DEVELOPMENT OF AN ANALYTICAL METHOD For the ANALYSIS OF ALKANOLAMINES IN SOIL

Phase III: Method Documentation

Prepared For:
Alberta Environment

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PROJECT SUMMARY:

The development of an Analytical method for the extraction of alkanolamines involved a three-phase approach. Each phase was designed to provide information that would facilitate completion of subsequent phases.

Phase I: Literature Search

- Only a few documents related directly to the analysis of alkanolamines in soil. None of these documents dealt with the principle problem of poor analytical recoveries in most soil types.
- Several documents regarding the behavior of other polar species such as aromatic amines were useful.
- A protocol for measuring the relative sorption of polar chemicals to soil was reviewed and subsequently adopted for this project.[1]
- Several soil and clay chemistry documents were reviewed and all confirmed that in many cases clay content and type of clay were the dominant factor controlling sorption of polar compounds.

Phase II: Preliminary Testing

- Despite their strong affinity and solubility for water the results of preliminary tests confirmed that aqueous extraction often did not yield satisfactory analytical recoveries.

[1] Sorption of Nonpolar and Polar Compounds to Soils: Processes, Measurements and Experience with the Applicability of the Modified OECD-Guideline 106

- Partitioning experiments based on procedures identified in phase 1 were established. Standard mixtures of alkanolamines were allowed to remain in contact with a high organic clay soil using various solvents. Each solvent system was tested in duplicate. The relative sorption of alkanolamines was measured by monitoring the loss of alkanolamines in the liquid phase. A schematic representation of the experiment is shown in figure 1.
- The relative efficiency of each solvent was determined by monitoring the partitioning of the alkanolamines between the solvent phase and the soil. The relative efficiencies of each solvent are shown in figure 2
- An alternative presentation of the data showing the relative molar sorption of alkanolamines to the high organic clay soil is shown in figure 3.
- The addition of organic solvent modifiers did not enhance the extraction efficiencies of the solvent systems. This observation reinforced the theory that portioning of the alkanolamines into the soil organic material was not a limiting sorption process.
- Ionic solvents such as $CaCl_2$ and HCl were most effective at releasing the alkanolamines from the soil matrix. This observation suggested that charged sites on the clay surfaces were likely the limiting sorption process.
- Successive extractions with ionic solvents did not yield substantially higher alkanolamines recoveries. Therefore, multiple liquid /solid extraction steps was ruled out as a potential analytical process.
- Extractions of soil samples with mid (~5 mg/kg) and high (~20 mg/kg) alkanolamines spikes were extracted in Dean Stark extraction apparatus using a dilute solution (0.01N) HCl. This

process was designed to take advantage of both heat and continuous extraction with fresh solvent. Recoveries of the alkanolamines exceeded 75% in all cases.

- The novel analytical process has been described as an *Ionic Reflux Extraction* (IRE).
- The high temperature reflux process does release more naturally occurring organic material than desired. The release of these compounds can create an interference for the analytical determination of alkanolamines by chromatographic techniques. Low levels of MEA are particularly vulnerable to this interference.

Phase III: Method Development

The method development process focused on the use of the IRE process identified in the Phase II of the project. Several different soil types and alkanolamines spiking levels were prepared. The method was optimized with respect to sample size, solvent volume and extraction time (# of solvent cycles). The development work was carried out in Dean Stark glassware equipped with cellulose thimble holders. Optimal sample sizes and solvent volumes were found to be approximately 10 grams of soil and 150 mL of 0.01N HCl. The Draft Analytical Method can be found in Appendix 1 - *Method for the Extraction of Alkanolamines in Soil by Ionic Reflux Extraction (IRE).*

Phase IV: Performance

Phase IV of the project involves performance testing of the extraction method developed in Phase III. Performance testing will include testing of the method using replicate analysis of a variety of soil types and 3 different alkanolamine spiking levels. The deliverable from Phase IV will be a finalized method

document and report including results of the performance testing. The report will include an opinion as to whether the method developed is suitable for commercial implementation.

