

**Table 1. Laboratory Key Elements for Sulfolane Analysis in Water**

<b>Key Element</b>	<b>Method Criteria</b>
<b>Reference Method</b>	SOP shall include references for method basis.
<b>Internal Standard (sulfolane-d8)</b>	Quantitation of sulfolane based on isotope dilution method using sulfolane-d8. Sulfolane-d8 added pre-extraction. Final extract concentration near the mid-point calibration concentration.  Use m/z 128 for quantifying and m/z 46, 62, and 64 as qualifier ions. See ion ratio criteria below.  In the case of dilution that results in a sulfolane-d8 that is less than 10x noise, then re-extract sample using a lesser volume. In these cases, holding time considerations are waived.
<b>Recovery Criteria for Internal Standard</b>	Absolute recovery (quantitation based on recovery standard) 40 – 100%.
<b>Recovery Standard</b>	Naphthalene-d8 added post-extraction.
<b>Recovery Criteria for Recovery Standard</b>	Area count -50 to +100% relative to the continuing calibration verification.
<b>Additional Surrogates – Pre-extraction</b>	A minimum of one surrogate (in addition to the internal standard sulfolane-d8) should be added pre-extraction. Suggested surrogate nitrobenzene-d5. Recovery criteria to be internally derived.
<b>Extraction Sample Amounts</b>	Extraction volume sufficient to meet detection criteria, generally, 100 mL to 1 L should be sufficient. Extraction volume and the final extract volume must be specified in SOP.
<b>Extraction Method</b>	At discretion of labs sufficient to meet data quality objectives.
<b>GC/MSD Method</b>	Full Scan Mode, recommended mass range m/z 40 to 250 or higher. Scan rate greater than 10 scans across peak (at 10% peak height). Daily tune MS consistent with laboratory quality assurance project plan (QAPP).
<b>GC/MSD Calibration</b>	Low calibration point needs to be able to quantitate 5 parts per billion (ppb) at a minimum in water. At least two calibration points need to be set below the action level, currently set at 25 ppb. The concentration of the internal standard, sulfolane-d8, should be the same in all calibration standards and sample extract. Off-site samples have been observed at concentrations up to approximately 300 ppb.

Key Element	Method Criteria
<b>Quant/Qual Ions for Sulfolane</b>	Quantification ion on m/z 120; Qualifier ions (QI) at m/z 41, 55 and 56. All four ions should be used and QI ratios defined.
<b>Ion Ratios (sulfolane and sulfolane-d8)</b>	<p>Relative intensities of the qualifier ions need to be within 30% of the daily reference standard for two of three QI. If do not meet ratio criteria in at least two QI, attempt to resolve the matrix interference. If matrix interference cannot be resolved, QI failure must be reported to DEC Project Managers within 1 week of failure. Ion ratios must be displayed in the raw data.</p> <p>If &lt;25% resolution relative to the sulfolane-d8 peak cannot be obtained attempt the following:</p> <ol style="list-style-type: none"> <li>1. Optimize chromatographic conditions in an attempt to enhance resolution, and</li> <li>2. Attempt additional cleanup techniques to remove the apparent interferences.</li> </ol> <p>If items 1 or 2 fail to achieve less than 25% resolution then for the primary quantitation ion (m/z 128) between sulfolane-d8 and an adjacent peak (naphthalene or other non-target analyte), the quantitation ion for sulfolane-d8 in the impacted sample should be switched to m/z 46 as long as baseline resolution is obtained for m/z 46. In these cases, quantitation using m/z 46 for sulfolane-d8 should be used for both sulfolane (as the internal standard) and sulfolane-d8 in the impacted sample as well as all associated calibration standards, calibration check standards, and quality control samples (laboratory control samples, method blanks, matrix spikes, laboratory duplicates, instrument blanks, etc.). As a result, some initial calibration standards, calibration check standards and quality control samples may need to be quantified and reported using both m/z 46 and m/z 128 for quantitation. Also, in these cases, the laboratory is not required to inform DEC of the presence of interference. Separation of sulfolane-d8 from the interferent should be defined, documented, and submitted as part of the final laboratory report, through chromatographs and ion ratio criteria.</p>

