

Sulfolane in Water and Soil Samples – PBM

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| Parameter | Sulfolane in Water and Soil | | | |
| Analytical Method | Analysis by Gas or Liquid Chromatography with Mass Spectrometric detection (GC/MS or LC/MS or LC/MS/MS). | | | |
| Introduction | <p>Sulfolane is a colourless, highly polar, water miscible compound with good chemical and thermal stability. It has a low volatility and Henry's Law constant. Sulfolane can be subject to aerobic biodegradation under appropriate conditions.</p> <p>Sulfolane has traditionally been used in the extraction of aromatics and in the removal of acid gases from a natural gas stream. Due to its combination of physical and chemical properties, sulfolane has also been used as an extraction distillation solvent, polymer solvent, polymer plasticizer, polymerization solvent, and in electronic/electrical applications (CCME 2006).</p> | | | |
| Method Summary | <p>Water and soil samples are extracted using dichloromethane after addition of a known amount of deuterium labeled sulfolane-d8 isotope (used either as isotope dilution standard or surrogate).</p> <p>Instrumental analysis is by Gas or Liquid Chromatography with Mass Spectrometric detection (GC/MS, LC/MS, or LC/MS/MS).</p> <p>This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.</p> | | | |
| MDL(s) and EMS Analyte Codes | <u>Analyte</u> Sulfolane | <u>CAS Number</u> 126-33-0 | <u>Approx. MDL</u> 10 ug/L water 0.05 mg/kg soil | <u>EMS Analyte Code</u> not yet defined |
| EMS Method Code(s) | ***Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes. | | | |
| Matrix | Freshwater, Groundwater, Drinking water, Soil and Sediment | | | |
| Interferences and Precautions | <p>Solvents, reagents, glassware and other sample processing materials must be demonstrated to be free from interferences by analyzing a method blank. Interferences may also be co-extracted from water samples. Chromatographic co-elution of such compounds, if they yield fragment ions common to an analyte, could potentially result in the reporting of artificially high results.</p> <p>Contamination of the analytical system can occur after high level samples are analyzed. Analysts should be aware of the degree of carryover that occurs on their instrument system, and should take appropriate steps to prevent the occurrence of false positives.</p> | | | |
| Sample Handling and Preservation | <p>Collect water samples in glass containers with Teflon lined lids (e.g. 250 mL amber glass).</p> <p>Collect soil samples in 120 mL or 250 mL glass jars with Teflon-lined lids.</p> <p>Preservation: Water samples may be preserved with solid sodium bisulfate (0.5% wt/vol).</p> | | | |
| Stability | <p>Holding Times:</p> <p>Waters: Water samples must be extracted within 7 days of the sampling if unpreserved, or within 14 days if preserved with sodium bisulfate. Extracts must be analyzed within 40 days of extraction.</p> <p>Soils: Soil samples must be extracted within 14 days of sampling. Extracts must be analyzed within 40 days of extraction.</p> <p>Storage: Refrigerate water and soil samples at ≤ 6°C (do not freeze). Store extracts refrigerated at ≤ 6°C or in a freezer at ≤ -10°C.</p> | | | |

Procedure

Water Sample Extraction Procedure

1. Add 100 mL of water sample into a clean 250 mL extraction bottle.
2. Add an appropriate amount of d8-sulfolane for use either as surrogate compound or as isotope dilution internal standard. If d8-sulfolane is used for isotope dilution purposes, then also add an appropriate amount of an alternate compound with similar chemical characteristics for use as a surrogate (e.g. dimethyl sulfone or diethyl sulfone).
3. Ensure pH of water sample is < 2 .
4. Add 100 mL of dichloromethane.
5. Shake sample for at least 1 hour on a vigorous mechanical shaker apparatus.
6. Allow phases to separate for approximately 5 minutes. Emulsions can be broken using a centrifuge if necessary.
7. Transfer the dichloromethane through a funnel filled with sodium sulfate into a solvent evaporation flask (e.g. turbvap tube or rotary evaporation flask).
8. Add another 100 mL of dichloromethane and repeat steps 4 to 6.
9. Add 2 mL of isooctane keeper solvent to the combined extracts and concentrate to 1.00 mL.
10. If required, add an appropriate amount of internal standard (e.g. dimethyl sulfone or diethyl sulfone). This step is not required if isotope dilution calibration with d8-sulfolane internal standard is used.
11. Analyze by GC/MS, LC/MS, or LC/MS/MS using internal standard with a minimum 4-point calibration.