Figure 1. Partitioning Experiment Schematic

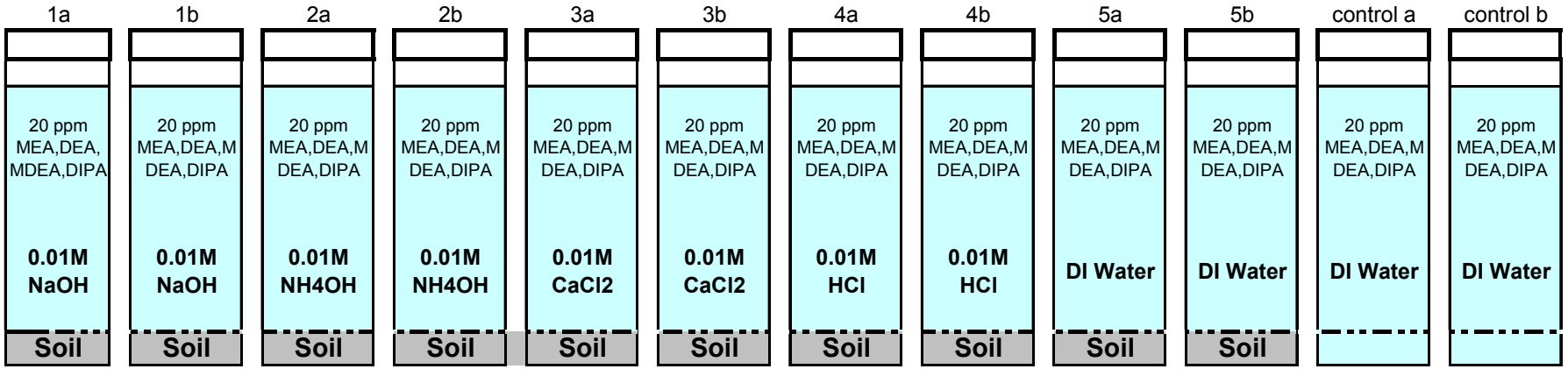


Figure 2: Alkanolamine Recovery Data

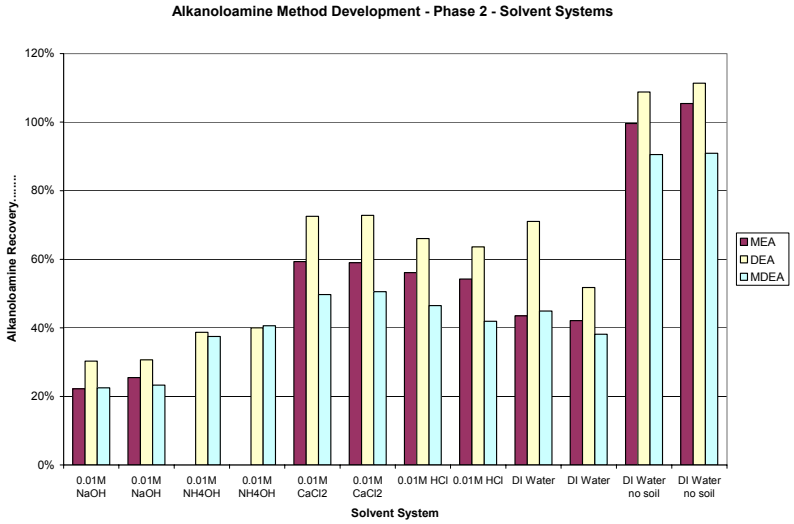
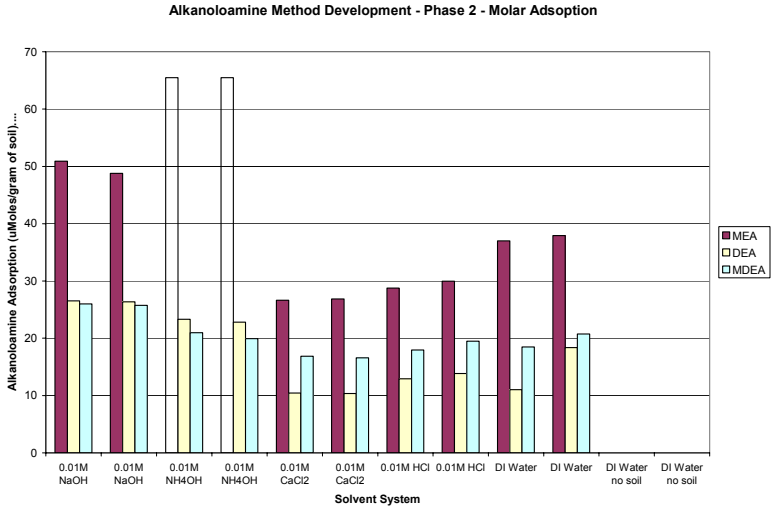


Figure 3: Alkanolamine Molar Adsorption



Maxxam Analytics Inc

Appendix 1

Draft Method

for

Extraction of Alkanolamines in Soil

by

Ionic Reflux Extraction (IRE)

Alberta Environment

Maxxam Designation: Alberta Environment Alkanolamine in Soil
Version: 1.01, February 2008

Method for the Extraction of Alkanolamines in Soil by Ionic Reflux Extraction (IRE)

1. Scope

1.1. Applicability

1.1.1 This method is applicable to the measurement alkanolamines in soil.

1.1.2 The results of the test procedure are reported in terms of mg/kg of individual alkanolamine species.

1.1.3 This method has been tested with several different alkanolamine species:

1.1.3.1 Monoethanolamine (MEA), CAS# 141-43-5
1.1.3.2 Diethanolamine (DEA), CAS# 111-42-2
1.1.3.3 Methyldiethanolamine (MDEA), CAS# 105-59-9
1.1.3.4 Diisopropanolamine (DIPA), CAS# 110-97-4

1.1.4 The method detection limits (MDL) range from 1 to 20 mg/kg on a dry soil basis. Detection limits will vary based on the alkanolamine species and the analytical technique employed following the extraction process.

