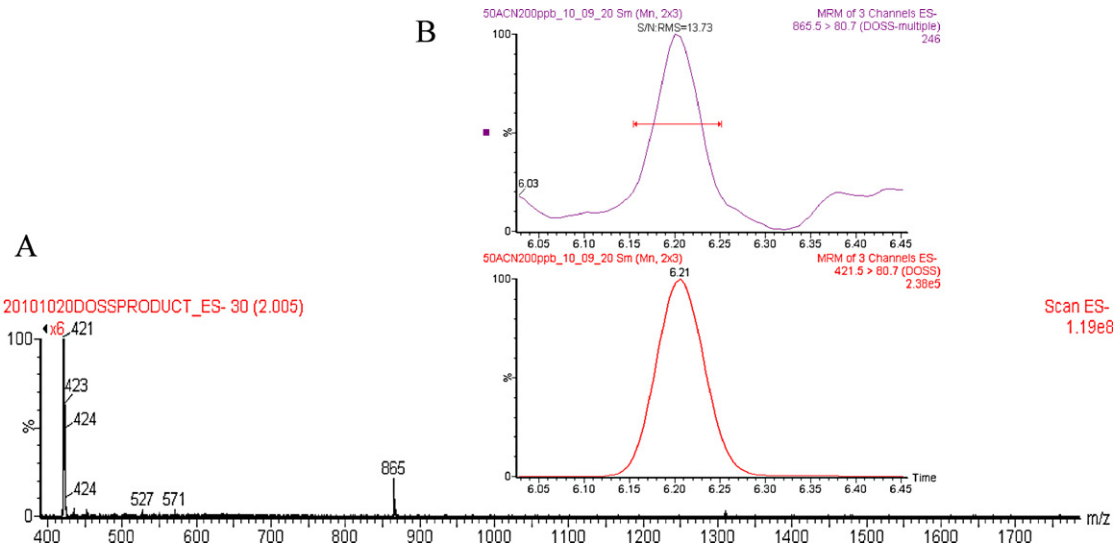

Fig. 2. Liquid chromatography–mass spectrometry (MS) of 200 μg/L dioctyl sulfosuccinate (DOSS) in 100% reagent water: (A) negative electrospray ionization scan, (B) selected reaction monitoring of DOSS anion (421 > 81) and singly charged sodium adduct $[DOSS_2 + Na_{(1)}]^-$ (865 > 81).

aggregates were not detected from injections of 50% ACN 200 μg/L DOSS samples, while aggregates were detected from 200 μg/L DOSS samples without ACN addition. DOSS aggregates $[DOSS_n + Na_{(n-1)}]^-$ with $2 \leq n \leq 4$ were observed (Fig. 2A), which was limited by the quadrupole range. Product scans of the 865 m/z precursor $[DOSS_2 + Na_{(1)}]^-$ confirmed the presence of DOSS (Fig. 2B). DOSS and aggregates eluted in the same solution which indicated that aggregates were collected from the samples without ACN addition, and eluted as aggregates. This observation confirms that these aggregates are stable through LC–MS/MS. Also, increased ACN in samples did not change the DOSS retention time.

Depending on the solution, either direct or reversed DOSS aggregates are energetically favorable [13]. The DOSS molecular structure does not change appreciably in polar or non-polar solvents [14]. Singly charged DOSS-sodium aggregates were identified in direct infusion of water as well as ACN. Aggregation of charged and neutral DOSS reduce the 421 > 81 m/z response. DOSS aggregates were not detected in 50% ACN over the calibration range of this method. Aggregates were detected at greater DOSS concentrations in 50% methanol solutions [13]. The linear nature of the calibration affirmed minimal aggregation over the calibration range. Higher DOSS concentrations that result in aggregation would result in quadratic curves. Addition of 50% ACN to samples increased sensitivity and reduced surface binding, therefore all standards and samples were prepared with 50% ACN.

