Designation: D7730 – 17

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 test method 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 test method. This test 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water

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 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *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).

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

3.3 *Abbreviations:*

3.3.1 *mM*—millimolar, 1×10^{-3} moles/L

3.3.2 *NA*—no addition

3.3.3 *ND*—non-detect

3.3.4 *ppb*—parts per billion, µg/L

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,

[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), 5301 Shawnee Rd., Alexandria, VA 22312, http://www.ntis.gov.

TABLE 1 Detection Verification Level (DVL) and Reporting Range

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

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.

5. Significance and Use

5.1 DOSS is an anionic detergent that is approved by the United States Food and Drug Administration (U.S. FDA) 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 U.S. EPA aquatic life benchmark for DOSS is 40 ppb.[5]

5.2 This test 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,[7] 2.1 × 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.[8] 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,[9,10] 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, 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

[4] Code of Federal Regulations—Title 21: Food and Drugs, Part 172, Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

[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, a trademark of the Waters Corporation, Milford, MA, 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] The Waters Atlantis dC18 is a trademark of the Waters Corporation, Milford, MA.

[8] A Waters Quattro Premier XE tandem quadrupole mass spectrometer, a trademark of the Waters Corporation, Milford, MA, 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.

[9] The sole source of supply of the Millex HV Syringe Driven Filter Unit PVDF 0.45 µm known to the committee at this time is Millipore Corporation, Catalog # SLHV033NS. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[10] Millex is a trademark of Merck KGAA, Darmstadt, Germany.