1.2 Interferences

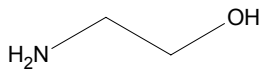
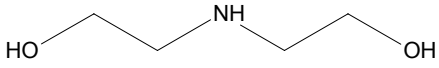
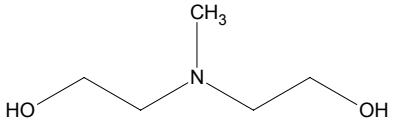
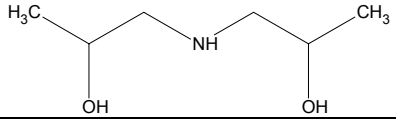
1.2.1 Interferences for the detection and quantitation of alkanolamines include any species with similar chromatographic retention time as the target alkanolamines.

1.2.2 Some interferences can be removed by pre-treating (cleaning) the soil extract with hexane.

2. Terminology

2.1. *Ionic Reflux Extraction*: A preparative technique in which acidified water is allowed to boil and recondense. The acidic condensate flows through the solid sample and is returned to the heated glassware on a continual basis.

2.2. *Alkanolamine structures*:

Common name	CAS #	Chemical structure
Monoethanolamine (MEA)	141-43-5	
Diethanolamine (DEA)	111-42-2	
Methyldiethanolamine (MDEA)	105-59-9	
Diisopropanolamine (DIPA)	110-97-4	

3. Summary of Test Method

3.1. *Sorption Processes*: Alkanolamines are bound to soil particles through several mechanisms. The three principle modes of sorption are *hydrophobic partitioning* of the neutral amine into organic material, *chemical bonding* with active surface groups and *cation exchange* of the positively charged amine with the negatively charged sites on the soil particles. Data collected during the literature search[i] and method development process[ii] identified cation exchange as the dominant mode of sorption limiting analytical recovery of alkanolamines spiked into soil samples

3.2. *Analytical Challenge*: Laboratory investigations have found alkanolamine recovery from soil samples to be generally poor and non-reproducible[iii]. Some preliminary testing (unpublished) found recoveries ranging from 10% to 60%, depending on soil type and alkanolamine species. These results were obtained using a 10:1 water extraction and mechanical agitation. Soil types with high clay contents produced the poorest alkanolamine recoveries. Organic solvent modifiers such as methanol and acetonitrile did not improve recoveries.

3.3. *Scientific Rationale and Approach*: The poor recovery in high clay soil samples suggested that cation exchange was the dominant sorption process. Strategies to

overcome the cation exchange involved elevated temperature and solvents capable of neutralizing the charged sites on the clay particles. Elevated temperatures and the use of dilute CaCl2 or HCl as extraction solvents produced improved recoveries (30 to 70% in moderate clay soils). Nonetheless, the liquid/solid extraction process seemed to reach an equilibrium point where further recovery of the alkanolamines could not occur. A reflux approach physically separates the bulk solvent from the soil and takes advantage of the equilibrium developed with fresh reflux solvent.

3.4. *Selection of extraction solvent*: Both CaCl2 and HCl showed comparable benefits as a solvent, however HCl was chosen as a reflux solvent because of its ability to partition into the vapour phase. The acidic vapour environment improves the recovery of alkanolamines from soil.

4. Significance and Use

4.1. Alkanolamines are widely used in the oil and gas sector to "sweeten" or remove acid gasses (H2S, CO2 etc) from a natural gas stream. The alkanolamine compounds most commonly used for this purpose are monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and diisopropanolamine (DIPA). These compounds may be released to the environment in the vicinity of facilities where they are used, and therefore sound environmental management of such sites requires that these compounds can be measured with confidence in soil samples.

5. Regulatory Criteria

5.1. Pending

6. Apparatus

6.1. Soxhlet Extraction Glassware or Dean Stark Extraction Glassware.
6.2. Standard laboratory glassware, Pipettes and Syringes
6.3. Cellulose extraction thimbles
6.4. Analytical balance

7. Reagents and Materials

7.1. All chemicals used for the preparation of reagents and standards are ACS grade or better unless otherwise stated.
7.2. Minimum Alkanolamine purity for standard preparation is 98%.

