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

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- Project leads at Maxxam – Phil Heaton and Dr. Barry Loescher

Outline

- Background
- Alkanolamine Structure and Properties
- Partitioning Experiments
- Analytical Method
- Method Performance

Background

- Alkanolamines are widely used in Alberta's oil and gas sector to "sweeten" or remove acid gases (H₂S, CO₂ etc) from a natural gas stream.
- Most commonly used for this purpose in Alberta 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.
- Prior to releasing environmental criterion, labs must be able to measure these compounds with confidence in soil and water samples and to the detection limits required to meet the criterion – with an acceptable amount of uncertainty.

Background

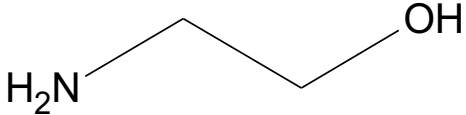
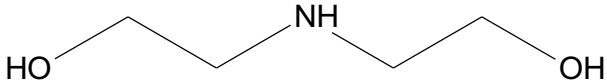
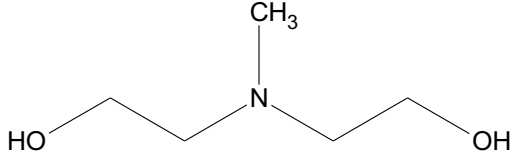
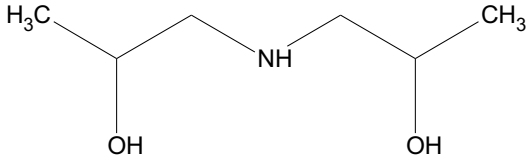
- Alkanolamines are small water-soluble molecules that create a significant analytical challenge. They can be accurately quantified once extracted into an aqueous matrix.
- Often exhibit poor recovery from various soil matrices. A need was identified for the development of a defensible and repeatable extraction procedure suitable for environmental monitoring and regulatory reporting.

Objective

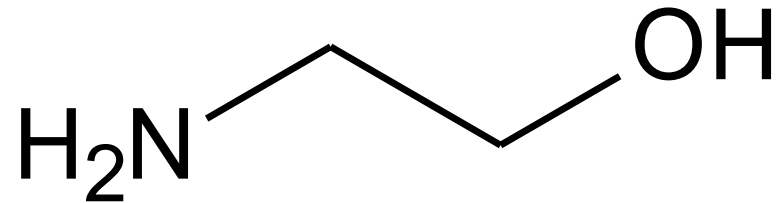
The method should have several characteristics:

1. Sufficient analytical recovery for quantitative analysis.
2. Applicable to a wide range of soil types.
3. Repeatable performance characteristics.
4. Publicly available methodology.
5. Method suitably rugged for wide application in commercial and government laboratories (ie must be able to be reproduced at small and big labs)

Alkanolamines

Compound	Structure
Monoethanolamine (MEA)	 <chem>NCCO</chem>
Diethanolamine (DEA)	 <chem>OCCNCCO</chem>
Methyldiethanolamine (MDEA)	 <chem>CCN(CC)CCO</chem>
Diisopropanolamine (DIPA)	 <chem>CC(C)CNC(C)CO</chem>

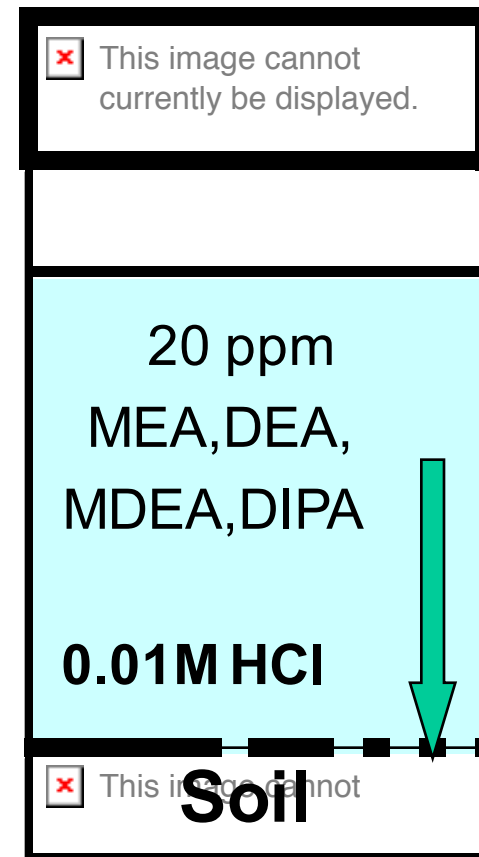
Small molecules = Big Properties



- Monoethanolamine
- Molecular Formula = C₂H₇NO
- Formula Weight = 61.08
- Surface Tension = 40 dyne/cm
- Boiling Point = 170 degrees C
- Water Miscibility = 100%