In the absence of NH_4CO_2H in samples, increasing sodium chloride (NaCl) concentration in reagent water and 50% ACN decreased DOSS response significantly ($p < 0.001$, Fig. 3). DOSS responses decreased 22% by increasing NaCl from 0 to 1%. DOSS responses decreased 67% by increasing NaCl from 1 to 2%. Sodium addition to reagent water resulted in adduct and aggregate formation that decreased DOSS response [15]. Scans of reagent water with increased Na addition indicated both adducts and aggregates as well as neutral loss accounted for the decreased DOSS response. Presence of Na-DOSS adducts and aggregates indicate varied Na effects in ESI negative analysis. Analyzing transitions for all of the possible adducts and aggregates would decrease the number of scans over the quantification ion 421 > 81 m/z thus reducing sensitivity. Surrogates were used to account for these matrix effects.

The near-shore Gulf of Mexico samples varied greatly. The concentration of Na varied significantly with collection location and date ($p < 0.0001$). For instance, the average Na concentration of samples collected July 13, 2010, from three sample locations was 5500 ± 1800 mg/L. Samples were collected the following day, July 14, 2010, in three different locations. The average Na content of two locations (1500 ± 1000 and 1700 ± 3300 mg/L, respectively) were significantly lower than the third (5900 ± 600 mg/L). The matrix spike sample Na concentration ranged from 0.8 mg/L to 11,200 mg/L with an average of 3700 ± 2800 mg/L. Extreme variance of Na in the near-shore Gulf of Mexico samples, were likely the result of environmental conditions such as rain and river flow rates, and needed to be addressed to assure accurate DOSS quantification.

The effect of seawater Na variability on DOSS response was tested. Increased Na content in reagent water reduced DOSS signal, therefore it was hypothesized that increases in seawater Na concentration would reduce DOSS recovery. The null hypothesis was matrix spike Na concentrations do not change DOSS recovery. The alternative hypothesis was matrix spike samples with higher Na concentration result in lower DOSS recovery. The matrix spike results failed to reject the null hypothesis ($p = 0.87$). The correlation of determination (R^2) was 0.0003 for Na/DOSS, which indicated that Na concentrations were not indicative of DOSS recovery (Fig. 4). Furthermore, calcium and potassium concentrations were not strongly correlated with matrix spike DOSS recovery. NH_4CO_2H reduced DOSS response (Figs. 1 and 3), but negated the effect of sea salt variability on DOSS recovery.

Previously, DOSS was found to bind glycine [16]. Various organic compounds may have been in the seawater samples resulting in decreased DOSS response; therefore DOSS-D34 was used to

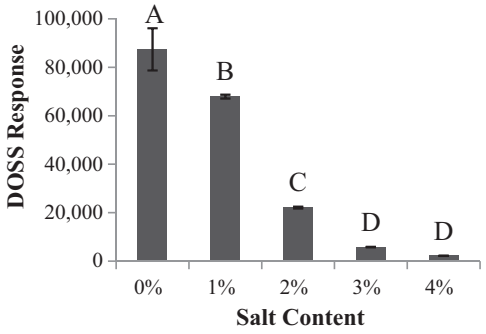

Fig. 3. Mean 100 μg/L dioctyl sulfosuccinate response with 0, 1, 2, 3, and 4% sodium chloride in reagent water with 50% acetonitrile. Treatments with the same letter are not significantly different.

