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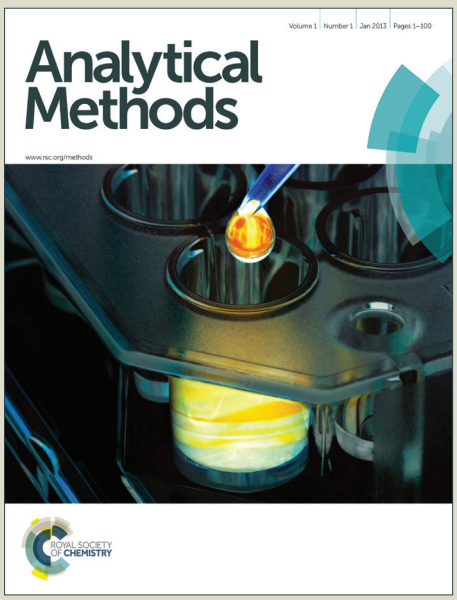

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Determination of COREXIT Components used in the Deepwater Horizon Cleanup by Liquid Chromatography-Ion Trap Mass Spectrometry

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Abstract

The oil spill dispersant, COREXIT 9500, used in the BP Deepwater Horizon oil spill, was analyzed by high-performance liquid chromatography-ion trap mass spectrometry with electrospray ionization. Two components present in the mixture, dioctyl sodium sulfonate (DOSS) and diproylene glycol butyl ether (DGBE), were recovered from spiked ocean water samples. Compounds were isolated from ocean water spiked with COREXIT 9500 by solid phase extraction using C_{18} cartridges prior to separation with high performance liquid chromatography-ion trap mass spectrometry using an acetonitrile and 0.1% formic acid gradient. Both compounds were identified using a simultaneous extraction procedure, as dioctyl sodium sulfonate is identified by negative electrospray-ion mode, and dipropylene glycol butyl ether by positive electrospray-ion mode. This method identifies trace levels of dispersants used in oil-spill cleanup efforts through the identification of two major components, which could provide validation for the correct identification of a dispersant mixture. This method was validated by recovering COREXIT components from spiked natural ocean water samples collected in the Gulf of Mexico. Oil-impacted ocean water samples were collected in Grand Isle, Louisiana at an oil-impacted beach, but no traces of COREXIT were identified.

Keywords: Environmental analysis; Surfactants; Oil-spill; Dioctyl sodium sulfonate; Dipropylene glycol butyl ether; LC/MS

1. Introduction

Following the explosion of the BP Deepwater Horizon Oil Rig in the Gulf of Mexico in April 2010, the company utilized the dispersants COREXIT 9500A and 9527A to separate the oil plume into smaller particles, thus assisting the clean-up and remediation. Approximately 2.1 million gallons of dispersant were applied to both the surface and the well head of the oil plume [1, 2]. Concern surrounding the toxicity of these dispersants has arisen because of their use in unprecedented quantities in the ocean environment, where natural degradation processes are not well understood [3, 4]. Due to the known environmental persistence of some surfactants that are present in the COREXIT mixture, it is important to be able to analytically detect these dispersants in ocean water matrices [5, 6].

Before the Environmental Protection Agency`s (EPA) release of information regarding the individual components that make up the dispersant mixture COREXIT 9500A and 9527A, analytical techniques could not be developed to analyze natural samples for known constituents [7]. Two of the major constituents found in both COREXIT 9500A and 9527A mixtures – the surfactants dioctyl sodium sulfonate (DOSS) and dipropylene glycol butyl ether (DGBE) (Figures 1-2 and 4, respectively) - are amenable to liquid chromatography-mass spectrometry (LC-MS) detection.