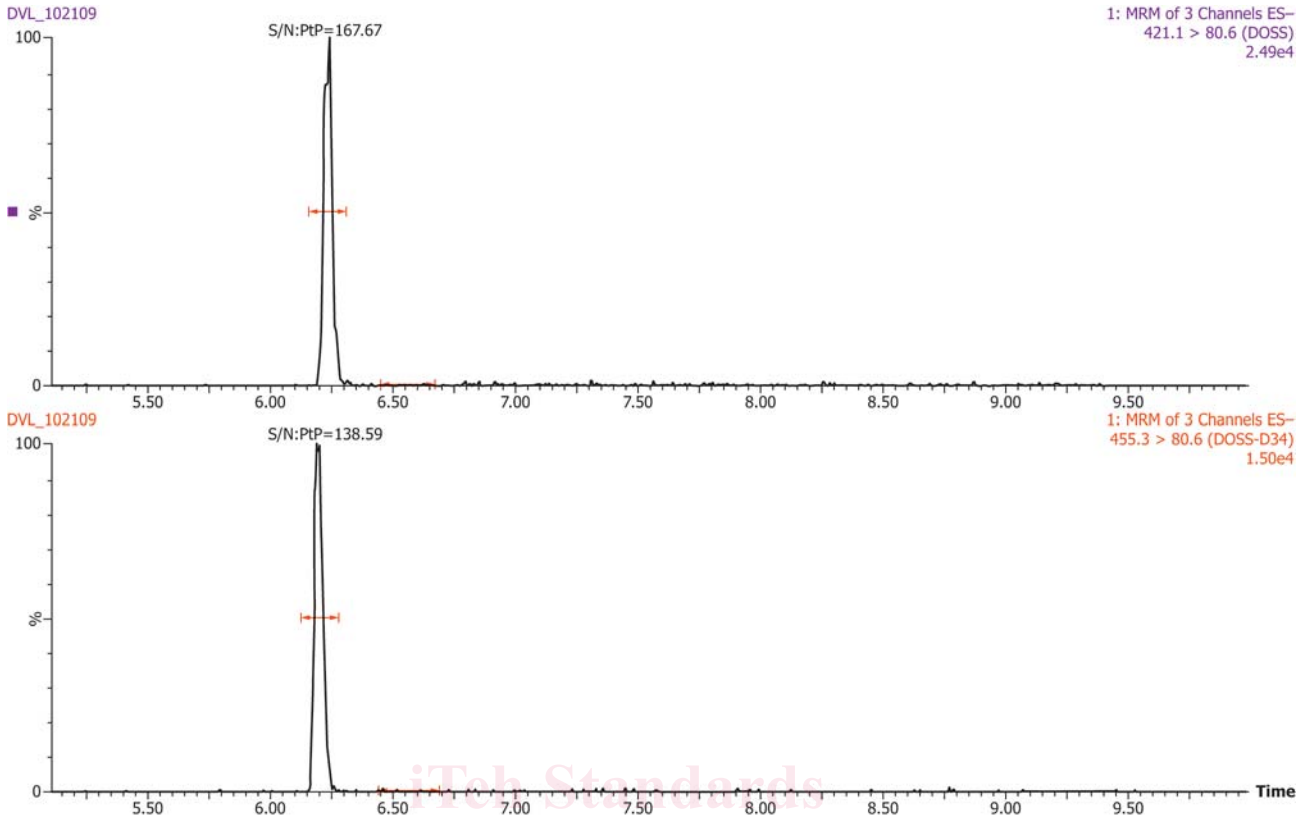

FIG. 1 Detection Verification Level Signal/Noise Ratio

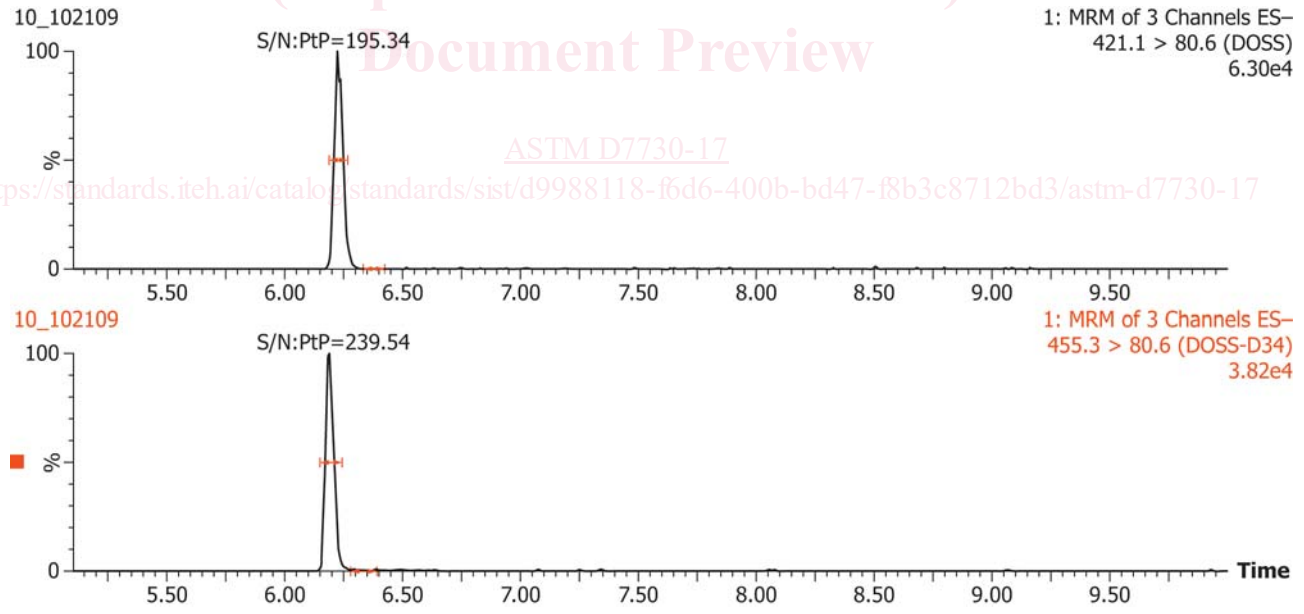

FIG. 2 Reporting Level Signal/Noise Ratio

American Chemical Society.[11] 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).

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 test 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 test method.

10. Sampling

10.1 *Sampling and Preservation*—Grab samples should be collected in 20-mL pre-cleaned glass vials with TFE-fluorocarbon–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 five 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] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

11.3 *Mass Spectrometer Parameters:*[8]

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 test 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
Ion Energy 2:	1.0
Multiplier:	650
Gas Cell Pirani Gauge:	7.0×10^{-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 in accordance with 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 this 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), and

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

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.

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

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 seven 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 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 this 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 quality control (QC) acceptance criteria in this test 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.

TABLE 6 Preliminary QC Acceptance Criteria

Analyte	Test Conc. (µg/L) in Reagent Water	Initial Demonstration of Performance			Lab Control Sample	
		Recovery (%)		Precision	Recovery (%)	
		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