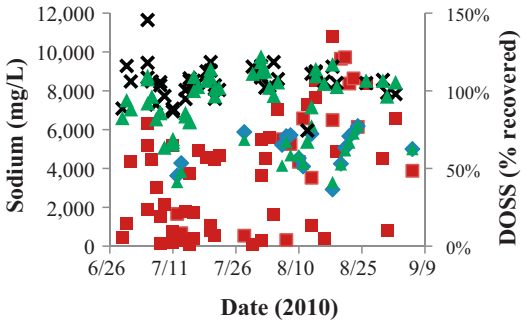

Fig. 4. Average matrix spike sodium concentration, dioctyl sulfosuccinate (100 μg/L, DOSS) and deuterated dioctyl sulfosuccinate surrogate (100 μg/L, DOSS-D34) recovery for selected collection dates: (■) sodium; (+) Chicago Regional Laboratory DOSS; (×) Houston Regional Laboratory DOSS; (▲) DOSS-D34. Note sodium concentration (mg/L) correspond to the left *y*-axis and DOSS and DOSS-D34 recoveries correspond to the right horizontal axis.

measure the matrix effect of each sample. DOSS-$^{13}C_4$ was not commercially released until the wellhead was capped.

Quality control results affirmed the robust nature of direct injection DOSS analysis. The CRL and HRL blank spike DOSS and DOSS-D34 recoveries were not significantly different. The quality control DOSS and surrogate mean recoveries were near 100% (Table 2). Although the CRL matrix spike recoveries were lower than laboratory control spike mean recoveries, the matrix spike DOSS/DOSS-D34 recoveries were strongly correlated, correlation of determination (R^2) 0.95. The strong correlation of CRL matrix spike results substantiated use of DOSS-D34 as an accurate measure of matrix effect. This was valuable as the near-shore sample variance was extreme (Fig. 4). The HRL R^2 was 0.34 for matrix spike samples and 0.27 for the laboratory control spike samples.

The notable differences in the CRL and the HRL analysis conditions were injection volume, analytical column and modifier. Substitution of 0.1% formic acid for NH_4CO_2H in mobile phase, using CRL conditions described in Section 2.9.2, increased both DOSS and DOSS-D34 response and retention time, but increased the DOSS/DOSS-D34 retention time difference 8-fold. NH_4-DOSS physical properties are measurably different than H-DOSS [8]. These differences explain increased retention time. Increased recovery using formic acid modifier was likely the result of sulfonate protonation, displacing response reducing cations. The low HRL DOSS/DOSS-D34 correlation in reagent and matrix spike at least partially a result of increased retention time difference. Sulfonate protonation likely magnified chemical and physical changes associated with deuteration. Although further investigation is needed to fully understand decreased DOSS/DOSS-D34 correlation, these findings are pertinent to maximize surrogate matrix effect measurement accuracy.

There was concern that the instrument sensitivity would decrease with numerous seawater analyses. However, calibration, matrix spike and laboratory control spike DOSS responses did not noticeably decrease during the 3 months of sample analysis. Additionally, no system deterioration was found during preventative maintenance after that period.

Table 2
United States Environmental Protection Agency Chicago and Houston Regional Laboratory control spike and matrix spike dioctyl sulfosuccinate and surrogate recovery.

	% Recovery DOSS	σ	% Recovery DOSS-D34	σ	n
Chicago Laboratory control spike	99%	11%	98%	13%	42
Chicago matrix spike	81%	14%	78%	15%	44
Houston Laboratory control spike	103%	9%	96%	11%	50
Houston matrix spike	105%	11%	97%	15%	49

Chicago = Chicago Regional Laboratory; Houston = Houston Regional Laboratory; DOSS = dioctyl sulfosuccinate; DOSS-D34 = deuterated dioctyl sulfosuccinate surrogate; σ = standard deviation; *n* = number of samples included in mean recovery.

3.2. Storage

Storage conditions were tested to determine if DOSS concentrations would decrease. Storage temperatures of 5 °C and 21 °C were evaluated. The mean DOSS recovery (100 μg/L spike) in seawater after 14 days of storage at 5 °C was 88%, while samples stored at 21 °C resulted in 70% mean DOSS recovery (Fig. SD4). A similar trend was observed when 200 μg/L DOSS in seawater was stored at 5 °C. After 14 days at 5 °C, 88% of the DOSS spike was recovered. DOSS stored at 21 °C resulted in lower recovery, after 3 weeks in seawater recoveries were as low as 60% (200 μg/L).

