Designation: D7730 – 11

Standard Test Method for Determination of Dioctyl Sulfosuccinate in Sea Water by Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)[1]

This standard is issued under the fixed designation D7730; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This procedure covers the determination of dioctyl sulfosuccinate (DOSS) in sea water by direct injection using liquid chromatography (LC) and detection with tandem mass spectrometry (MS/MS). This analyte is qualitatively and quantitatively determined by this method. This method adheres to selected reaction monitoring (SRM) mass spectrometry.

1.2 The Detection Verification Level (DVL) and Reporting Range for DOSS are listed in Table 1.

1.2.1 The DVL is required to be at a concentration at least 3 times below the Reporting Limit (RL) and have a signal/noise ratio greater than 3:1. Fig. 1 and Fig. 2 display the signal/noise ratio of the selected reaction monitoring (SRM) transition.

1.2.2 The reporting limit is the concentration of the Level 1 calibration standard as shown in Table 5 for DOSS, taking into account the 50% sample preparation dilution factor.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

2.2 *Other Standards:*[3]

EPA publication SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

3. Terminology

3.1 *Definitions:*

3.1.1 *detection verification level, DVL, n*— a concentration that has a signal/noise ratio greater than 3:1 and is at least 3 times below the Reporting Limit (RL).

3.1.2 *reporting limit, RL, n*—the concentration of the lowest-level calibration standard used for quantification.

3.2 *Abbreviations:*

3.2.1 *ppb*—parts per billion, µg/L

3.2.2 *mM*—millimolar, 1 x 10^{-3} moles/L

3.2.3 *NA*—no addition

3.2.4 *ND*—non-detect

4. Summary of Test Method

4.1 This is a performance based method, and modifications are allowed to improve performance.

4.2 For DOSS analysis, samples are shipped to the lab between 0°C and 6°C and analyzed within 5 days. In the lab, the entire collected 20 mL sample is spiked with surrogate, ammonium formate buffer solution and brought to a volume of 40 mL with acetonitrile. This prepared sample is then filtered using a syringe driven filter unit, and analyzed by LC/MS/MS. If visible oil is present, the prepared sample is allowed to settle resulting in an oil layer at the top of the 40 mL solution. A portion of the aqueous (bottom) layer is filtered, leaving the oil layer behind, through a syringe driven filter assembly and analyzed by LC/MS/MS.

4.3 DOSS and DOSS surrogate are quantitated by retention time and one SRM transition. The final report issued for each sample lists the concentration of DOSS and the surrogate recovery.

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA, 22161 or at http://www.epa.gov/epawaste/hazard/testmethods/index.htm

TABLE 1 Detection Verification Level and Reporting Range

Analyte	DVL (µg/L)	Reporting Range (µg/L)
DOSS	3	20-400

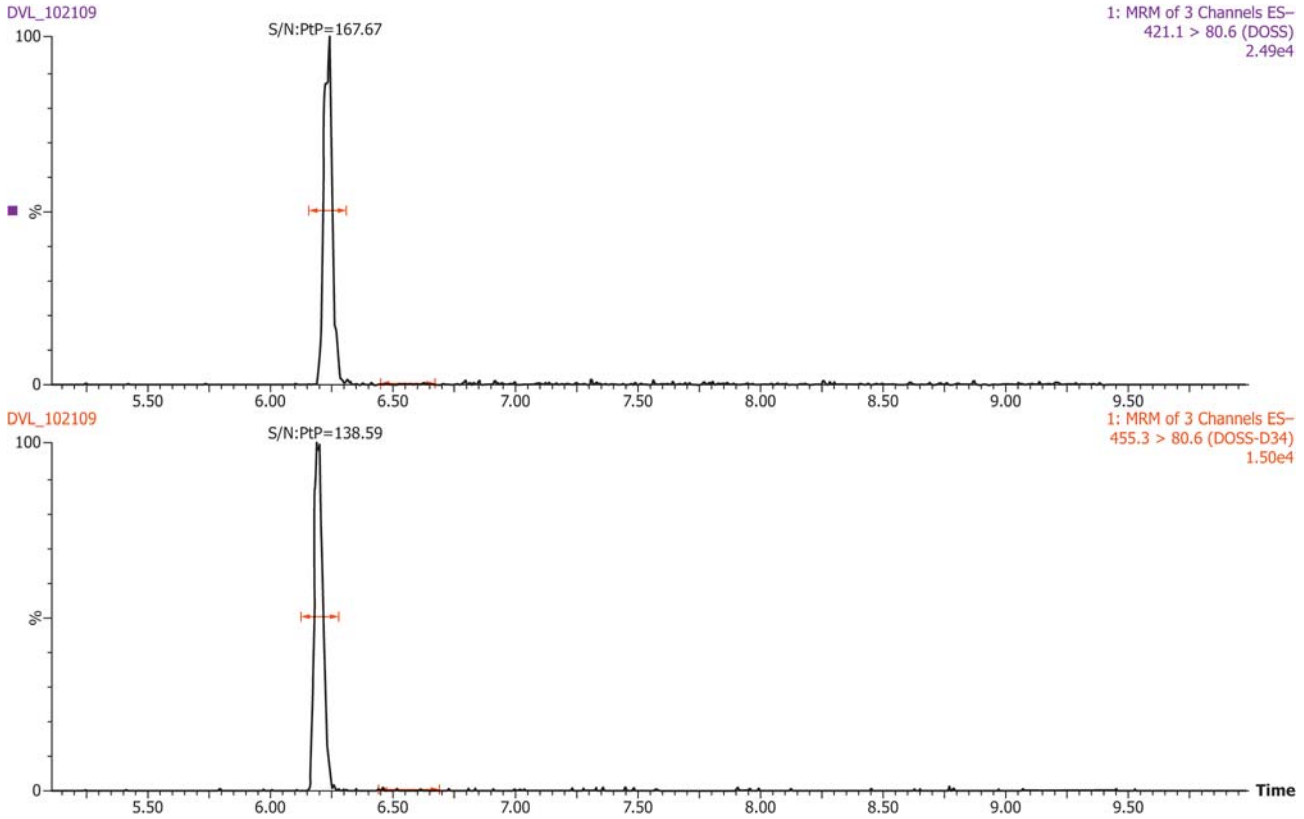

FIG. 1 Detection Verification Level Signal/Noise Ratio.