Key Element	Method Criteria
<b>Detection Limit (DL)</b>	DL not to exceed 5 ppb in water. LOQ (limit of quantitation) not to exceed 10 ppb in water. Report J-values between DL and LOQ.
<b>Tailing criteria and integration</b>	Sulfolane and sulfolane-d8 peak tailing not to exceed a factor of two calculated on the unmodified software integrated peak (consistent with tailing factor equation from SW-846 Method 8270D). Manual integration only performed if necessary. Submit before and after extracted ion current profile (EICP) documentation with the report.
<b>Minimum Separation Criteria</b>	For standards and as part of each initial calibration, a demonstration of 10 ng of naphthalene and 25 ng sulfolane-d8 when monitoring all target mass ions for sulfolane-d8. Full baseline chromatographic resolution must be achieved.
<b>Data flagging</b>	Data flagged based on laboratory standard practices. All flags used should be defined.
<b>Sample Collection, Handling, and Preservation</b>	Pre-cleaned appropriate sized amber bottle. Placed on ice and kept above freezing but below 6°C. Samples must be extracted within 7 days and the extract must be analyzed within 40 days of extraction.
<b>Demonstration Criteria</b>	For initial demonstration of performance, analyze a minimum of five extracted LCS QC samples at 25 ppb, each showing recoveries of $\pm 20\%$ and $RSD \leq 30\%$ .

**Table 2. Quality Control Requirements**

<b>Description</b>	<b>Frequency</b>	<b>Criteria</b>	<b>Corrective Action</b>
<b>Initial Calibration</b>	As needed	For regression: $r^2 \geq 0.99$ or $r \geq 0.995$ ; For average RRF: $RSD \leq 15\%$	Repeat initial calibration.
<b>Initial Calibration Verification (ICV)</b>	Immediately following Initial Calibration	Second source, $\%Drift \leq 20\%$	Investigate, reanalyze, recalibrate.
<b>Continuous Calibration Verification (CCV)</b>	After MS tuning and before sample analysis, every 20 injections thereafter, and at end of analytical sequence, or within a 12 hour tuning period, whichever is shorter. CCV concentration at action level, equivalent to 25 ppb in a sample.	$\%Drift \leq 20\%$	Reanalyze CCV. If second re-analysis fails then perform initial calibration. Samples that were not bracketed by acceptable CCV must be reanalyzed.
<b>Method Blank (MB)</b>	Every preparation batch/event, or 20 samples, whichever is less	< DL	Re-analyze MB. If MB > DL or LOQ but ND (<DL) in samples then no action needed. If MB > DL then re-extract and re-analyze batch. Flag data with "B" qualifier, if insufficient sample for extraction.
<b>Laboratory Control Sample (LCS)</b>	Every preparation batch/event, or 20 samples, whichever is less. LCS concentration at action level, equivalent to 25 ppb in a sample. Spiking standard is prepared in water or a water-miscible solvent.	70 – 120%	Re-analyze LCS. If %R > acceptance criteria but ND (<DL) in samples no action needed. Otherwise re-extract and re-analyze batch.
<b>Surrogate (additional, i.e.,</b>	Each sample and QC	In-house developed limits	Re-analyze and evaluate. If

Description	Frequency	Criteria	Corrective Action
<b>nitrobenzene-d5)</b>		TBD, not to exceed 50 – 150%	second analysis fails criteria, re-exact and reanalyze.
<b>Matrix Spike/Matrix Spike Duplicate (MS/MSD) and Laboratory Duplicate Sample (DUP)</b>	An MS/MSD pair every preparation batch with 10 or more samples, up to 20. If preparation batch is less than 10 samples, analyze laboratory sample duplicate. Spiking standard is prepared in water or a water-miscible solvent.	RPD for DUP and MS/MSD $\leq$ 25%; MS/MSD Recovery 60 – 140%	Qualify data and narrative any obvious matrix effects.
<b>Internal Standard (sulfolane-d8) Recovery</b>	Each sample and QC. Spiking standard is prepared in water or a water-miscible solvent.	40-100%	Re-extract and flag if second re-extraction/re-analysis fails criteria.
<b>Recovery Standard (naphthalene-d8)</b>	Each sample and QC	Area Count -50 – +100% relative to the continuing calibration verification	Re-analyze and flag if second analysis fails criteria.