Soil Sample Extraction Procedure

1. Add 10 - 12 g of field-moist soil sample into a 50mL centrifuge tube. Determine the dry weight extracted as a function of measured soil moisture content.
2. Add 1mL of deionized water to sample and vortex vigorously for 10 seconds.
3. Add an appropriate amount of d8-sulfolane for use either as surrogate compound or as isotope dilution internal standard. If d8-sulfolane is used for isotope dilution purposes, then also add an appropriate amount of an alternate compound with similar chemical characteristics for use as a surrogate (e.g. dimethyl sulfone or diethyl sulfone).
4. Add 10 mL dichloromethane and shake for 15 minutes using a vigorous mechanical shaker.
5. Add approximately 10 g of 1:1 anhydrous sodium sulfate and sodium chloride.
6. Shake for another 15 minutes by vigorous mechanical shaker.
7. Centrifuge sample at $\sim 2,000$ rpm for 5 minutes or until clarified.
8. Place 1.00 mL of extract into autosampler vial.
9. If required, add an appropriate amount of internal standard (e.g. dimethyl sulfone or diethyl sulfone). This step is not required if isotope dilution calibration with d8-sulfolane internal standard is used.
10. Analyze by GC/MS, LC/MS, or LC/MS/MS using internal standard with a minimum 4-point calibration.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements, and apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80-120% or better for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or $\leq 15\%$ relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

| Summary of QC Requirements | | |
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| QC Component | Minimum Frequency | Minimum Data Quality Objectives |
| Internal Standard Area Checks | All samples and QC (not required if isotope dilution with d8-sulfolane is used) | Peak area counts for all internal standards in all injections must be 50-200% of the initial calibration (average or mid-point) or initial CVS |
| Isotope Dilution Standards | All samples (if used) | Absolute recovery of all isotope dilution standards used for recovery correction must be 10% - 130%. |
| Surrogate Compounds | All samples | 50 - 140% recovery |
| Calibration Verification Standard (CVS) – 2 nd source | 1 per initial calibration | 80 - 120% recovery |
| Method Blank (MB) | One per batch (max 20 samples) | Less than reported DL |
| Lab Control Sample (LCS) | One per batch (max 20 samples) | 70 – 130% (waters) 60 – 140% (soils) |
| Lab Duplicates (DUP) | One per batch (max 20 samples) | 30% RPD (waters) 50% RPD (soils) [or within 2x reported DL for low level results] |
| Matrix Spike (MS) or Reference Material (RM) | One per batch (max 20 samples) | 50 – 140% |
| Continuing Calibration Verification (CCV) | At least every 12 hours (max 20 samples), and at end of each batch. | 80 - 120% for mid-level standards |
| If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount. | | |

Prescribed Elements

The following components of this method are mandatory:

1. Mass spectrometric detection must be used. GC/MS, LC/MS, or LC/MS/MS are all acceptable.
2. Sulfolane-d8 must be added to all samples prior to sample preparation or extraction, either as an isotope dilution standard or as a surrogate. If sulfolane-d8 is used as an isotope dilution internal standard (i.e. for recovery correction purposes), then an alternate compound with similar chemical characteristics to sulfolane must be used as surrogate (e.g. dimethyl sulfone or diethyl sulfone).
3. Stated calibration requirements must be met. Calibration standards must be solvent-matched with sample extracts unless equivalency is demonstrated.
4. Sample container materials, preservation, storage, and hold time requirements may not be modified. Samples analyzed beyond the stated holding time must be qualified. Refer to latest version of "BC MOE Sample Preservation and Hold Time Requirements" for updates.

5. All stated Performance Requirements and Quality Control requirements must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

1. Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), United States Environmental Protection Agency Office Revision 5, July 2014.
2. Method 3511: Organic Compounds in water by Microextraction, United States Environmental Protection Agency Office November 2002.
3. CCME 2006. Canadian Environmental Quality Guidelines for Sulfolane: Water and Soil. Scientific Supporting Document, PN 1368.

Revision History

Sept 15, 2017 First version added to BC Lab Manual in support of 2017 CSR updates.