Diisopropanolamine (DIPA) in Water and Soil Samples by HPLC - PBM

Parameter

Diisopropanolamine (DIPA) in Water and Soil

Analytical Method

High Performance Liquid Chromatography with UV or Fluorescence Detection.

Introduction

DIPA is a secondary alkanolamine which is a hygroscopic polar solvent that is completely miscible in water. DIPA has a wide variety of applications such as a solvent used in the Sulfinol process by the petroleum industry to remove acid gases from natural gas streams through chemical absorption. The neutralizing capacity of DIPA salts, their high foaming properties and low level of skin irritation allow them to be commonly used as components of cosmetics, personal care products and detergents (CCME 2006).

Method Summary

This method uses a derivatization step which transforms mono and diethanolamines into products with strong UV absorbance and fluorescence properties by reaction with 9-fluorenylmethyloxycarbonyl (FMOC-CL). The derivatized products are injected directly into an HPLC system with separation on an octadecylsilyl (C18) column and using UV or fluorescence detection.

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

Analyte	CAS Number	Approx. MDL	EMS Analyte Code
Diisopropanolamine (DIPA)	110-97-4	100 ug/L (waters) 0.10 mg/kg (soils)	defined on request

EMS Method Code(s)

***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

Solvents, reagents, glassware and other sample processing materials must be demonstrated to be free from interferences by analysis of a method blank.

Any UV absorptive or fluorescent compound with similar retention time to FMOC-CL derivatized DIPA (including unknown FMOC-CL derivatives within a sample) can be a potential interference by this method. Retention time alone does not constitute definitive proof of chemical identity by this method. If interference is suspected, analysis by an alternate HPLC column or using mass spectrometric detection is recommended for confirmation.

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.

Sample Handling and Preservation

Sample Containers:

Water Samples: Collect water samples in Polypropylene (PP), Polyethylene Terephthalate (PET), High-Density Polyethylene (HDPE), or amber glass bottles with Teflon-lined lid. Consult the laboratory for sample volume requirements.

Soil Samples: Collect soil samples in glass jars with a Teflon-lined lids. 125 mL or 250 mL soil jars containing at least 50 g of soil are recommended.

Preservation:

Water Samples: No chemical preservation is required. Samples may be preserved with NaHSO4 or HCl to pH <2 to extend hold times (200 mg solid NaHSO4 per 40 mL sample is recommended).

Soil Samples: No chemical preservation is used.

Stability

Holding Time: DIPA is known to biodegrade under aerobic conditions when sufficient concentrations of nutrients are present. Rates of biodegradation are expected to slow at reduced temperature.

Water Samples: Extract unpreserved samples within 7 days from date of sampling. Acid preservation extends hold times to 14 days from sampling. Sample extracts may be analyzed up to 40 days after date of extraction if extracts are acidified or exchanged to an organic solvent to halt biodegradation.

Soil Samples: Extract soil samples within 14 days from date of sampling. Sample extracts may be analyzed up to 40 days after date of extraction if extracts are acidified or exchanged to an organic solvent to halt biodegradation.

Storage: Sample temperature should be chilled to ≤ 10°C immediately after sampling and during transit to the laboratory. In the laboratory, samples must be refrigerated at ≤ 6°C. Avoid freezing to prevent sample breakage.

Procedure

Borate Buffer Preparation:

Prepare a solution of 19.108 g Na2B4O7·10H2O in 1 L of water, and a second solution of 12.404 g H3BO3 and 9.925 g NaCl in 1 L of water. Mix equal volumes of the two solutions and adjust to pH 9.5 using 20% NaOH.

Derivatization Reagent Preparation:

Prepare 2.5 mmol FMOC-Cl solution in acetonitrile. Store FMOC-CL solution in a freezer at ≤ -10°C. Shelf life is one year.

Water Samples:

Filter a small portion of as-received water sample into a 10 mL test tube using a syringe and 0.45 um syringe filter. To facilitate derivatization, check or adjust sample pH such that it is >6 (add a minimum volume NaOH if necessary to avoid dilution of sample). Using a pipette, transfer 0.50 mL of the filtered sample into a 1-2 mL vial for derivatization and analysis (e.g. PTFE filter vial).

Solids Extraction:

Accurately weigh approximately 10 g of well-mixed soil (avoiding large stones or non-representative material) into a cellulose thimble, and transfer to clean Soxhlet or Dean Stark extraction glassware. Add 100 mL of 0.01 N HCl, and reflux for a minimum 1 hour period, beginning when the solvent begins to boil. Cool and filter a portion of the extract into a 10 mL test tube using a syringe and 0.45 um syringe filter. To facilitate derivatization, adjust extract pH such that it is >6 (add a minimum volume of NaOH to avoid dilution of extract). Using a pipette, transfer 0.50 mL of the filtered sample extract into a 1-2 mL vial for derivatization and analysis (e.g. PTFE filter vial).

Derivatization and Analysis:

Add 25 uL of borate buffer for every 0.5 mL of sample, add 100 uL of FMOC-CL derivatization agent of every 0.5 mL of sample. Incubate the vials under low heat for about 30 minutes.

After incubation, remove the filter vial caps and add 10 uL of 30% HCl for every 0.5 mL of sample, vortex and analyze the samples by HPLC-UV using an octadecylsilyl (C18) reverse phase column.

Calibration standards must be derivatized using the same procedure.

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 Requirements: Laboratories must demonstrate method accuracy (measured as average recovery) of 80-120% or better for Lab Control Samples or 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.

Initial Validation Requirement for Alternative Extraction Methods (Soils): For soils using alternative extraction methods to the technique described here, prepare and analyze DIPA Matrix Spike samples on a minimum of three different predominantly clay-matrix soil samples (each conducted in triplicate) to validate effectiveness of the extraction technique on samples with high cation exchange potential. Matrix Spikes must be equilibrated with soil sub-samples for at least 12 hours prior to initiating the extraction process. Average DIPA recoveries for the three or more samples evaluated must be 70-130% for this performance verification.

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**
Surrogate Compounds	Recommended	Not specified
Calibration Verification Standard (CVS) – 2nd source	1 per initial calibration	80 - 120%
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Laboratory Control Sample (LCS)	One per batch (max 20 samples)	70 – 130%
Laboratory Duplicate (DUP)	One per batch (max 20 samples)	30% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	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% 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. All stated Performance Requirements and Quality Control requirements must be met.
2. Where samples or extracts require filtration or any pre-extraction cleanup, QC samples must be processed in the same manner.
3. 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

1. CCME 2006. Canadian Environmental Quality Guidelines for Diisopropanolamine (DIPA): Water and Soil, Scientific Supporting Document, PN 1367, Canadian Council of Ministers of the Environment, 2006.
2. AE 2010. Soil and Groundwater Remediation Guidelines for Monoethanolamine and Diethanolamine, Alberta Environment, Dec 2010.

3. CCME 2016. Guidance Manual for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment, Volume 4 Analytical Methods, PN 1557, Canadian Council of Ministers of the Environment, 2016.

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