**Table 1. Laboratory Key Elements for Sulfolane Analysis in Soil**

<b>Key Element</b>	<b>Decision</b>
<b>Reference Method</b>	8270D Analytical with SW846 Preparation 3540C or 3550C, preference is 3540. SOP shall include references for method basis.
<b>Extraction Solvent</b>	MeCl <sub>2</sub>
<b>Internal Standard (sulfolane-d8)</b>	<p>Quantitation of sulfolane based on isotope dilution method using sulfolane-d8. Sulfolane-d8 added pre-extraction. Final extract concentration near the mid-point calibration concentration. Use m/z 128 for quantifying and m/z 46, 62, and 64 as qualifier ions. See ion ratio criteria below.</p> <p>Laboratory shall notify project manager to discuss extracting or analyzing a sample outside holding time criteria. Samples should not be extracted or analyzed outside holding time criteria without preapproval from the project manager. Consider using the Solid Phase Extraction Cleanup procedure if sample contains fuel interference.</p>
<b>Recovery Criteria for Internal Standard</b>	Absolute recovery (quantitation based on recovery standard) 50 – 120%.
<b>Recovery Standard</b>	Naphthalene-d8 added post-extraction.
<b>Recovery Criteria for Recovery Standard</b>	Area count -50 to +100% relative to the continuing calibration verification.
<b>Additional Surrogates – Pre-extraction</b>	A minimum of one surrogate (in addition to the internal standard sulfolane-d8) should be added pre-extraction. Suggested surrogate nitrobenzene-d5. Quantitation should be based on the recovery standard. Recovery criteria to be internally derived.
<b>Extraction Sample Amounts</b>	Extraction mass sufficient to meet detection criteria, generally, 10 to 30 g should be sufficient. Extraction mass and the final extract volume must be specified in SOP. Percent solids determined and results reported on a dry-weight basis.
<b>Extraction Method</b>	Sonication or soxhlet, with preference to soxhlet.
<b>GC/MSD Method</b>	Daily tune MS consistent with laboratory quality assurance project

Key Element	Decision
<b>GC/MSD Calibration</b>	<p>plan (QAPP). Dwell Time per ion: 25 to 100 <math>\mu</math>S.</p> <p>Low calibration point needs to be able to quantitate billion 10 (ppb) at a minimum in soils. At least two calibration points need to be set below the screening level of 69 ppb. The concentration of the internal standard, sulfolane-d8, should be the same in all calibration standards and sample extract.</p>
<b>Quant/Qual Ions for Sulfolane</b>	<p>Quantification ion on m/z 120; Qualifier ions (QI) at m/z 41, 55 and 56. All four ions should be used and QI ratios defined.</p>
<b>Ion Ratios (sulfolane and sulfolane-d8)</b>	<p>Relative intensities of the qualifier ions need to be within 30% of the daily reference standard for two of three QI. If they do not meet ratio criteria in at least two QI, attempt to resolve the matrix interference. If matrix interference cannot be resolved, QI failure must be reported to DEC Project Managers within 1 week of failure. Ion ratios must be displayed in the raw data.</p> <p>If &lt;25% resolution relative to the sulfolane-d8 peak cannot be obtained attempt the following:</p> <ol style="list-style-type: none"> <li>1. Optimize chromatographic conditions in an attempt to enhance resolution, or</li> <li>2. Attempt additional cleanup techniques to remove the apparent interferences.</li> </ol> <p>If items 1 or 2 fail to achieve less than 25% resolution then for the primary quantitation ion (m/z 128) between sulfolane-d8 and an adjacent peak (naphthalene or other non-target analyte), the quantitation ion for sulfolane-d8 in the impacted sample should be switched to m/z 46 as long as baseline resolution is obtained for m/z 46. In these cases, quantitation using m/z 46 for sulfolane-d8 should be used for both sulfolane (as the internal standard) and</p>