Analytical methods have been previously developed utilizing gas chromatography-mass spectrometry (GC-MS) [8] and LC-MS [2] for DOSS. DOSS is also known to be used in textile printing and dyeing processes because of its excellent wetting properties [9], as well as being found in many products requiring a surfactant. However, another compound that could be used as a challenge compound for the identification of COREXIT surfactant mixtures, DGBE, has no known LC-MS detection method and could also help identify COREXIT from other environmental sources.

In this paper analytical methods for the extraction and determination of two compounds in the COREXIT mixture by HPLC-MS are shown, and compared to known analytical standards. Known standards were spiked into natural ocean water samples, to test for percent recovery by the extraction method developed. Natural ocean water samples taken from the oil laden beach, on Grand Isle, Louisiana, in October 2010 were tested using newly developed extraction and HPLC-MS methods.

2. Experimental

2.1 Sample collection

Ocean water samples were collected from Grand Isle State Park in Louisiana on October 11, 2010 from both an oil-spill impacted and non-impacted control beach. Samples were collected into 1L amber bottles that were previously baked at 500°C for 3 hours, and rinsed 3 times with the sample prior to filling. The samples were stored on ice and shipped overnight to the University of Colorado, Boulder, CO, USA. Samples were then stored for up to 1 month at 4°C until extraction by solid-phase extraction (SPE) and analysis by HPLC-MS.

2.2 Chemicals and reagents

HPLC-grade acetonitrile, methanol, water, and reagent-grade acetic acid were obtained from Honeywell Burdick & Jackson (Morristown, NJ, USA). Analytical standards were ordered for dioctyl sulfosuccinatesodium salt (DOSS, Sigma Chemical Co., St. Louis, MN, USA) and dipropylene glycol butyl ether (DGBE, Aldrich Chemical Co., Milwaukee, WI, USA). The COREXIT 9500 mixture was obtained directly from the manufacturer (Nalco Inc., Sugarland TX, USA).

2.3 Sample extraction

The solid-phase extraction (SPE) procedure was performed using a manual extraction manifold with C_{18} cartridges (Agilent AccuBond II, Santa Clara, CA, USA). They contained 500 mg

of 40-µm C_{18} bonded silica. All C_{18} cartridges were prepared by rinsing 5-mL of methanol, followed by 5-mL of deionized water. A 100-mL sample was passed through the cartridge at a flow rate of 10 mL/min, and sent to waste. The cartridge was then washed with 3 mL of deionized water to remove salts, and the cartridge was purged with air to remove any excess water. The cartridge was eluted using 5-mL of methanol at a flow rate of 2 mL/min and the sample was collected. The eluate was evaporated to 500-µL using a high throughput evaporator (Zymark Turbovap LV ZW700, Hopkinton, MA). The sample was then filtered prior to HPLC analysis using a 0.2 µm nylon membrane filter (Pall Life Sciences, Ann Arbor, MI, USA). An aliquot of 20 uL was injected into the LC-MS system.

Sediment samples were also collected from the beaches at the same location as the water samples. These samples were then weighed into 100 g (wet weight) aliquots into amber glass bottles with 250 mL of laboratory grade water. The bottles were then rotated continuously for 7 days in order to allow any COREXIT components to leach from the sediment phase into the aqueous phase. The aqueous layer was then tested for COREXIT components using the developed analytical method.

2.4 LC-MS Analysis

Liquid chromatography-ion trap mass spectrometry, in both positive and negative ion mode of operation was used to separate and identify two components of the dispersant mixture COREXIT 9500. The analytes were separated using an HPLC series 1100 (Hewlett-Packard, Palo Alto, CA, USA) equipped with a reversed-phase C_8 analytical column (Eclipse XDB-C_8, Agilent Technologies, Wilmington, DE, USA) of 3.0 X 50 mm and 1.8-µm particle diameter. Column temperature was maintained at 25 °C. The mobile phase used for eluting the analytes from the HPLC column consisted of acetonitrile and 0.1% formic acid in laboratory grade water, at a flow-rate of 0.4 mL/min. A gradient elution was performed as follows: from 30% A (acetonitrile) and 70% B (1% formic acid in water) to 100% A in 12 minutes. This HPLC system was connected to an ion trap mass spectrometer,