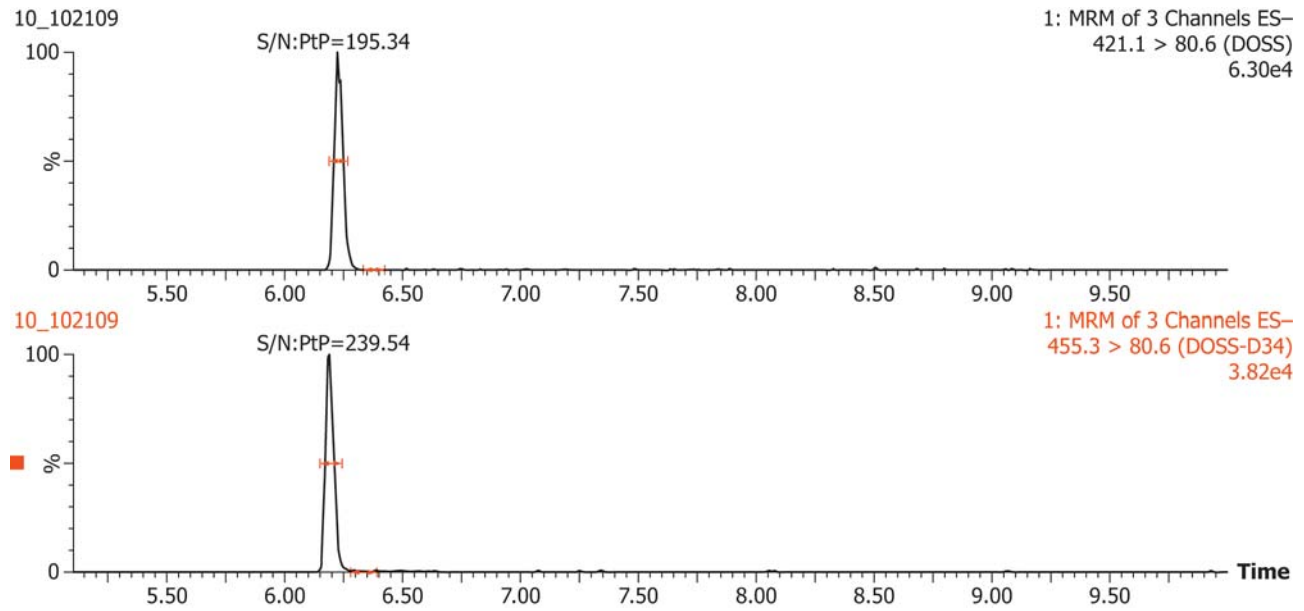

FIG. 2 Reporting Level Signal/Noise Ratio.

5. Significance and Use

5.1 DOSS is an anionic detergent that is approved by the Food and Drug Administration and is used widely as a laxative, emulsifying, solubilizing and dispersing agent, and is used in the cosmetic industry.[4] DOSS may also be used as a dispersing agent to treat oil. DOSS may be released into the environment at levels that may be harmful to aquatic life. The US EPA aquatic life benchmark for DOSS is 40 ppb.[5]

5.2 This method has been investigated for use with reagent and sea water.

6. Interferences

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other apparatus producing discrete artifacts or elevated baselines. All of these materials are demonstrated to be free from interferences by analyzing laboratory reagent blanks under the same conditions as samples.

6.2 All glassware is washed in hot water with detergent and rinsed in hot water followed by distilled water. The glassware is then dried and heated in an oven at 250°C for 15 to 30 minutes. All glassware is subsequently cleaned with methanol or 50% acetonitrile/50% water, or both.

6.3 System contamination and surface binding are problematic as DOSS is a surface active compound. It is important to thoroughly rinse sample containers with organic solvent to accurately measure DOSS concentrations. Thorough rinsing of all lab equipment is necessary to reduce contamination. Carefully analyze blanks to ensure that the method minimizes DOSS carryover.

6.4 All reagents and solvents should be pesticide residue purity or higher to minimize interference problems.

6.5 Matrix interferences may be caused by contaminants in the sample. The extent of matrix interferences can vary considerably from sample source depending on variations of the sample matrix.

6.6 Sulfonate filters contribute significantly to background interference and should be avoided for this standard. In addition to sample filtration, sulfonate filters may be present in water purification systems.

7. Apparatus

7.1 LC/MS/MS System

7.1.1 *Liquid Chromatography System*—A complete LC system is needed in order to analyze samples.[6] Any system that is capable of performing at the flows, pressures, controlled temperatures, sample volumes, and requirements of the standard may be used.

7.1.2 *Analytical Column—Waters*—Atlantis™ dC18, 2.1 x 150 mm, 3 µm particle size was used to develop this test method. Any column that achieves baseline resolution of these analytes may be used. Baseline resolution simplifies data analysis and can reduce the chance of ion suppression, leading to higher limits of detection. The retention times and order of elution may change depending on the column used and need to be monitored.

7.1.3 *Tandem Mass Spectrometer System*—A MS/MS system capable of MRM analysis.[7] Any system that is capable of performing at the requirements in this standard may be used.

7.2 *Filtration Device*

7.2.1 *Hypodermic syringe*—A Lock Tip Glass Syringe capable of holding a Millex® HV Syringe Driven Filter Unit PVDF 0.22 µm or similar may be used.

7.2.1.1 A Lock Tip Glass Syringe was used in this test method.

7.2.2 *Filter*—Millex® HV Syringe Driven Filter Unit PVDF 0.22 µm (Millipore Corporation, Catalog # SLGV033NS) or similar may be used.

8. Reagents and Materials

8.1 *Purity of Reagents*—High Performance Liquid Chromatography (HPLC) pesticide residue analysis and spectrophotometry grade chemicals shall be used in all tests. Unless indicated otherwise, it is intended that all reagents shall conform to the Committee on Analytical Reagents of the American Chemical Society.[8] Other reagent grades may be used provided they are first determined to be of sufficiently high purity to permit their use without affecting the accuracy of the measurements.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type 1 of Specification D1193. It must be demonstrated that this water does not contain contaminants at concentrations sufficient to interfere with the analysis.

8.3 *Gases*—Ultrapure nitrogen and argon.

8.4 Acetonitrile (CH_3CN, CAS # 75-05-8).

8.5 Methanol (CAS # 67-56-1).

8.6 Ammonium formate (NH_4CO_2H, CAS # 540-69-2).

8.7 2-Propanol (CAS # 67-63-0).

8.8 Dioctyl sulfosuccinate (DOSS) purchased as the sodium salt (CAS # 577-11-7).

8.9 Dioctyl sulfosuccinate-$^{13}C_4$, (bis(2-ethylhexyl) sulfosuccinate (Fumaric acid-$^{13}C_4$) sodium salt (Unlabeled CAS # 577-11-7), (Optional Surrogate, custom synthesis).