Key Element	Decision
	<p>sulfolane-d8 in the impacted sample as well as all associated calibration standards, calibration check standards, and quality control samples (laboratory control samples, method blanks, matrix spikes, laboratory duplicates, instrument blanks, etc.). As a result, some initial calibration standards, calibration check standards and quality control samples may need to be quantified and reported using both m/z 46 and m/z 128 for quantitation. Also, in these cases, the laboratory is not required to inform DEC of the presence of interference. Separation of sulfolane-d8 from the interferent should be defined, documented, and submitted as part of the final laboratory report, through chromatographs and ion ratio criteria.</p>
<b>Qualitative Identification</b>	<p>If significant non-target analytes precludes the proper identification of sulfolane as defined above, the laboratory must notify DEC within two business days of discovery for discussion with DEC regarding the applicability of alternate extraction procedures, such as water extraction followed by solid-phase extraction cleanup (note SOPs for alternative extraction and cleanup procedures must be submitted to and approved by DEC prior to receiving samples).</p>
<b>Detection Limit (DL)</b>	<p>DL not to exceed 5 ppb in soil. LOQ (limit of quantitation) not to exceed 10 ppb in soil. Report J-values between DL and LOQ. Annual DL and quarterly verification at 1 to 2 times the DL with 70 – 130% recovery is recommended, subject to revision. Annual DL must be immediately followed with verification.</p>
<b>Tailing criteria and integration</b>	<p>Sulfolane and sulfolane-d8 peak tailing not to exceed a factor of two calculated on the unmodified software integrated peak (consistent with tailing factor equation from SW-846 Method 8270D). Manual integration only performed if necessary. Submit before and after extracted ion current profile (EICP) documentation</p>

Key Element	Decision
	with the report.
<b>Minimum Separation Criteria</b>	For standards and as part of each initial calibration, a demonstration of 10 ng of naphthalene and 25 ng sulfolane-d8 when monitoring all target mass ions for sulfolane-d8. Full baseline chromatographic resolution must be achieved.
<b>Data flagging</b>	Data flagged based on laboratory standard practices. All flags used should be defined.
<b>Sample Collection, Handling, and Preservation</b>	<p>8 oz. glass jar or equivalent with Teflon-lined lid. Placed on ice and kept above freezing but below 6°C. Samples must be extracted within 14 days and the extract must be analyzed within 40 days of extraction.</p> <p>Storage of soil samples at less than -10°C should be considered on a project specific basis.</p>
<b>Demonstration Criteria</b>	For initial demonstration of performance, analyze a minimum of five extracted LCS QC samples at 50 ppb, each showing recoveries of $\pm 20\%$ and $RSD \leq 30\%$ . Provide Level IV data package.

**Table 2. Quality Control Requirements for Soil**

<b>Description</b>	<b>Frequency</b>	<b>Criteria</b>	<b>Corrective Action</b>
<b>Initial Calibration</b>	As needed	For regression: $r^2 \geq 0.99$ or $r \geq 0.995$ ; For average RRF: $RSD \leq 15\%$	Repeat initial calibration.
<b>Initial Calibration Verification (ICV)</b>	Immediately following Initial Calibration	Second source, %Drift $\leq 20\%$	Investigate, reanalyze, recalibrate.
<b>Continuous Calibration Verification (CCV)</b>	After MS tuning and before sample analysis, every 20 injections thereafter, and at end of analytical sequence, or within a 12 hour tuning period, whichever is shorter. CCV concentration at action level, equivalent to 50 ppb in a sample.	%Drift $\leq 20\%$	Reanalyze CCV. If second re-analysis fails then perform initial calibration. Samples that were not bracketed by acceptable CCV must be reanalyzed.
<b>Method Blank (MB)</b>	Every preparation batch/event, or 20 samples, whichever is less	< DL	Re-analyze MB. If MB > DL or LOQ but ND (<DL) in samples then no action needed. If MB > DL then re-extract and re-analyze batch. Flag data with “B” qualifier, if insufficient sample for extraction.
<b>Laboratory Control Sample (LCS)</b>	Every preparation batch/event, or 20 samples, whichever is less. LCS concentration equivalent to 50 ppb in a sample, near action level. Spiking standard is prepared in water or a	70 – 120%	Re-analyze LCS. If %R > acceptance criteria but ND (<DL) in samples no action needed. Otherwise re-extract and re-analyze batch.