an Agilent Technologies LC/MSD Trap XCT Plus (Agilent Technologies, Wilmington, DE, USA) system equipped with an electrospray ionization (ESI) probe operated in positive and negative ionization mode. Selected operating conditions of the MS system were optimized in full-scan mode (m/z scan range: 50-1000) by flow injection (400 µL/min) analysis of each selected compound at 25 µg/L concentrations. Final injection volume for each sample was 20 uL.

3. Results and discussion

3.1 DOSS MS Optimization

Figures 1a and b show the chromatographic results and mass spectrum obtained when analyzing COREXIT 9500 in negative ion mode. The mass identification of DOSS was achieved in the COREXIT 9500 mixture, at an ion peak of 421 m/z. The mass of the DOSS compound is 421 m/z, showing the lack of a proton from negative ionization mode. The DOSS eluted from the column at 8.2 minutes when in the COREXIT 9500 mixture, and at 8.2 minutes as a standard. In the COREXIT mixture, only one peak was observed in negative ion mode at the same retention time as the standard, 8.2 minutes. A sulfur isotope belonging to DOSS was observed at 423 m/z, at an intensity of 5% of the C_{12} isotope at 421 m/z (Figure 1).

Structural identification was performed by MS/MS experiments after the parent ion was isolated and fragmented for DOSS. The fragmentation of the 421 m/z ion, going to 81 m/z peak, as shown in Figure 2, belongs to the sulfonic acid group of DOSS. This MS/MS fragmentation was observed by Place et al. and confirmed in these MS/MS experiments [8]. The corresponding bond of fragmentation and products are structurally represented in Figure 2, with the mass ion of the sulfonate group being 81 m/z.

The limit of detection (LOD) for the DOSS analytical standard in laboratory grade water was 1002 ng/L without concentration by SPE. A calibration curve with concentrations ranging between 1002 ng/L to 400,000 ng/L was made using the manually-integrated area under the curve of the m/z signal. Figure 3 shows an n=10 point calibration curve of DOSS, with an R^2 value of 0.994, and linear regression fitted line (y = 149666*x + 616785).

3.2 DGBE MS Optimization

The expected molecular ion, 213 m/z was determined in positive-ion electrospray by observing a sodium adduct, which is attached to the molecule during analysis from the parent compound (190 m/z + 23 m/z = 213 m/z). A peak at 213 m/z is expected, as well as a smaller peak < 10% at 214 m/z to account for the ^{13}C isotopes. The DGBE peak in Figure 4a eluted at 3.2 minutes in the COREXIT mixture and as a pure standard. No proton adduct was found for this compound, only the sodium adduct was present. No MS/MS fragmentation was seen for the 213 m/z ion in positive ion mode.

The LOD for the DGBE analytical standard using LC-MS analysis was 9990 ng/L without concentration by SPE. A calibration curve with concentrations ranging between 9990 ng/L to 400,440 ng/L was made using the manually-integrated area under the curve of the m/z signal. Figure 5 shows an n=8 point calibration curve of DGBE, with an R^2 value of 0.9985, and linear regression fitted line (y = 20301*x + 248627).

3.3 Solid-phase extraction recovery

Solid-phase extraction (SPE) was performed first with DOSS and DGBE in laboratory grade water, for method development, followed by non-oil impacted natural ocean water samples collected in Grand Isle, Louisiana. DOSS and DBGE analytical standards were spiked into both laboratory and ocean water at concentrations at or greater than the limit of detection for analytical standards in laboratory grade water. Table 1 shows the percent recovery after SPE was performed. Percent

recovery was calculated by taking the known concentration spiked into the sample, and after evaporation of solvent, weighing the liquid left, approximately 500-µL, and correcting for density to determine the amount of concentrated compound. This sample was then analyzed with a known standard by HPLC, and the difference was the percent recovery of the compound. Percent recovery in laboratory grade water samples was higher than ocean water samples, possibly because the compounds could interact with unknown elements in the ocean water and not be removed during the methanol wash step. An alternate explanation for this lower recovery could be the result of analyte sorption to the column being disrupted by unknown elements in the ocean water. After concentration by SPE and evaporation, the method detection limits in ocean water for DOSS was 300 ng/L ± 10 ng/L and 2000 ng/L ± 30 ng/L for DGBE.