[4] Code of Federal Regulations-Title 21: Food and Drugs, Part 172 available at http://www.gpoaccess.gov/cfr/index.html.

[5] Additional information about DOSS is available at http://www.epa.gov/bpspill/dispersant-methods.html (2010)

[6] A Waters ACQUITY UltraPerformance Liquid Chromatography (UPLC®) System was used to develop this test method. All parameters in this test method are based on this system and may vary depending on your instrument.

[7] A Waters Quattro Premier™ XE tandem quadrupole mass spectrometer was used to develop this test method. All parameters in this test method are based on this system and may vary depending on your instrument.

[8] Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D.C. For Suggestions on the testing of reagents not listed by the American Chemical Society, see Annual Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulators, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.10 Dioctyl sulfosuccinate-D_{34}(DOSS-D_{34}), bis(2-ethylhexyl-D_{17}) sulfosuccinate sodium salt (Unlabeled CAS # 577-11-7).

9. Hazards

9.1 Normal laboratory safety applies 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.

10. Sampling

10.1 *Sampling and Preservation*—Grab samples should be collected in 20 mL pre-cleaned glass vials with Teflon® lined septa caps demonstrated to be free of interferences. This test method is based on a 20 mL sample size per analysis. Each sample should be collected in duplicate and a quadruplicate sample must be included with each sample batch of 10 for MS/MSD quality control analyses. Store samples between 0°C and 6°C from the time of collection until analysis. Analyze the sample within 5 days of collection.

10.2 DOSS is surface active. The surface activity results in DOSS adhering to many materials. Sampling techniques that expose samples to materials other than the sample container may reduce DOSS concentration in samples. Sampling techniques such as peristaltic pumping expose the sample to large surface areas compared to sample volume. Grab sampling techniques should be used. Transferring of sample from an initial collection device to sampling vial may result in biased low DOSS concentrations and must be avoided.

11. Preparation of LC/MS/MS

11.1 LC Chromatograph Operating Conditions[6]

11.1.1 Injection volumes of all calibration standards and samples are made at 50 µL volume using a full loop injection. "Full loop" mode is the preferred technique when performing quantitative analyses. Multiple blank samples should be analyzed at the beginning of a run to remove residual DOSS from the system. The first sample analyzed after the calibration curve is a blank to ensure there is negligible (Less than the DVL) DOSS carry-over. The gradient conditions for the liquid chromatograph are shown in Table 2. Divert the column flow away from the electrospray source for 0 to 5 minutes after injection. Flow diversion to waste may be done using the mass spectrometer divert valve, divert tubing configurations vary from manual injection. Test the divert valve configuration and operation prior to analysis. Seawater samples contain nonvolatile salts; the elution from injection to 5 minutes after injection is diverted to waste in order to prevent mass spectrometer source contamination. If there is carry-over from one sample to another, greater than half the reporting limit, the initial percentage of acetonitrile should be raised as shown in Table 3 to try and remove the carry-over. This will shorten the elution time of DOSS approximately 1 minute; therefore it is necessary reduce the flow diversion and adjust the MRM time. Increasing the initial acetonitrile gradient concentration does not increase the DVL or reporting limit.

11.2 *LC Sample Manager Conditions :*

11.2.1 *Wash Solvents*—Weak wash is 4.0 mL of 50% water/50% acetonitrile. Strong wash is 2.0 mL of 60% acetonitrile/40% 2-propanol. The strong wash solvent is needed to eliminate carry-over between injections of DOSS samples. The weak wash is used to remove the strong wash solvent. Instrument manufacturer specifications should be followed in order to eliminate sample carry-over.

11.2.2 *Temperatures*—Column, 35°C; Sample compartment, 15°C.

11.2.3 *Seal Wash*—Solvent: 50% acetonitrile/50% water; Time: 2 minutes.

11.3 *Mass Spectrometer Parameters*[7]:

11.3.1 To acquire the maximum number of data points per SRM channel while maintaining adequate sensitivity, the tune parameters may be optimized according to your instrument. Each peak requires at least 10 scans per peak for adequate quantitation. This procedure will contain one surrogate, which is isotopically labeled DOSS, DOSS-quantitation and DOSS-confirmation are in one MRM acquisition function to optimize sensitivity. Variable parameters regarding retention times, SRM transitions, and cone and collision energies are shown in Table 4. Mass spectrometer parameters used in the development of this method are listed below:

The instrument is set in the Electrospray negative source setting.

Capillary Voltage: 3.5 kV
Cone: Variable depending on analyte (Table 4)
Extractor: 2 Volts
RF Lens: 0.3 Volts
Source Temperature: 120°C
Desolvation Temperature: 350°C
Desolvation Gas Flow: 800 L/hr
Cone Gas Flow: 25 L/hr
Low Mass Resolution 1: 14.0
High Mass Resolution 1: 14.0
Ion Energy 1: 0.8
Entrance Energy: -1
Collision Energy: Variable depending on analyte (Table 4)
Exit Energy: 0
Low Mass Resolution 2: 14.0
High Mass resolution 2: 14.0

TABLE 2 Gradient Conditions for DOSS Liquid Chromatography

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

TABLE 3 Gradient Conditions for DOSS Liquid Chromatography Starting with a Higher Acetonitrile Concentration

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	50	50
2.0	0.3	50	50
5.0	0.3	0	100
8.0	0.3	0	100
8.3	0.3	50	50
10.0	0.3	50	50

TABLE 4 Retention Times, SRM transitions, and DOSS-Specific Mass Spectrometer Parameters

Analyte	Retention time (min)	Cone Voltage (Volts)	Collision Energy (eV)	SRM Mass Transition (Parent > Product)
DOSS	6.44	36	24	421.1 > 80.6
DOSS-confirmatory[A]	6.44	36	15	421.1>183.1
DOSS-D_{34}(Surrogate)	6.16	37	26	455.3 > 80.6
DOSS-^{13}C (Optional Surrogate)	6.44	36	24	425.3> 80.6

[A]DOSS-confirmatory SRM transition observed at higher DOSS concentrations, not required for DOSS identification.

Ion Energy 2: 1.0
Multiplier: 650
Gas Cell Pirani Gauge: 7.0 x 10^{-3} Torr
Inter-Channel Delay: 0.02 seconds
Inter-Scan Delay: 0.01 seconds
Dwell: 0.1 seconds
Solvent Delay: 5 minutes

12. Calibration and Standardization

12.1 The mass spectrometer must be calibrated per manufacturer specifications before analysis. In order to obtain accurate analytical values through using this test method within the confidence limits, the following procedures must be followed when performing the test method. Prepare all solutions in the lab using Class A volumetric glassware.