Description	Frequency	Criteria	Corrective Action
	water-miscible solvent.		
<b>Surrogate (additional, i.e., nitrobenzene-d5)</b>	Each sample and QC	In-house developed limits TBD, not to exceed 50 – 150%	Re-analyze and evaluate. If second analysis fails criteria, re-exact and reanalyze.
<b>Matrix Spike/Matrix Spike Duplicate (MS/MSD) and Laboratory Duplicate Sample (DUP)</b>	An MS/MSD pair every preparation batch with 10 or more samples, up to 20. If preparation batch is less than 10 samples, analyze laboratory sample duplicate. Spiking standard is prepared in water or a water-miscible solvent.	RPD for DUP and MS/MSD $\leq 25\%$ ; MS/MSD Recovery 60 – 140%	Qualify data and narrative any obvious matrix effects.
<b>Internal Standard (sulfolane-d8) Recovery</b>	Each sample and QC. Spiking standard is prepared in water or a water-miscible solvent.	50-120%	Re-extract and flag if second re-extraction/re-analysis fails criteria.
<b>Recovery Standard (naphthalene-d8)</b>	Each sample and QC	Area Count -50 – +100% relative to the continuing calibration verification	Re-analyze and flag if second analysis fails criteria.

**Table 1. Laboratory Key Elements for Sulfolane Analysis in Plant Material**

Key Element	Decision
<b>Reference Method</b>	<p>SW846 8270D Analytical. Extraction procedure references include Headley et al. (2002) and Doucette et al. (2005). SOP shall include references for method basis.</p> <p>References:            Doucette, W.J., J.K. Chard, B.J. Moore, W.J. Staudt, and J.V. Headley. 2005. Uptake of sulfolane and diisopropanolamine (DIPA) by cattails (<i>Typha latifolia</i>). <i>Microchemical Journal</i>. Volume 81, pp. 41– 49.</p> <p>Headley, John V, Leslie C. Dickson, and Kerry M. Peru. 2002. Comparison of Levels of Sulfolane and Diisopropanolamine in Natural Wetland Vegetation Exposed to Gas-Condensate Contaminated Groundwater. <i>Communications in Soil Science and Plant Analysis</i>. Vol. 33, Nos. 15–18, pp. 3531–3544.</p>
<b>Extraction</b>	<p>Extraction procedure to include the following:</p> <ul style="list-style-type: none"> <li>• Process plant material as a whole sample and grind/cut-up to minimize the sample size (&lt;1/2” pieces in size) and to assist in the pulverization process.</li> <li>• Liquid nitrogen should be added to the pieces to freeze the vegetables until the vegetables are solidified.</li> <li>• Once frozen, sample should be pulverized using a blender (consistency of the vegetable should resemble a powder).</li> <li>• 20 grams of the pulverized, frozen vegetable should be weighed and placed into a 250 mL jar.</li> <li>• The sample should be allowed to thaw.</li> <li>• Add internal standard (sulfolane-d8) after weighing 20 g aliquot of pulverized material.</li> </ul>