3.4 Natural sample determination

Sediment and water samples collected on an oil-impacted beach with visible oil slicks and tar balls in Grand Isle State Park in Grand Isle, LA were extracted and analyzed for both DOSS and DGBE using the methods developed. Figure 6 shows the sampling locations for both oil-impacted and non-impacted beach samples. Both sediment and water samples collected were not found to contain COREXIT components DOSS and DGBE despite visual oil contamination in collected samples. This could be the result of no occurrence of the chemical in the waters sampled, the compound being diluted out lower than the detection limit, or the compounds could have been degraded prior to reaching the sampling locations. Samples spiked with DOSS and DGBE analytical standards, in a concentration range of 30 ng/L to 100 ng/L showed good compound recovery, indicating that the method described herein for extraction and analysis of COREXIT in natural ocean water is robust for use in future studies where compounds are present at the limit of detection or greater. The method could be improved upon by ensuring the applicability with oil-impacted ocean

water samples, where this dispersant mixture is likely to be found. The method reported in this paper can be easily used to identify and quantify both dispersants in ocean waters and sediments at low concentration ranges. Furthermore, the relative concentration ratio obtained for both compounds could represent a positive identification of the commercial mixture (COREXIT) used in oil spill events if environmentally present.

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"Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation."

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Figure and Table Captions

Figure 1. (a) Extracted 421 m/z ion chromatogram in negative ion mode of COREXIT 9500 mixture (b) Extracted 421 m/z ion from COREXIT 9500 sample mixture.

Figure 2. Fragmentation of 421 m/z ion for accurate identification of DOSS sulfonic acid group in COREXIT 9500 mixture, observed as 81 m/z.

Figure 3. Ten-point calibration curve of DOSS, with varying concentrations (1.00 µg/L to 400.00 µg/L) and corresponding m/z areas of integration (R^2 = 0.9938; y = 149666*x + 616785).

Figure 4. (a) Extracted ion chromatogram in positive mode at 213 m/z from COREXIT 9500 mixture (b) extracted ion 213 m/z from COREXIT 9500 mixture.

Figure 5. Eight-point calibration curve of DGBE, with varying concentrations (9.99 µg/L to 399.6 µg/L) and corresponding m/z areas of integration (R^2 = 0.9985; y = 20301*x + 248627).

Figure 6. Location for both oil-impacted (red star) and non-impacted (green star) water and sediment samples collected on October 11, 2010 and used for LC-MS method development.

Table 1. Solid-phase extraction results of DOSS and DGBE in both laboratory and ocean water samples.

