

Glycols in Soil and Water - PBM

Parameter Glycols in soil and water.

Analytical Method Direct injection – Gas chromatography with Flame Ionization Detection (GC/FID) - PBM.

Introduction This method is applicable to the quantitative determination of glycols in soil and water.

Method Summary A portion of the water or aqueous soil extract is transferred to an autosampler vial, and is injected into the GC inlet (on-column or splitless), for direct analysis by GC/FID using a polar stationary phase (e.g. DB-Wax or DB-624 or equivalent). This method yields reporting limits that are suitable to meet BC CSR standards. If lower reporting limits are required, samples may be analyzed by GC/MS or by HPLC/MS (US EPA Method 8321B) with a large volume injection.

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.

MDL(s) and EMS Analyte Codes	<u>Analyte</u>	<u>CAS No.</u>	<u>Approx. Soil MDL (µg/g)</u>	<u>Approx. Water MDL (µg/L)</u>	<u>EMS Analyte Code</u>
		Ethylene glycol	107-21-1	5	2,000
	Propylene glycol, 1,2-	57-55-6	5	2,000	P020
	Diethylene glycol	111-46-6	5	2,000	E220
	Triethylene glycol	112-27-6	5	2,000	E320

Note: This method may also be applicable to the analysis of other BC CSR substances such as glycol monoalkyl ethers.

EMS Method Code GLYC (Glycols in Soil and Water by GC/FID)
***Refer to [EMS Parameter Dictionary](#) on the ministry website for all current EMS codes.

Matrix
Soil: Soil, Sediment, Sludge, Solid waste.
Water: Freshwater, Seawater, Groundwater, Wastewater.

Interferences and Precautions

1. Glycols by GC-FID may be subject to interferences by any substance with similar boiling points and chromatographic characteristics that may co-elute under the conditions of the analysis (e.g. by alkanolamines or petroleum hydrocarbons). Matrix spikes and/or GC/MS confirmation is recommended to assist with correct identification of target compounds in samples if co-eluting interferences are suspected.
2. Hydrocarbon interferences may be removed with a hexane pre-extraction cleanup step, using brief physical agitation.
3. Propylene glycol and ethylene glycol can be difficult to separate when one analyte is found at significantly higher concentration than the other.
4. Contamination of the analytical system can occur after high level samples are analyzed. Analysts should be aware of the degree of carry-over that occurs on their instrument and should take appropriate steps to prevent the occurrence of false positives.
5. Samples with high salt or total dissolved solids content can cause contamination of the GC inlet and column, resulting in degradation of chromatographic performance.

Sample Handling and Preservation

Sample Containers:
Soil: Glass jar with Teflon (or foil) lined lid, 125 – 250 mL recommended.
Water: 40-60 mL glass vial with Teflon lined lid.

Preservation:
Soil: Soil samples are not chemically preserved.

Water: Water samples may be preserved with NaHSO₄, HCl, or H₂SO₄ to pH <2 to extend hold times.

Storage: Store samples at ≤ 10°C during shipment to the laboratory and at ≤ 6°C at the laboratory. Avoid freezing to prevent sample breakage.

Stability

Holding Time:

Soil: Analyze soil samples within 14 days after collection. If organic solvent extraction is conducted, samples must be extracted within 14 days, and extract hold time is 40 days.

Water: Analyze unpreserved water samples within 7 days after collection. Acid preservation extends hold times to 14 days from sampling.

Where holding times are exceeded, test results must be qualified.

Procedure

Soils: Soil samples are subjected to aqueous extraction prior to direct injection of the aqueous extract. Soils are extracted using deionized water using a 2:1 ratio of water to field-moist soil. Soil samples are physically agitated using a mechanical shaker for a minimum of 30 minutes. Suspended solids may be removed by filtration, or sample extracts may be centrifuged until clear. Moisture content analysis is performed on a separate aliquot. Test results are corrected for moisture content and are reported on a dry weight basis. Include sample moisture content in the aqueous extract volume for data calculation purposes.

Waters: Water samples are analyzed by direct aqueous injection by gas chromatography with flame ionization detection (GC/FID). Suspended solids may be removed by filtration, or samples may be centrifuged until clear.

Detailed instrumental analysis procedures are not provided for this method. The procedures described in EPA Method 8015D (see references) are suitable for general guidance.

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
Method Blank (MB) - matrix specific	One per batch (max 20 samples)	Less than reported DL
Calibration Verification Standard (CVS) – 2 nd Source	One per initial calibration	85 – 115%
Continuing Calibration Verification (CCV) – mid-level	At least every 12 hours (max 20 samples), and at end of each batch.	80 – 120%

Laboratory Control Sample (LCS)	One per batch (max 20 samples)	60-140% (soils) 70-130% (water)
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	50% RPD (soils) 30% RPD (water) [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	60-140%
Surrogate Compounds	Recommended	Not specified
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.		

Recommended surrogate compounds include tetramethylene glycol or 1,3-propylene glycol.

Prescribed Elements The following components of this method are mandatory:

1. Calibrations must consist of a minimum of 4 calibration standards.
2. For soil extractions, soil moisture content must be accounted for in the extraction solvent volume if using extraction by water or a water-miscible solvent.
3. For FID analysis, at least 80% baseline chromatographic separation must be achieved for all target parameters in calibration standards (valley height of peak overlap must not exceed 20% of maximum peak height).
4. Where sample extracts require filtration or pre-extraction hexane cleanup, QC samples must be processed in the same manner.
5. All stated performance requirements and quality control requirements must be met.
6. 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.

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 US EPA method 8015D, Nonhalogenated organics using GC/FID (Revision 4, June 2003).

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