

Sulfolane in Water and Soil Samples by GC/MS - PBM

Parameter	Sulfolane in Water and Soil			
Analytical Method	Analysis by Gas Chromatography/Mass Spectroscopy (GC/MS).			
Introduction	<p>Sulfolane is a colourless, highly polar compound with good chemical and thermal stability. It has a low volatility and Henry's Law constant. Industrially, sulfolane is synthesized by hydrogenation of 3-sulfolene (C₄H₆SO₂), which is prepared through the reaction of butadiene (C₄H₆) and Sulphur dioxide (SO₂). The total worldwide production of sulfolane was estimated between 18,000 and 36,000 tones per year.</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.</p>			
Method Summary	<p>Water samples are extracted using a known volume of Acetonitrile/Dichloromethane with a known amount of deuterium labeled d8-sulfolane isotope added prior to extraction. Salt is added to the extraction to assist with separation of the Acetonitrile/DCM and water phase and the final extract is dried with magnesium or sodium sulfate.</p> <p>Soil samples are extracted with a known volume of Acetonitrile/Dichloromethane with a known amount of deuterium labeled d8-sulfolane isotope added prior to extraction.</p> <p>Samples are analyzed by Gas Chromatography/Mass Spectroscopy with a ZB-Semivolatiles column.</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	Analyte Sulfolane	CAS Number 126-33-0	Approx. MDL 0.01 ug/L water 10 mg/kg soil	EMS Analyte Code defined on request
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>Sampling should be done by qualified personnel. Samples must be collected and stored such that degradation or alteration of the sample is minimized. Collect the sample in two 40 ml glass vials or one 250 ml clean glass or amber high density polyethylene container, and tightly cap immediately after sampling.</p> <p>Soil samples require 120 ml or 250 ml glass jar with a Teflon-lined lid containing at least 50 g of soil.</p>			

Preservation: Water samples can be preserved with 0.5% sodium bisulfate

Stability

Holding Time:

Water samples are to be extracted as soon as possible upon receipt and within 7 days of the original sampling date, or 14 days if preserved with sodium bisulfate. The analysis of extracts is to be completed within 30 days of the extraction date.

Soil samples are to be extracted within 14 days of the original sampling date and the analysis of extracts is to be completed within 10 days of the extraction date.

Storage: Refrigerate in the dark at $\leq 6^{\circ}\text{C}$ (do not freeze)

Procedure

Sulfolane extraction salt: Mix 10:1 sodium sulphate : sodium chloride by weight

Liquid/Liquid Extraction

Transfer 30mL of water sample into 40mL vial with 10g of Sulfolane extraction salt, add Sulfolane d-8 internal standard and vortex for 1 minute. Add 6 mL of 2:1 Acetonitrile/DCM mix, vortex for 1 minute, shake on a wrist action shaker for 30 minutes then allow to settle or centrifuge at 1000rpm for 5 minutes.

Transfer sample extract (top layer) into culture tube with anhydrous sodium sulphate, shake for 30 minutes then centrifuge at 1000rpm for 5 minutes.

Transfer 1.00 mL of dry sample extract into a GC vial. Analyze extract for Sulfolane by GC/MS.

Solids Extraction

Transfer 5.0g of solids sample into a 40 mL vial. Add 10mL of acetonitrile and one scoop of anhydrous sodium sulphate to all vials. Shake samples for 30 minutes on a wrist action shaker then allow to settle or centrifuge at 1000rpm for 5 minutes. Transfer 1mL of acetonitrile extract into pre-labelled GC vial, add 0.5mL of DCM and internal standard Sulfolane d-8, cap and shake. The extract can be analyzed for Sulfolane by GC/MS.

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 better than 20% 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		
QC Component	Minimum Frequency	Minimum Data Quality Objectives
Internal Standard Area Checks	All samples and QC	Within 50% of initial calibration or last CCV

Surrogate Compounds	Sulfolane-d8	80 - 120% recovery
Calibration Verification Standard (CVS)	1 per initial calibration	80 - 120% recovery
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS) or Reference Material (RM)	One per batch (max 20 samples)	70 – 130%
Lab Duplicates (DUP)	One per batch (max 20 samples)	20% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS)	One per batch (max 20 samples)	60 – 140%
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch.	80 - 120% recovery 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. Sample holding times must be adhered to. Samples analyzed beyond the stated holding time must be qualified.
2. An internal standard, Sulfolane-d8 is required to be added to all samples prior to analysis. Stated calibration requirements must be met. Calibration standards must be solvent-matched with samples unless equivalency is demonstrated.
3. Samples that exceed the calibration range must be diluted and re-analyzed, or reported as estimated or minimum values.
4. 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. Laboratories must disclose to their clients where modified or alternative methods are employed.

- References**
1. Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), United States Environmental Protection Agency Office January 1998.
 2. Method 3511: Organic Compounds in water by Microextraction, United States Environmental Protection Agency Office November 2002.

Revision History Mar 17, 2017 First version of method.