The storage study was performed before the DOSS-D34 surrogate was available. In order to assess DOSS extraction, DOSS-D34 was added after storage and analyzed. The mean surrogate recovery from samples stored 7 days was 100% and for samples stored 14 days recovery was 99%. DOSS surrogate recoveries indicated that DOSS was collected from the sample containers. Environmental DOSS abiotic and biodegradation have been reported [17]. Increased lipase activity indicated Gulf of Mexico surface microbial community had the ability to hydrolyze DOSS [18]. Reduced DOSS recovery with storage was likely the result of degradation. More than 90% of the DOSS was recovered from samples stored in 20 mL glass vials at 5 °C for 7 days, therefore samples were held at or below 5 °C and analyzed within a week of collection.

3.3. Subsurface sample collection

Sample collection greatly impacted quantitation of DOSS. Polypropylene tubing was used to collect subsurface water samples. Seventy-nine μg/L DOSS spiked seawater siphoned through 2.2 m polypropylene tube resulted in a loss of 26%. When the tube was rinsed with 50% ACN the DOSS spike remainder was recovered. Other factors including tubing materials, flow rate and sampling tools may affect DOSS losses due to sample collection. Sample contact with surfaces other than the sample container should be avoided to minimize low bias.

3.4. Partitioning

Since dispersant was applied near the wellhead, extractions were performed on crude oil to determine DOSS partitioning between oil and seawater. Oil from the wellhead exposed to the dispersant was used to prepare duplicate 10% oil/seawater mixtures. The seawater did not contain DOSS prior to oil exposure. DOSS was not detected in the subsample of the water below the oil. Extraction of the whole sample resulted in 2.3 ± 1.5 mg/L. Therefore the oil contained approximately 23 mg/L DOSS by calculation. The majority of DOSS in the crude oil did not transfer to the seawater.

The high affinity of DOSS for crude oil was also exhibited by DOSS-D34. DOSS-D34 was not detected in the water subsample, but 97% was recovered from 50% ACN extracts of the whole sample. The majority of DOSS-D34 added to seawater associated with oil despite high DOSS concentration in the oil. The high affinity of DOSS to oil may partially explain why no near-shore surface water samples were found to contain DOSS at or above 40 μg/L.

3.5. Gulf of Mexico sample results

More than 600 near-shore Gulf of Mexico samples were analyzed. None of the samples had DOSS concentrations more than the 20 ppb reporting limit[19]. Direct injection LC–MS/MS greatly reduced sample preparation time, increasing sample throughput, and allowed results to be reported within 24 h of sampling. No dipropyl glycol butyl ether or ethylene glycol monobutyl ether peaks were detected with a signal to noise ratio of 2 and peak area greater than 2. The near-shore results were comparable to the near-well sample results [20], but did not require model correction for DOSS lost in sample preparation.

4. Conclusions

The reported method is the first to identify the effect of DOSS aggregation on LC–MS/MS quantification. Sample preparation conditions for amphiphilic compounds, such as surfactants and phosphorylated biomolecules, should be optimized to minimize aggregation. Despite great sodium potassium variance in the seawater samples tested, NH_4CO_2H efficiently counteracted DOSS response suppression. Ammonium cation displacement allows direct injection LC–MS/MS sulfonate analysis in various complex samples. Isobaric interferents highlighted the value of confirmatory transitions to support DOSS identification.

Surrogates are used to evaluate data quality, and conditions must be selected to ensure surrogates strongly correlate with target analytes. NH_4CO_2H not only reduced sodium interference, but also buffered solutions enabling high DOSS/DOSS-D34 correlation. Ammonium formate should be used for DOSS analysis rather than formic acid to assess DOSS matrix effect by DOSS-D34.

Acknowledgements

The views expressed in this article are those of the authors and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2012.01.088.

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