



Designation: ~~D7730~~—~~11~~ 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This ~~procedure~~ ~~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~~ ~~detection verification level~~ (DVL) and ~~Reporting Range~~ ~~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~~ ~~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%~~ ~~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~~ ~~safety, health, and health~~ ~~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 <http://www.astm.org/standards/sist/d9988118-f6d6-400b-bd47-f8b3c8712bd3/astm-d7730-17>

[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; 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:~~ *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~~ ~~reporting limit~~ (RL).

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> 5301 Shawnee Rd., Alexandria, VA 22312, <http://www.ntis.gov>.

TABLE 1 Detection Verification Level and Reporting Range

Analyte	DVL ($\mu\text{g/L}$)	Reporting Range ($\mu\text{g/L}$)
DOSS	3	20-400

TABLE 1 Detection Verification Level (DVL) and Reporting Range

Analyte	DVL ($\mu\text{g/L}$)	Reporting Range ($\mu\text{g/L}$)
DOSS	3	20-400

3.2.2 *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, $\mu\text{g/L}$

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

3.2.3 *NA*—no addition

3.2.4 *ND*—non-detect

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3.3.4 *ppb*—parts per billion, $\mu\text{g/L}$

4. Summary of Test Method

4.1 This is a ~~performance-based~~ 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~~ 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~~ 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. ~~30-17~~

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% 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.

⁴ Code of Federal Regulations—Title Regulations—Title 21: Food and Drugs, Part 172 available at <http://www.gpoaccess.gov/cfr/index.html>, 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)

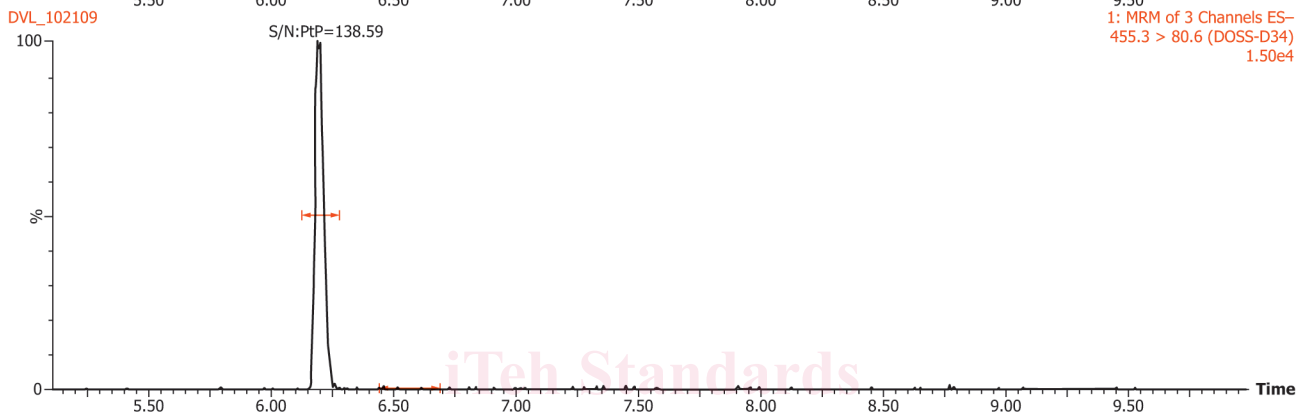
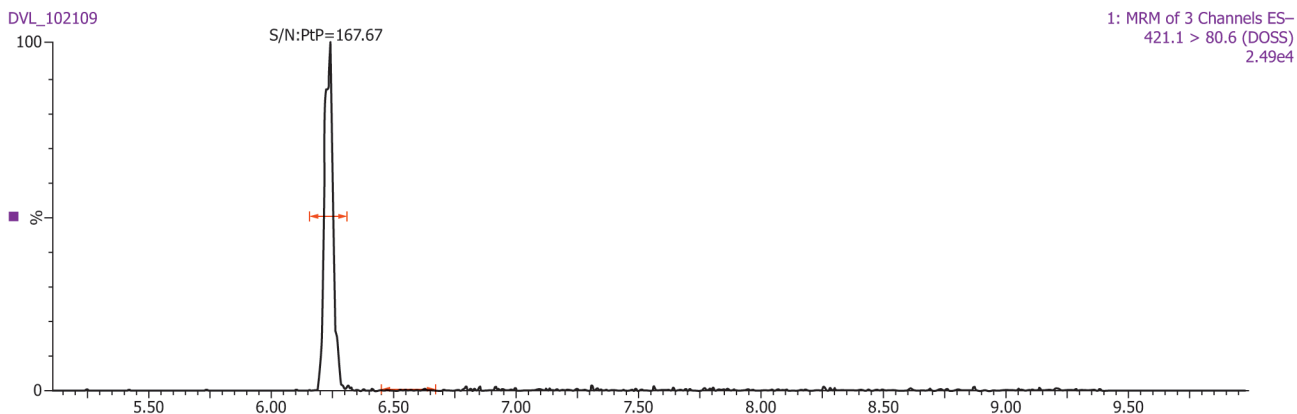