12.1.1 Account for the purity and sodium mass of the DOSS standards. The DOSS anion is quantitated, therefore the calibrations standards should be the DOSS anion concentration. For example:

10.76 mg of 98% pure dioctyl sulfosuccinate sodium salt standard contains 10.54 mg of dioctyl sulfosuccinate sodium salt (577-11-7),

10.54 mg of dioctyl sulfosuccinate sodium salt (577-11-7) contains 10.00 mg of dioctyl sulfosuccinate (DOSS),

10.00 mg of DOSS in 50.0 mL 50 % acetonitrile/50% water contains 200.0 ppm DOSS.

12.2 Calibration and Standardization– To calibrate the instrument, analyze seven calibration standards; the calibration standards nominal concentrations are detailed in Table 5. A calibration solution is prepared from standard materials or certified solutions. Level 7 calibration solution containing the DOSS and surrogate is prepared and aliquots of that solution are diluted to prepare Levels 1 through 6 and the DVL. The following steps will produce standards with the concentration values shown in Table 5. The analyst is responsible for recording initial component weight, calculating dilutions and preparing appropriate solutions. The DOSS 421.1 > 80.6 transition (Table 4) shall be used for DOSS quantitation. The DOSS confirmatory transition (421.1>183.1) serves to support DOSS identification, but is not required due to low sensitivity and may not be seen at lower concentrations.

12.2.1 Prepare Level 7 calibration stock standard at 200 ppb by adding to a 10 mL volumetric flask individual solutions of the following: 100 µL of DOSS and DOSS-D_{34} each at 20 ppm in 50% water/50% acetonitrile and dilute to 10 mL with a solution of 5 millimolar ammonium formate in 50% water/50% acetonitrile. The preparation of the stock standard can be accomplished using different volumes and concentrations of stock solutions as is accustomed in the individual laboratory. Depending on the prepared stock concentrations, the solubility at that concentration will have to be ensured.

12.2.2 Aliquots of Level 7 calibration stock standard are then diluted with 5 millimolar ammonium formate in 50% water/50% acetonitrile to prepare the desired calibration levels in 2 mL amber glass autosampler vials. The calibration vials must be used within 24 hours to ensure optimum results. Stock calibration standards are routinely replaced every 7 days if not previously discarded for quality control failure. Calibration standards are not filtered.

12.2.3 Inject each standard and obtain its chromatogram. An external calibration technique is used to monitor the SRM transitions of each analyte. Calibration software is utilized to conduct the quantitation of the target analytes and surrogates using the SRM transition. The calibration software manual should be consulted to use the software correctly. The quantitation method is set as an external calibration using the peak

TABLE 5 Concentrations of Calibration Standards (PPB)

Analyte/Surrogate	DVL	LV 1	LV 2	LV 3	LV 4	LV 5	LV 6	LV 7
DOSS	3	10	20	40	60	100	150	200
DOSS-D_{34}(Surrogate)	3	10	20	40	60	100	150	200

areas in ppb units. Concentrations may be calculated using the data system software to generate linear regression or quadratic calibration curves. Forcing the calibration curve through the origin is not recommended.

12.2.4 Linear calibration may be used if the coefficient of determination, r^2, is >0.98 for the analyte. The point of origin is excluded and a fit weighting of 1/X is used in order to give more emphasis to the lower concentrations. If one of the calibration standards other than the high or low point causes the r^2 of the curve to be <0.98, this point must be re-injected or a new calibration curve must be regenerated. If the Level 1 or Level 7 calibration result is excluded, minimally a five point curve is acceptable but the reporting range must be modified to reflect this change.

12.2.5 Quadratic calibration may be used if the coefficient of determination, r^2, is >0.99 for the analyte. The point of origin is excluded, and a fit weighting of 1/X is used in order to give more emphasis to the lower concentrations. If one of the calibration standards causes the curve to be <0.99, this point must be re-injected or a new calibration curve must be regenerated. At least six calibration points are required for quadratic regression. If the Level 1 or Level 7 calibration result is excluded, the reporting range must be modified to reflect this change. Each calibration point used to generate the curve must have a calculated percent deviation less than 25% between the nominal concentration and the regression calculated result.

12.2.6 The retention time window of the SRM transitions must be within 5% of the retention time of the analyte in a midpoint calibration standard. If this is not the case, re-analyze the calibration curve to determine if there was a shift in retention time during the analysis and the sample needs to be re-injected. If the retention time is still incorrect in the sample, refer to the analyte as an unknown.

12.2.7 A calibration check standard (near the midpoint, for example: 60 or 100 ppb) must be analyzed at the end of each batch of 20 samples or within 24 hours after the initial calibration curve was generated. The end calibration check should be the same calibration standard that was used to generate the initial curve. The regression result from the end calibration check standard must have a percent deviation less than 35% from the target analyte and surrogate nominal concentration. If the results are not within these criteria, the problem must be corrected and either all samples in the batch must be re-analyzed against a new calibration curve or the affected results must be qualified with an indication that they are not within the performance criteria of the test method. If the analyst inspects the vial containing the end calibration check standards and notices that the samples evaporated affecting the concentration, a new end calibration check standard may be made and analyzed. If this new end calibration check standard has a percent deviation less than 35% from the calculated concentration for the target analyte and surrogate, the results may be reported unqualified.

12.3 If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

12.3.1 Analyze at least four replicates of a sample solution containing the DOSS and surrogate at a concentration in the calibration range of Levels 3 to 5. The Level 5 concentration was used to set the QC acceptance criteria in this method. The matrix and chemistry should be similar to the solution used in this test method. Each replicate must be taken through the complete analytical test method including any sample pre-treatment steps.

12.3.2 Calculate the mean (average) percent recovery and relative standard deviation (RSD) of the four values and compare to the acceptable ranges of the QC acceptance criteria for the Initial Demonstration of Performance in Table 6.

12.3.2.1 This study should be repeated until the single operator precision and mean recovery are within the limits in Table 6.

12.3.2.2 The QC acceptance criteria for the Initial Demonstration of Performance in Table 6 are preliminary until more data and multi-laboratory study is completed. Data generated from a single-laboratory validation from reagent and sea water matrices are shown in the Precision and Bias Section 16. It is recommended that the laboratory generate their own in-house QC acceptance criteria which meets or exceeds the criteria in this standard. A Reference on how to generate QC acceptance criteria is in Method 8000B in EPA publication SW-846.