8. Safety

8.1. This method does not purport to address all of the safety considerations associated with its use. It is the responsibility of the user to establish appropriate health and safety practices.

9. Sample Handling, Preservation and Holding Times

Matrix	Sample Container	Minimum Volume	Holding Time (days)	Storage Conditions	Preservation
Soil	Glass or Plastic	100 grams	TBD	<10C	None
Soil Extracts	Glass or HDPE	N/A	TBD	4C	None

10. Procedure

10.1. Sample Preparation

10.1.1. Soil Extraction

10.1.1.1. Using a spatula, mix the sample as well as possible.
10.1.1.2. Accurately weigh out approximately 10 grams of soil, avoiding twigs, large stones and any other non-representative material.
10.1.1.3. Place the 10g sub-sample into a clean cellulose thimble
10.1.1.4. Place the thimble in clean Dean Stark or Soxhlet extraction glassware
10.1.1.5. Add 100mL of 0.01N HCl and reflux for 1 hour. Begin the 1-hour duration from the time the solvent begins to boil. This duration is intended to provide a minimum of 20 cycles of the extraction solvent.
10.1.1.6. Allow the extract to cool to a safe temperature before transferring to a suitable glass or HDPE extract vial.
10.1.1.7. Filter a suitable portion, approximately 10mL, of the extract is into a glass or HDPE test tube using a 0.45um syringe filter. This process will remove fine clay particles and may remove some color from the extracts.

10.1.1.8. Add 1 mL of hexane to the test tube and mix with a vortex mixer for approximately 10 seconds. Allow to separate. This hexane clean-up step helps to remove organic material that can interfere with the chromatographic measurement of alkanolamines, particularly MEA.

10.1.1.9. Using a disposable pipette or syringe, remove enough of the lower aqueous layer for the analytical determination step.

10.1.2. Matrix Spike

10.1.2.1. Prepare a suitable stock spiking solution containing each of the alkanolamines being tested. The spiking level should fall near the mid level of the analytical calibration range.

10.1.2.2. Spike a 10 gram sample of a randomly selected soil sample with a maximum of 0.5mL of the stock alkanolamine solution. Spike volumes greater than 0.5mL (5%) may alter the soil moisture content and influence the sorption of alkanolamines.

10.1.2.3. Prepare one per batch of 20 samples or less

10.1.3. Duplicates

10.1.3.1. Prepare a duplicate using a sample chosen at random.

10.1.3.2. Prepare one per batch of 20 samples or less.

10.1.4 *Method Blank*

10.1.4.1 Accurately weigh 8 -10 g of clean sand into a clean cellulose thimble and carry through the entire analytical process

10.1.4.2 Prepare one per batch of 20 samples or less

11. Calibration

11.1. This method describes the extraction process only. Calibration procedures should consistent with the laboratory analytical method employed for the determination of Alkanolamines in Water

11.2. Suitable analytical techniques include reverse phase liquid chromatography or gas chromatography.

12. Quality Control Requirements

12.1. Method Blank

12.1.1. A method blank is used to ensure there is no systematic contamination throughout the preparation and analysis procedure. The results for the blank must remain below the detection limit.

12.1.1.1. If positive blanks are detected at levels > 10% of sample values, the impacted samples must be re-extracted. Do not subtract blank.

12.2. Matrix Spike

12.2.1. A matrix spike is prepared using a sample from the set to be analyzed. The matrix spike is used to test the effectiveness of the extraction and measurement process. Acceptance limits to be determined.

12.3. Duplicates

12.3.1. The acceptable Relative Percent Difference (RPD) of the duplicate samples is 30% or less for values greater than 5 x the reporting limit (RDL).

13. Calculations and reporting

13.1. Results are quantitated using the external standard method. Alkanolamine content is reported as mg/kg. Data is typically reported on a dry basis: The report must indicate the basis of reporting.

[Amine] (mg/kg) = A × D × V / W
A = Calculated concentration in the extract (mg/L)
D = Dilution factor (if any)
V = Volume of extract (mL)
W (dry weight) = wet sample weight (g) × (1 – moisture)
(express moisture as a decimal, e.g. 8.5% → 0.085)

14. Detection Limits:

14.1. To be determined in Phase IV

15. Precision and Bias

15.1. To be determined in Phase IV

16. Attachments

16.1.

[i] DEVELOPMENT OF AN ANALYTICAL METHOD FOR THE ANALYSIS OF ALKANOLAMINES IN SOIL Phase I: Literature Review, Maxxam Analytics, November 2007,
[ii] DEVELOPMENT OF AN ANALYTICAL METHOD FOR THE ANALYSIS OF ALKANOLAMINES IN SOIL Phase II: Preliminary Testing, Maxxam Analytics, January 2008,
[iii] MAGG project report, PTAC Soil and Groundwater Forum, 2006