FIG. 1 Detection Verification Level Signal/Noise Ratio:Ratio

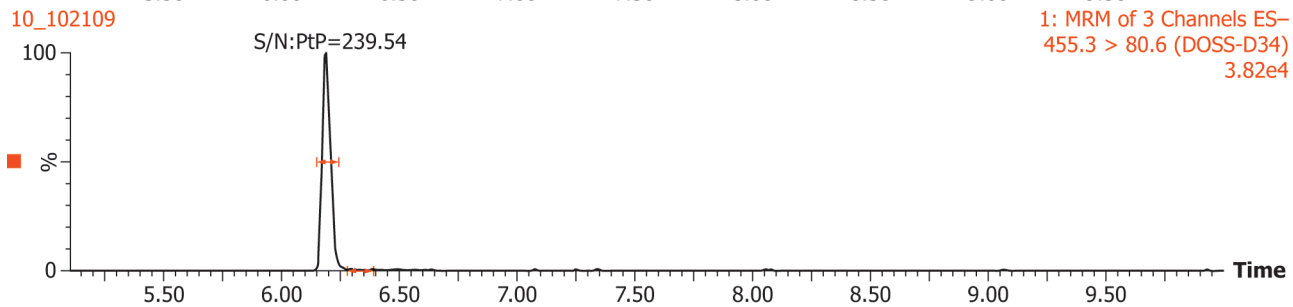
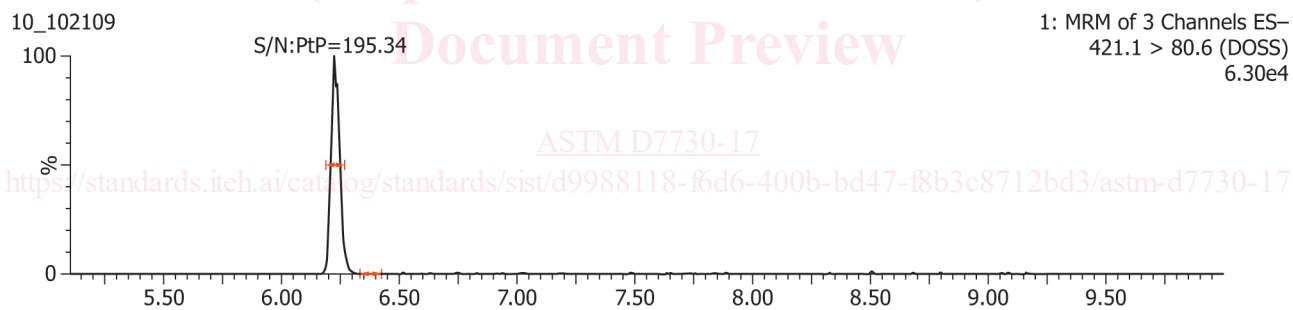


FIG. 2 Reporting Level Signal/Noise Ratio:Ratio

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—Column—Atlantis™* Waters Atlantis dC18,⁷ 2.1 × 150 mm, 3-~~µm~~ 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* ~~Device~~:

7.2.1 *Hypodermic syringe*—A Lock Tip Glass Syringe capable of holding a ~~Milllex®~~ Milllex 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*—~~Milllex®~~ Milllex HV Syringe Driven Filter Unit PVDF 0.22 ~~µm~~ (Millipore Corporation, Catalog # SLGV033NS) or similar ~~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 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 (CH₃CN, CAS # 75-05-8).