12.4 *Surrogate Spiking Solution:*

12.4.1 A surrogate spiking solution, 50% water/50% CH_3CN, containing DOSS-D_{34} is added to all samples. A stock surrogate spiking solution is prepared at 20 ppm. Spiking 200 µL of this spiking solution into a 20 mL water sample results in a concentration of 200 ppb of the surrogate in the sample. The result obtained for the surrogate recovery must fall within the limits of Table 6. If the limits are not met, the affected results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.5 *Method Blank:*

12.5.1 Analyze a reagent water blank with each batch of 20 or fewer samples. The DOSS measured in the blank must be less than the DVL. If the concentration of DOSS is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance

TABLE 6 Preliminary QC Acceptance Criteria

		Initial Demonstration of Performance			Lab Control Sample	
		Recovery (%)		Precision	Recovery (%)	
Analyte	Test Conc. (µg/L) in Reagent Water	Lower Limit	Upper Limit	Maximum % RSD	Lower Limit	Upper Limit
DOSS	200	50	150	30	50	150
DOSS-D_{34} (Surrogate)	200	50	150	30	50	150

criteria of the test method. DOSS has been found to carry-over in LC systems. A rigorous washing of the injector with stronger wash solvents has been shown to work well as described in this method. If you have an older LC system or have carry-over problems, the LC conditions listed in Table 3 should be investigated to remove background.

12.6 *Laboratory Control Sample (LCS):*

12.6.1 To ensure that the test method is in control, analyze a LCS prepared with the DOSS at a concentration in the calibration range of Levels 3 to 5. The LCS is prepared following the analytical method and analyzed with each batch of 20 samples or less. Prepare a stock matrix spiking solution in 50% water/50% acetonitrile containing the DOSS at 20 ppm. Spike 200 µL of this stock solution into 20 mL of water to yield a concentration of 200 ppb for the DOSS in the sample. The LCS result must be within the limits in Table 6. Matrix spiking solutions are routinely replaced every 7 days if not previously discarded for quality control failure.

12.6.2 If the LCS regression result is not within Table 6 limits, analysis of samples is halted until the problem is corrected, and either all samples in the batch must be re-analyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.7 *Matrix Spike/Matrix Spike Duplicate (MS/MSD):*

12.7.1 To check for interferences in the specific matrix being tested, perform a MS/MSD on at least one sample from each batch of 10 or fewer samples by spiking the sample with a known concentration of DOSS and following the analytical method. Prepare a stock matrix spiking solution in 50% water/50% acetonitrile containing the DOSS at 20 ppm. Spike 200 µL of this stock solution into 20 mL of water to yield a concentration of 200 ppb of the DOSS in the sample.

12.7.2 If the spiked concentration plus the background concentration exceeds that of the Level 7 calibration standard, the sample must be diluted to a level near the midpoint of the calibration curve.

12.7.3 Calculate the spike percent recovery (P) using Equation 1:

$$P = 100\,\frac{|A(V_S + V) - BV_S|}{CV}$$

Where:

A = concentration found in spiked sample
B = concentration found in unspiked sample
C = concentration of analyte in spiking solution
V_S = volume of sample used
V = volume of spiking solution added
P = percent recovery

12.7.4 The percent recovery of the spike shall fall within the limits in Table 7. If the percent recovery is not within these limits, matrix interference may be present in the selected sample. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

12.7.5 The matrix spike/matrix spike duplicate (MS/MSD) limits in Table 7 are preliminary until more data is acquired. The data generated by a single-laboratory using sea water samples are in the Precision and Bias Section 16. The matrix variation between the different waters may have a tendency to generate significantly wider control limits than those generated by a single-laboratory in one water matrix. It is recommended that the laboratory generate their own in-house QC acceptance criteria which meets or exceeds the criteria in this standard. Surrogates should be used to identify and measure matrix affect.

12.7.5.1 The laboratory should generate their own in-house QC acceptance criteria after the analysis of 15-20 matrix spike samples of a particular surface water matrix. References on how to generate QC acceptance criteria is in Method 8000B in EPA publication SW-846.

12.8 *Duplicate:*

12.8.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch of 20 or fewer samples. If the sample contains the analyte at a level greater than 5 times the detection limit of the method, the sample and duplicate may be analyzed unspiked; otherwise, an MSD should be used.

12.8.2 Calculate the relative percent difference (RPD) between the duplicate values (or MS/MSD values) as shown in Eq. 2. Compare to the RPD limit in Table 7.

$$RPD = \frac{|MSR - MSDR|}{(MSR + MSDR)/2}$$

where:

RPD = relative percent difference
MSR = matrix spike recovery
$MSDR$ = matrix spike duplicate recovery

12.8.3 If the result exceeds the precision limit, the batch must be re-analyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13. Procedure

13.1 This test method is based upon a 20 mL sample size per analysis. Any sample size may be used such as a half filled VOA vial as long as the QC spikes and sample preparation volumes are adjusted accordingly. Samples shall be analyzed within 5 days of collection. If the samples are above 6°C when

TABLE 7 Preliminary MS/MSD QC Acceptance Criteria

		MS/MSD		
		Recovery (%)		Precision
Analyte	Test Conc. (µg/L)	Lower Limit	Upper Limit	Maximum RPD (%)
DOSS	200	30	150	30
DOSS-D_{34} (Surrogate)	200	30	150	30

received or during storage, or not analyzed within 5 days of collection, it is noted in the case narrative that accompanies the data.

13.2 In the laboratory, the entire 20 mL sample, collected in a 20 mL glass collection vial, is poured into a 50 mL graduated cylinder. The surrogate, as described in Section 12, is added to the sample in the original sample container and 0.2 mL of 1.0 M ammonium formate. The laboratory control and matrix spike samples are then spiked with the target compound as described in Section 12. The vial is rinsed with two 6 to 8 mL portions of acetonitrile to collect DOSS remaining in the collection vial. These 2 portions are added to the 50 mL graduated cylinder. The samples are then diluted to 40 mL final volume with acetonitrile and mixed thoroughly. The prepared sample is filtered through the syringe driven filter unit fitted with a PVDF filter cartridge into a glass storage vial.

13.3 For samples that are not biphasic, the entire 40 mL volume is filtered through the filtration device described in 7.2 into a pre-cleaned collection vial (such as a VOA vial). A portion of that filtered sample is added to an amber glass LC vial with a Teflon® lined cap which is analyzed. A new filter unit is used for each sample.