Figures and Tables

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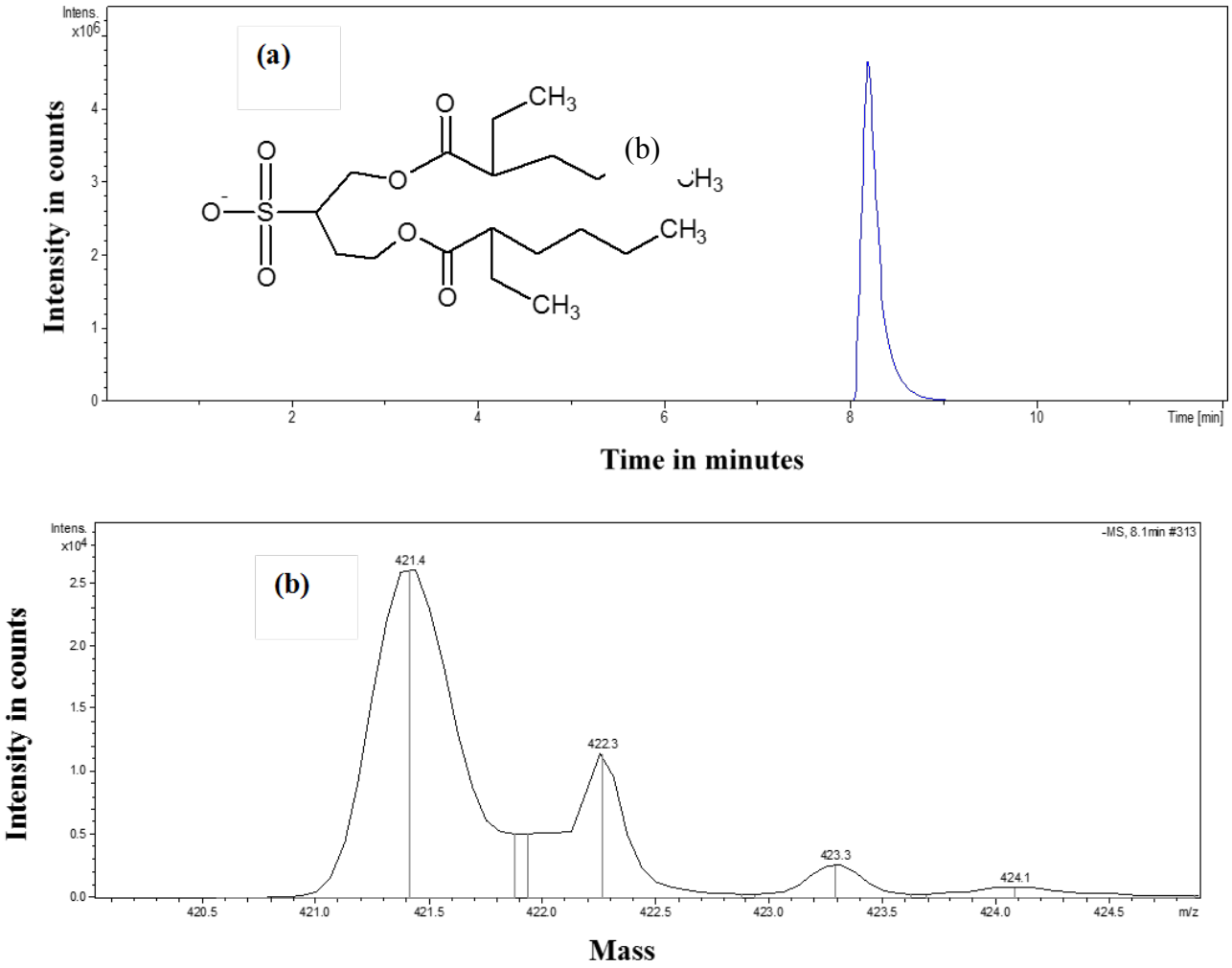