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

8.6 Ammonium formate (NH₄CO₂H, 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-¹³C₄, (bis(2-ethylhexyl) sulfosuccinate (Fumaric acid-¹³C₄) sodium salt (Unlabeled CAS # 577-11-7), (Optional Surrogate, custom synthesis).

8.10 Dioctyl sulfosuccinate-D₃₄(DOSS-D₃₄), bis(2-ethylhexyl-D₁₇) 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~~ 20-mL pre-cleaned glass vials with ~~Teflon® lined~~ TFE-fluorocarbon-lined septa caps demonstrated to be free of interferences. This test method is based on a ~~20-mL~~ 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 ~~five~~ days of collection.

⁶ A Waters ACQUITY UltraPerformance Liquid Chromatography (~~UPLC®~~) System—(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™~~ Premier XE tandem quadrupole mass ~~spectrometer~~ 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 Milllex 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 Milllex is a trademark of Merck KGAA, Darmstadt, Germany.

¹¹ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D.C. For ~~Suggestions~~ suggestions on the testing of reagents not listed by the American Chemical Society, see ~~Annual~~ Annual *Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulators' Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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*LC Chromatograph Operating Conditions:*

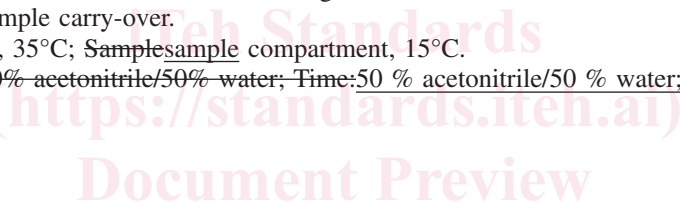
11.1.1 Injection volumes of all calibration standards and samples are made at ~~50 μ L~~ 50 μ L volume using a full loop injection. “Full loop” mode is the preferred technique when performing quantitative analyses. Multiple blank samples should be analyzed at the beginning of a run to remove residual DOSS from the system. The first sample analyzed after the calibration curve is a blank to ensure there is negligible (~~less~~ 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~~ *Conditions:*

11.2.1 *Wash Solvents*—Weak wash is 4.0 mL of ~~50% water/50% 50 % water/50 %~~ acetonitrile. Strong wash is 2.0 mL of ~~60% acetonitrile/40%~~ 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~~ sample compartment, 15°C.

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



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<https://standards.iteh.ai/catalog/standards/sist/d9988118-f6d6-400b-bd47-f8b3c8712bd3/astm-d7730-17>

TABLE 2 Gradient Conditions for DOSS Liquid Chromatography

Time (min)	Flow (mL/min)	Percent 95% Water/ 5% <u>95 % Water/ 5 %</u> CH ₃ CN, 5 mM NH ₄ CO ₂ H	Percent 95% 95 % CH₃CN/ 5% <u>95 % CH₃CN/ 5%</u> Water, 5 mM NH ₄ CO ₂ H
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 ₃ CN, 5 mM NH ₄ CO ₂ H	Percent 95% CH ₃ CN/5% Water, 5 mM NH ₄ CO ₂ H
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 Parameters⁸:

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 x 10⁻³ Torr

Inter-Channel Delay: 0.02 seconds

Inter-Scan Delay: 0.01 seconds

Dwell: 0.1 seconds

Solvent Delay: 5 minutes

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

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-confirmatory ^A	6.44	36	15	421.1 > 183.1
DOSS-D _{3,4} (Surrogate)	6.16	37	26	455.3 > 80.6
DOSS- ¹³ C (Optional Surrogate)	6.44	36	24	425.3 > 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.