13.4 For biphasic samples, the lower aqueous layer is filtered through the filtration device described in 7.2 into a pre-cleaned collection vial (such as a VOA vial). The upper oil layer is left behind and is not added to the filtration device. A portion of that filtered sample is added to an amber glass LC vial with a Teflon® lined cap which is analyzed. A new filter unit is used for each sample.

13.5 Samples may be encountered that have more than one phase. Those samples may be prepared for analysis using one or a multiple of the following options:

13.5.1 *Whole Sample:*

For a 20 mL sample, add 0.2 mL of 20 ppm DOSS surrogate to the sample in the sample container. Cap the container and mix to ensure homogeneity. Transfer the contents of the sample container to a graduated cylinder record the sample volume. Subsequently, add 0.2 mL of 1.0 M ammonium formate to the graduated cylinder. Rinse the sample collection vial twice with 6 to 8 mL of acetonitrile, which is added to the prepared sample to compose ~ 50% acetonitrile solution to ensure quantitative sample transfer. Bring the prepared sample volume to 40 mL using acetonitrile, and then mix thoroughly. If different sample sizes are used, spiking solution, ammonium formate, and acetronitrile volume shall be adjusted proportionally. The sample must be thoroughly mixed and then allowed to settle. A portion of the aqueous fraction (bottom) should be transferred to a glass syringe for filtration. Filter the sample using a 0.22 µm PVDF filter into an autosampler vial, or another glass vial and then transfer to an autosampler vial. If a high concentration of DOSS is detected in oil, the filtered solution should be diluted for a preliminary analysis. Transfer 20 µL of the filtered prepared sample into an autosampler vial, and add 1.98 mL of 5 mM ammonium formate in 50% acetonitrile/50% water. If the DOSS result of the preliminary analysis is below the reporting limit, analyze the filtered-prepared sample directly or an appropriate dilution.

13.5.2 *Water Subsample:*

Collect a 10 mL subsample of the water fraction (bottom) using a needle and a glass syringe. To reduce the oil exposure, invert the vial and tap gently to cause the oil to move away from the septum. Insert needle through septum and collect 10 mL of the water layer; place the aliquot removed in a graduated cylinder. Then add 100 µL of 20 ppm DOSS surrogate to the sample in the graduated cylinder. Subsequently, add 100 µL of 1.0 M ammonium formate to the graduated cylinder. Add 10 mL acetonitrile to the prepared sample to compose ~ 50% acetonitrile solution to ensure quantitative prepared sample transfer. If different sample sizes are used, spiking solution, ammonium formate, and acetronitrile volume shall be adjusted proportionally. Filter the sample using a 0.22 µm PVDF filter into an autosampler vial, or another glass vial and then transfer to an autosampler vial.

13.5.3 *Oil Subsample:*

Add 1.5 mL of HPLC grade water to graduated cylinder. Collect a 0.5 mL subsample of oil (top), and place in a graduated cylinder. Then add 20 µL of 20 ppm surrogate to the sample in the graduated cylinder. Subsequently, add 20 µL of 1.0 M ammonium formate to the graduated cylinder. Add 2 mL acetonitrile to the prepared sample to compose ~ 50% acetonitrile solution to ensure quantitative prepared sample transfer. If different sample sizes are used, spiking solution, ammonium formate, and acetonitrile volume shall be adjusted proportionally. The sample should be thoroughly mixed and then allowed to settle. A portion of the aqueous fraction (bottom) should be transferred to a glass syringe for filtration. Filter the sample using a 0.22 µm PVDF filter into another vial (filtered-prepared sample). If a high concentration of DOSS is detected in oil, the filtered solution should be diluted for a preliminary analysis. Transfer 20 µL of the filtered-prepared sample into an autosampler vial, and add 1.98 mL of 5 mM ammonium formate in 50% acetonitrile/50% water. If the DOSS result of the preliminary analysis is below the reporting limit, analyze the filtered-prepared sample directly or an appropriate dilution.

13.6 The syringe must be cleaned between each filtration. It is the analyst's responsibility to ensure that the syringe is clean. A suggested method for cleaning the syringe between filtrations is to first rinse with at least 5 syringe volumes of water, followed by at least 3 volumes of 50% water/50% acetonitrile.

13.7 Once a passing calibration curve is generated the analysis of samples may begin. An order of analysis may be: method blank, laboratory control sample and duplicate, method blank, up to 20 samples, matrix spike sample(s) and duplicate followed by an end calibration check standard and a method blank.

14. Calculation or Interpretation of Results

14.1 For DOSS and surrogate analysis, the SRM transitions are identified by comparison of retention times in the sample to those of the standards. Calibration curves are used to calculate the amounts of DOSS and surrogate. Calculate the concentration in µg/L (ppb) for each analyte. The sample concentration was diluted by two fold by the addition of surrogates, ammonium formate, acetonitrile, and target compound spike where applicable. The two fold dilution must be accounted for when

reporting the concentration. DOSS may be reported if present at or above the reporting limit. If the concentration of the analyte is determined to be above the calibration range, the sample is diluted with 5 mM ammonium formate in 50% acetonitrile/50% water to obtain a concentration near the mid-point of the calibration range and re-analyzed. This method uses one surrogate, DOSS-D_{34}, to monitor performance and matrix affect. The surrogate recoveries are provided with all data generated from this test method.

14.1.1 A surrogate is used to monitor the performance of DOSS. If the surrogate meets the quality control criteria in this test method, the data may be reported unqualified for DOSS if all other quality control in this test method is acceptable. If the surrogate does not meet the quality control criteria of the test method, the data is qualified for DOSS.

15. Report

15.1 Determine the results in units of µg/L (ppb) in a water sample. Calculate the concentration in the sample using the linear or quadratic calibration curve. All data that does not meet the specifications in the test method must be appropriately qualified.

16. Precision and Bias

16.1 Standard Test Methods under the jurisdiction of the ASTM committee D19 may be published for a maximum of five years to the completion of a full collaborative study validation. Such Standards are deemed to have met all other D19 qualifying requirements but have not completed the required validation studies to fully characterize the performance of the methods across multiple laboratories and matrices. Publication of standards that have been fully validated is done to make current technology accessible to users of Standards, and to solicit additional input from the user community. The determination of precision and bias was conducted through EPA and generated applicable data to determine the precision and bias as described in D2777.

16.2 The determination of precision and bias was conducted through US EPA Region 5 Chicago Regional Laboratory.

16.3 This test method was tested by CRL on reagent water. The samples were spiked with the DOSS to obtain a 200 ppb concentration of each as described in Section 12. Table 8 contains the recoveries and standard deviation (SD) for the target compound.