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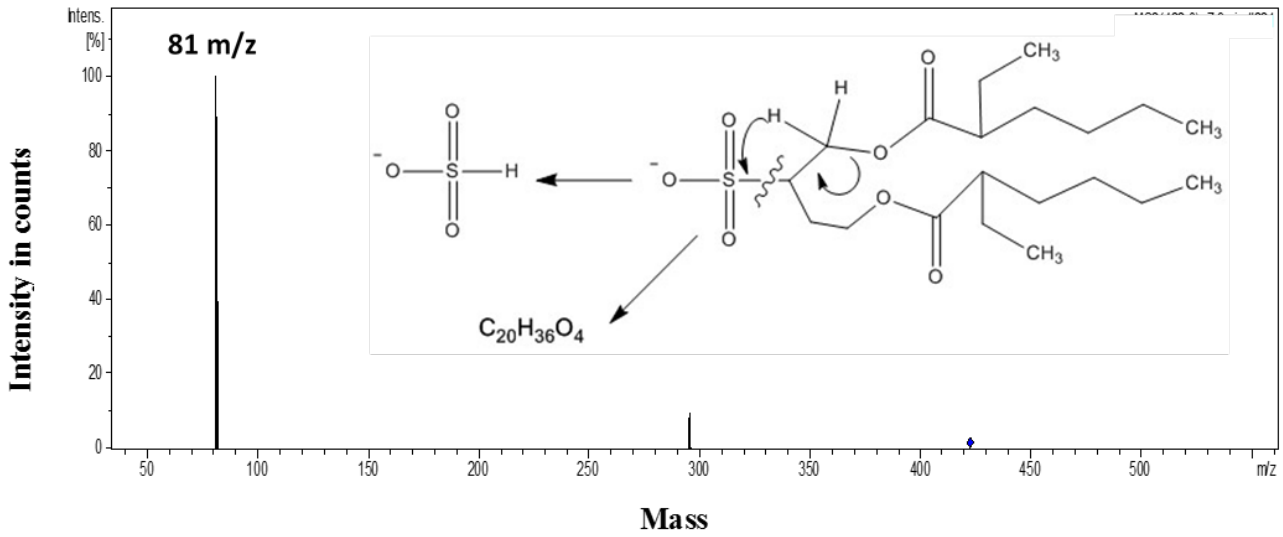

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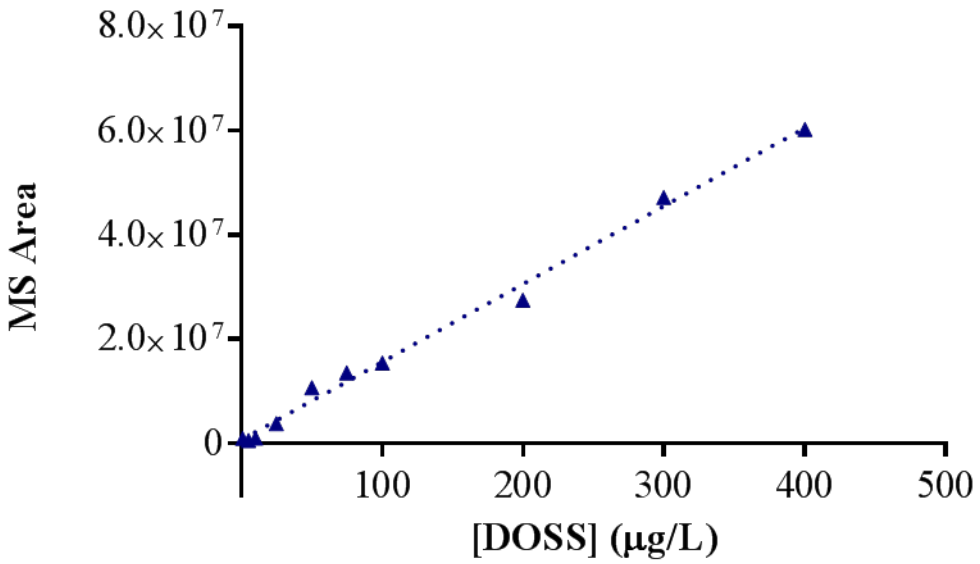