Key Element	Decision
	<ul style="list-style-type: none"> <li>• Add 200 mL of DI water to the 20 gram sample and place sample on a mechanical shaker for 30 minutes</li> <li>• Vacuum filter sample through a Buchner funnel using a Whatman No 41 filter paper (or equivalent) into a 500 mL filtration flask.</li> <li>• The water portion of the sample should then be extracted with methylene chloride, in accordance with the Department approved analysis of sulfolane in water SOP.</li> </ul> <p>Previous analyses with separatory funnel backwash have shown emulsions occurring for most vegetable matrices, requiring separation by mechanical means (e.g. centrifugation). How emulsions will be handled should be addressed in the SOP.</p>
<b>Internal Standard (sulfolane-d8)</b>	<p>Internal standard in water or water-miscible solvent. Quantitation of sulfolane based on isotope dilution method using sulfolane-d8. Sulfolane-d8 added pre-extraction. Final extract concentration near the mid-point calibration concentration. Use m/z 128 for quantifying and m/z 46, 62, and 64 as qualifier ions. See ion ratio criteria below.</p> <p>In the case of dilution that results in a sulfolane-d8 that is less than 10x noise, then re-extract sample using a lesser mass. Laboratory shall notify project manager to discuss extracting or analyzing a sample outside holding time criteria. Samples should not be extracted or analyzed outside holding time criteria without preapproval from the project manager. In these cases, holding time considerations are waived.</p>
<b>Recovery Criteria for Internal Standard</b>	Absolute recovery (quantitation based on recovery standard) 50 – 120%.
<b>Recovery Standard</b>	Naphthalene-d8 added post-extraction.
<b>Recovery Criteria for Recovery Standard</b>	Area count -50 to +100% relative to the continuing calibration verification.

Key Element	Decision
<b>Extraction Sample Amounts</b>	Extraction mass sufficient to meet detection criteria, generally, 10 to 30 g should be sufficient. Extraction mass and the final extract volume must be specified in SOP.
<b>GC/MSD Method</b>	Daily tune MS consistent with laboratory quality assurance project plan (QAPP). Dwell Time per ion: 25 to 100 $\mu$ S.
<b>GC/MSD Calibration</b>	Low calibration point needs to be able to quantitate billion 10 (ppb) at a minimum in plant material. At least two calibration points need to be set below the screening level of 62 ppb. The concentration of the internal standard, sulfolane-d8, should be the same in all calibration standards and sample extract.
<b>Quant/Qual Ions for Sulfolane</b>	Quantification ion on m/z 120; Qualifier ions (QI) at m/z 41, 55 and 56. All four ions should be used and QI ratios defined.
<b>Ion Ratios (sulfolane and sulfolane-d8)</b>	<p>Relative intensities of the qualifier ions need to be within 30% of the daily reference standard for two of three QI. If they do not meet ratio criteria in at least two QI, attempt to resolve the matrix interference. If matrix interference cannot be resolved, QI failure must be reported to DEC Project Managers within 1 week of failure. Ion ratios must be displayed in the raw data.</p> <p>If &lt;25% resolution relative to the sulfolane-d8 peak cannot be obtained attempt the following:</p> <ol style="list-style-type: none"> <li>1. Optimize chromatographic conditions in an attempt to enhance resolution, or</li> <li>2. Attempt additional cleanup techniques to remove the apparent interferences.</li> </ol> <p>If items 1 or 2 fail to achieve less than 25% resolution then for the primary quantitation ion (m/z 128) between sulfolane-d8 and an adjacent peak (non-target analytes), the quantitation ion for</p>

Key Element	Decision
	<p>sulfolane-d8 in the impacted sample should be switched to m/z 46 as long as baseline resolution is obtained for m/z 46. In these cases, quantitation using m/z 46 for sulfolane-d8 should be used for both sulfolane (as the internal standard) and sulfolane-d8 in the impacted sample as well as all associated calibration standards, calibration check standards, and quality control samples (laboratory control samples, method blanks, matrix spikes, laboratory duplicates, instrument blanks, etc.). As a result, some initial calibration standards, calibration check standards and quality control samples may need to be quantified and reported using both m/z 46 and m/z 128 for quantitation. Also, in these cases, the laboratory is not required to inform DEC of the presence of interference. Separation of sulfolane-d8 from the interferent should be defined, documented, and submitted as part of the final laboratory report, through chromatographs and ion ratio criteria.</p>
<b>Detection Limit (DL)</b>	<p>DL not to exceed 5 ppb in plant material. LOQ (limit of quantitation) not to exceed 10 ppb in plant material. Report J-values between DL and LOQ. Annual DL and quarterly verification at 1 to 2 times the DL with 70 – 130% recovery is recommended, subject to revision. Annual DL must be immediately followed with verification.</p>
<b>Tailing criteria and integration</b>	<p>Sulfolane and sulfolane-d8 peak tailing not to exceed a factor of two calculated on the unmodified software integrated peak (consistent with tailing factor equation from SW-846 Method 8270D). Manual integration only performed if necessary. Submit before and after extracted ion current profile (EICP) documentation with the report.</p>
<b>Minimum Separation Criteria</b>	<p>For standards and as part of each initial calibration, a demonstration of 10 ng of naphthalene and 25 ng sulfolane-d8 when monitoring</p>