16.4 This test method was tested by CRL on Gulf of Mexico sea water. The samples were spiked with target compound as described in Section 12. Table 9 contains the recoveries for the target compound.

16.5 This test method was used by CRL on Gulf of Mexico sea water sampling during the summer of 2010. The samples were prepared as described in this test method. Fig. 3, Fig. 4, Fig. 5, and Fig. 6 show the recoveries for the surrogate and target compound from those sample analysis.

17. Keywords

17.1 Dioctyl Sulfosuccinate; Liquid Chromatography; Mass Spectrometry; Water

TABLE 8 Single-Laboratory Recovery Data in Reagent Water using Chromatography Conditions Outlined in Table 2 and Table 3

Precision and Accuracy Samples	Measured ppb from 200 ppb DOSS Spikes in Reagent Water					
	Table 2				Table 2	
	Retention time (min)	DOSS measured (ppb)	Percent Recovery	Retention time (min)	DOSS measured (ppb)	Percent Recovery
1	6.38	182.6	91.3%	5.41	196.1	98.0%
2	6.37	232.9	116.5%	5.41	232.8	116.4%
3	6.37	224.6	112.3%	5.41	225.8	112.9%
4	6.37	226.8	113.4%	5.41	238.9	119.5%
Average Recovery:		216.7	108.4%		223.4	111.7%
Standard Deviation:		23.0			19.0	
% Relative SD		10.6%			8.5%	

TABLE 9 Single-Laboratory Recovery Data in Gulf of Mexico Sea Water using Chromatography Conditions Outlined in Table 2 and Table 3

	Measured ppb from 200 ppb DOSS Spikes in Gulf Water					
		Table 2			Table 3	
Precision and Accuracy		DOSS measured			DOSS measured	
Samples	Retention time (min)	(ppb)	Percent Recovery	Retention time (min)	(ppb)	Percent Recovery
1	6.37	189.1	94.6%	5.4	257.2	128.6%
2	6.37	251.4	125.7%	5.4	251.4	125.7%
3	6.37	253.2	126.6%	5.41	263.0	131.5%
4	6.37	257.0	128.5%	5.4	262.4	131.2%
5	6.37	250.7	125.4%	5.4	255.0	127.5%
Average Recovery:		250.7	120.1%		257.8	128.9%
Standard Deviation:		250.7			4.9	
% Relative SD		11.9%			1.9%	