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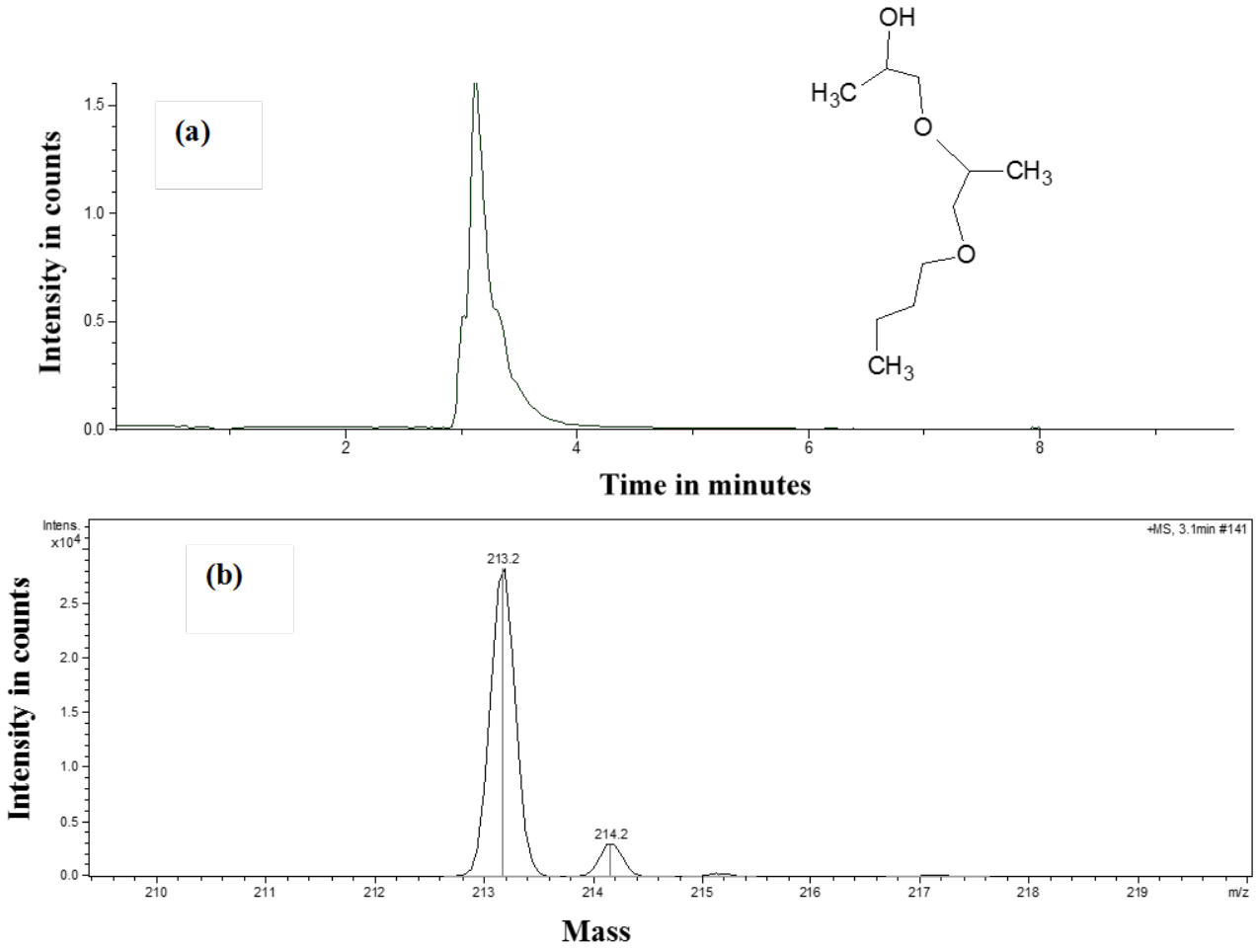
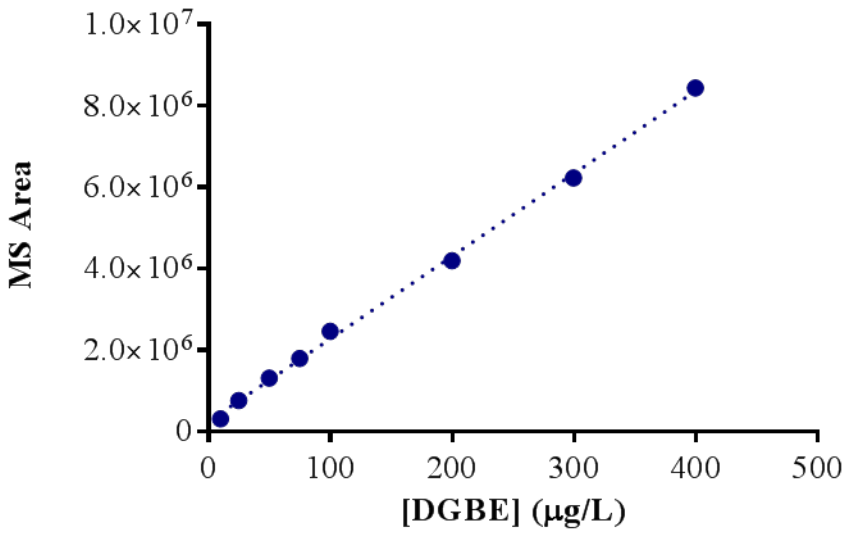