Key Element	Decision
	all target mass ions for sulfolane-d8. Full baseline chromatographic resolution must be achieved.
<b>Data flagging</b>	Data flagged based on laboratory standard practices. All flags used should be defined.
<b>Sample Collection, Handling, and Preservation</b>	Appropriate sample containers should be used. Placed on ice and kept above freezing but below 6°C. Samples must be extracted within 14 days and the extract must be analyzed within 40 days of extraction. Archive sample at conclusion of initial sample extraction. Archive remaining residual sample in a freezer at -20°C until such time the sample would normally be disposed. At that time, contact Project Manager for further instruction regarding continuing retaining or disposal of sample.
<b>Demonstration Criteria</b>	For initial demonstration of performance, analyze a minimum of five extracted LCS QC samples at 50 ppb, each showing recoveries of $\pm 20\%$ and $RSD \leq 30\%$ . Provide Level IV data package.

**Table 2. Quality Control Requirements for Plant Material**

<b>Description</b>	<b>Frequency</b>	<b>Criteria</b>	<b>Corrective Action</b>
<b>Initial Calibration</b>	As needed	For regression: $r^2 \geq 0.99$ or $r \geq 0.995$ ; For average RRF: $RSD \leq 15\%$	Repeat initial calibration.
<b>Initial Calibration Verification (ICV)</b>	Immediately following Initial Calibration	Second source, %Drift $\leq 20\%$	Investigate, reanalyze, recalibrate.
<b>Continuous Calibration Verification (CCV)</b>	After MS tuning and before sample analysis, every 20 injections thereafter, and at end of analytical sequence, or within a 12 hour tuning period, whichever is shorter. CCV concentration at screening level, equivalent to 62 ppb in a sample.	%Drift $\leq 20\%$	Reanalyze CCV. If second re-analysis fails then perform initial calibration. Samples that were not bracketed by acceptable CCV must be reanalyzed.
<b>Method Blank (MB)</b>	Every preparation batch/event, or 20 samples, whichever is less	< DL	Re-analyze MB. If MB > DL or LOQ but ND (<DL) in samples then no action needed. If MB > DL then re-extract and re-analyze batch. Flag data with “B” qualifier, if insufficient sample for extraction.
<b>Laboratory Control Sample (LCS)</b>	Every preparation batch/event, or 20 samples, whichever is less. LCS concentration at screening level, equivalent to 62 ppb in a sample. Spiking standard	70 – 120%	Re-analyze LCS. If %R > acceptance criteria but ND (<DL) in samples no action needed. Otherwise re-extract and re-analyze batch.

Description	Frequency	Criteria	Corrective Action
	is prepared in water or a water-miscible solvent.		
<b>Matrix Spike/Matrix Spike Duplicate (MS/MSD) and Laboratory Duplicate Sample (DUP)</b>	An MS/MSD pair every preparation batch with 10 or more samples, up to 20. If preparation batch is less than 10 samples, analyze laboratory sample duplicate. Spiking standard is prepared in water or a water-miscible solvent.	RPD for DUP and MS/MSD $\leq 25\%$ ; MS/MSD Recovery 60 – 140%	Qualify data and narrative any obvious matrix effects.
<b>Internal Standard (sulfolane-d8) Recovery</b>	Each sample and QC. Spiking standard is prepared in water or a water-miscible solvent.	50-120%	Re-extract and flag if second re-extraction/re-analysis fails criteria.
<b>Recovery Standard (naphthalene-d8)</b>	Each sample and QC	Area Count -50 – +100% relative to the continuing calibration verification	Re-analyze and flag if second analysis fails criteria.