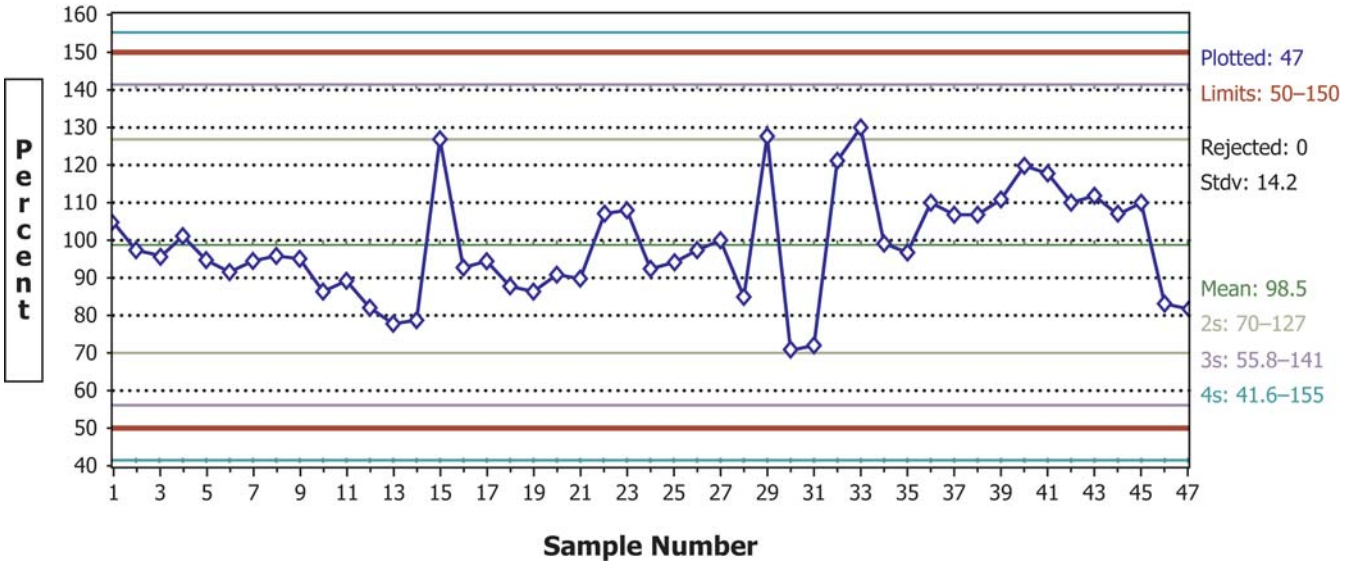

FIG. 3 Single-Laboratory DOSS –D_{34} Recovery Data in Reagent Water

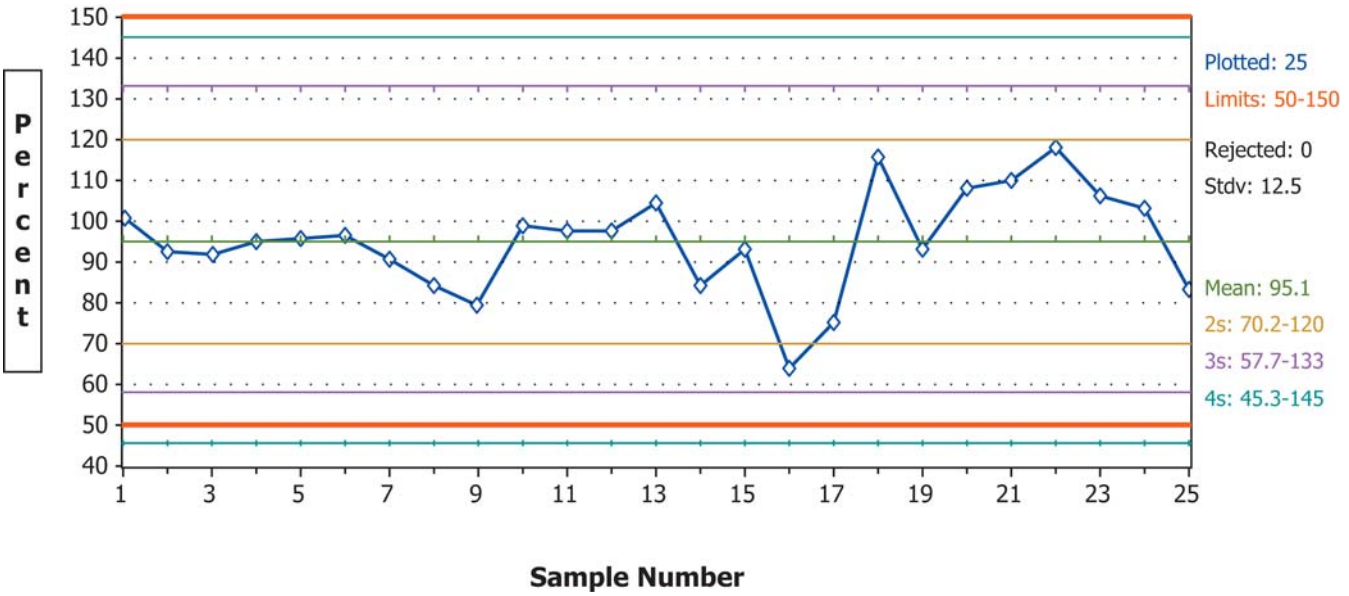

FIG. 4 Single-Laboratory DOSS Recovery Data in Reagent Water

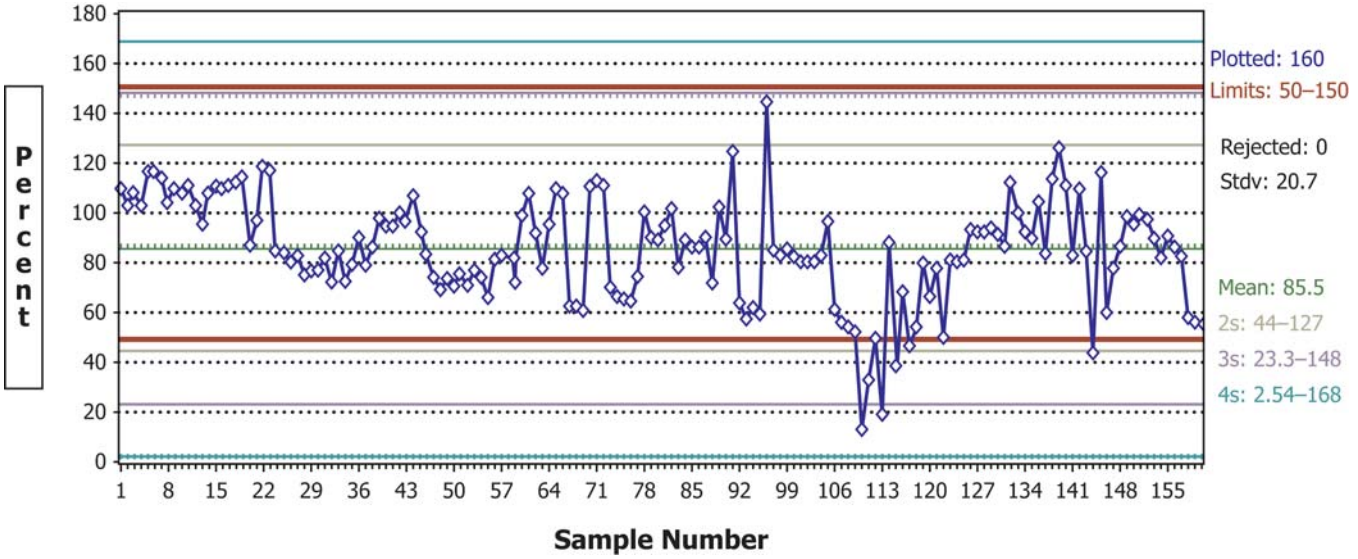

FIG. 5 Single-Laboratory DOSS $-D_{34}$ Recovery Data in Gulf of Mexico Sea Water

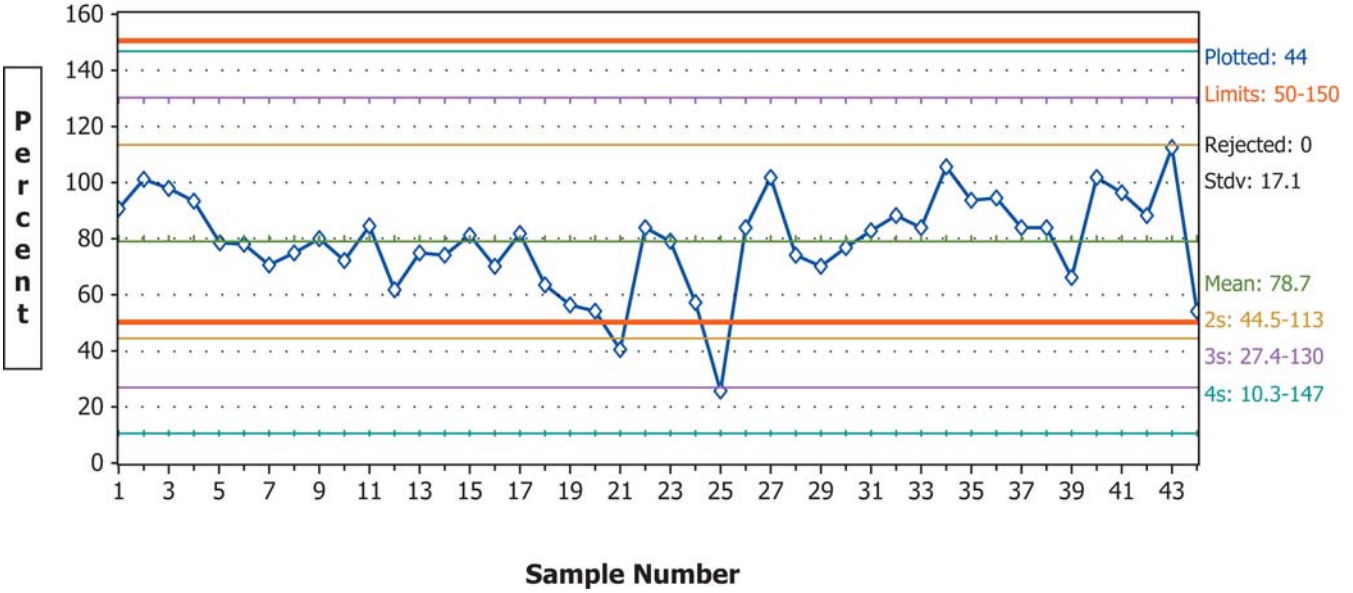

FIG. 6 Single-Laboratory DOSS Recovery Data in Gulf of Mexico Sea Water