Figure 4. (a) Extracted ion chromatogram in positive mode at 213 m/z from COREXIT 9500 mixture (b) extracted ion 213 m/z from COREXIT 9500 mixture.

Figure 5.



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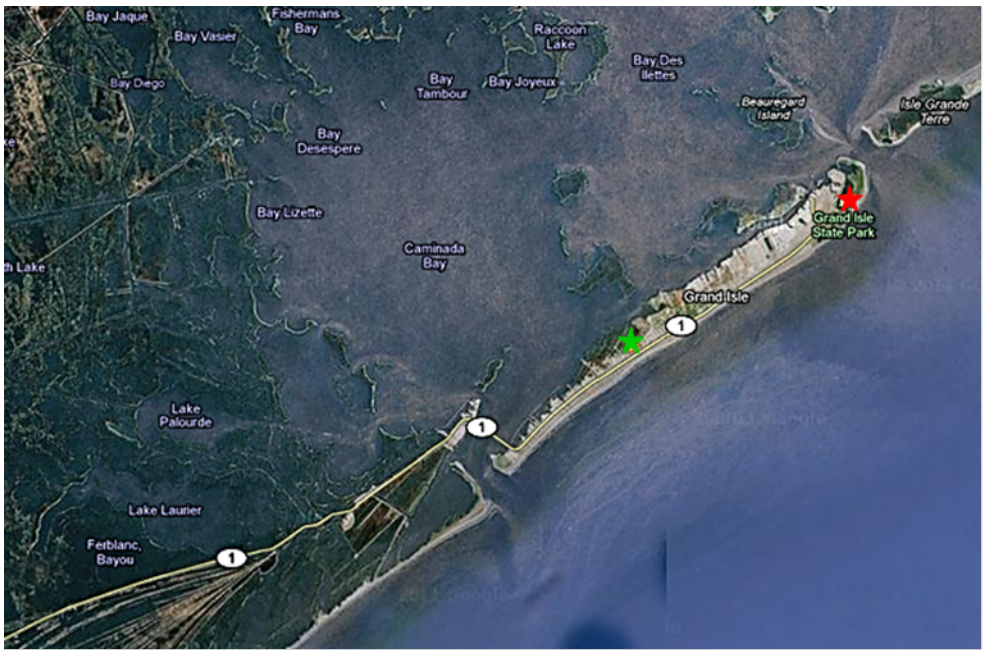

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Table 1.

Table 1. Solid-phase extraction results of DOSS and DGBE in both laboratory and ocean water samples.

	Percent Recovery (%)					
Sample	Lab-1	Lab-2	Lab-3	Ocean-1	Ocean-2	Ocean-3
DOSS	67	63	70	54	57	60
DGBE	60	58	65	48	52	50