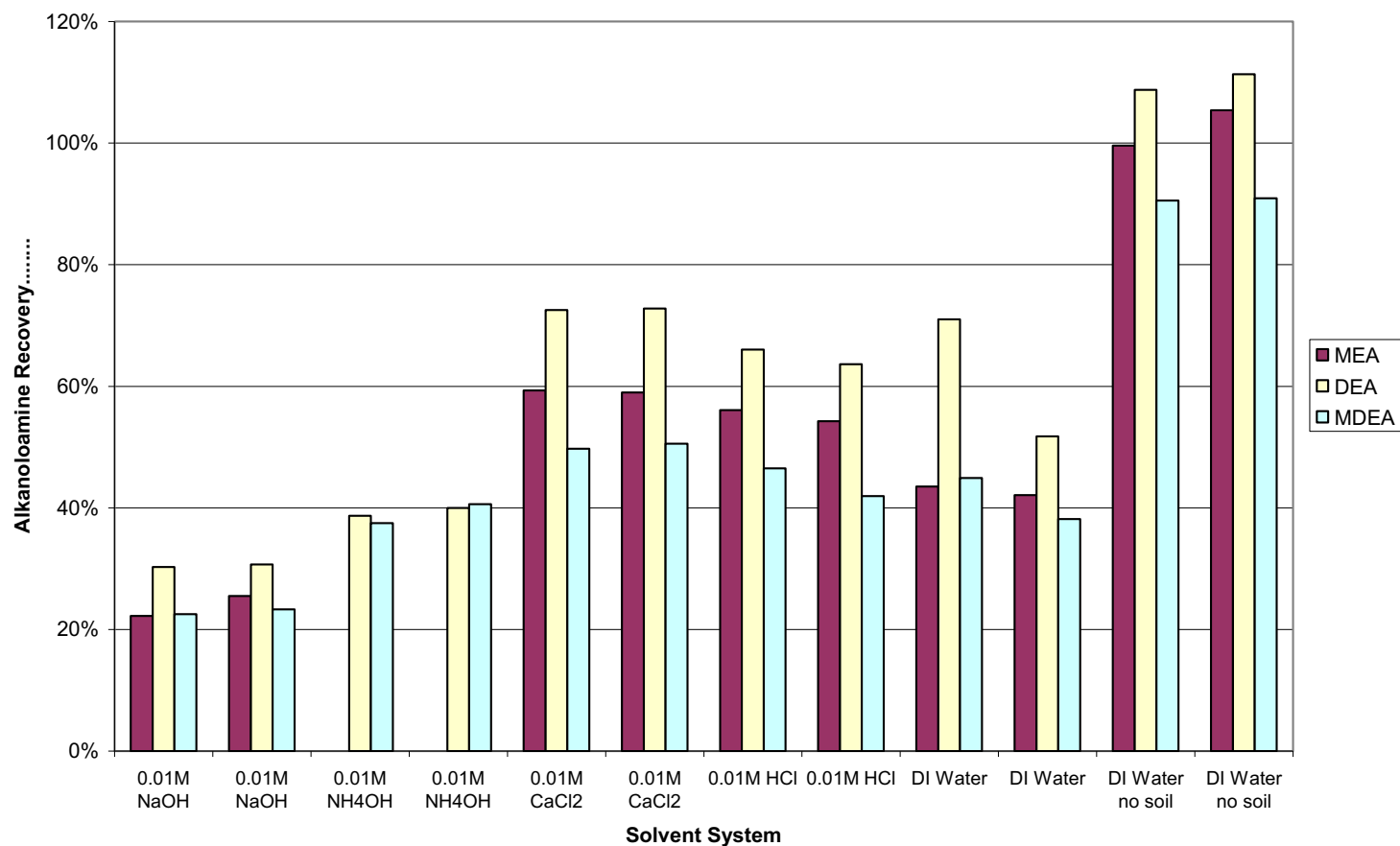
Partitioning Experiment

- Experiment designed to compare solvents (0.01 molar)
 - NaOH, NH₄OH, CaCl₂ and HCl
- Solvent samples spiked with 20 ppm of alkanolamines
- Allowed to remain in contact with soil for 48 hours
 - Loss of alkanolamines was monitored by LC
- HCl and CaCl₂ were the most effective
 - Supports cation exchange theory



Partitioning Experiment Results

Alkanoloamine Method Development - Phase 2 - Solvent Systems



Preliminary Testing Conclusions

- Cation exchange is the principal factor controlling adsorption of alkanolamines to soil.
- Organic solvents will not improve recoveries.
- Ionic solvents work best but are unlikely to achieve high recoveries with single or a few extraction cycles.

Method Development

- Elected to combine ionic solvents with temperature and multiple extraction cycles
- **Ionic Reflux Extraction (IRE)**
 - Solvent 0.01N HCl
 - Apparatus: Dean Stark or Soxhlet
- **Hexane Clean Up**
- **Measurement**
 - Liquid Chromatography (IC or LC)
 - Pulsed Amperometric Detection

Maxxam Designation: Alberta Environment Alkanolamine in Soil
Version: 1.02, March 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.

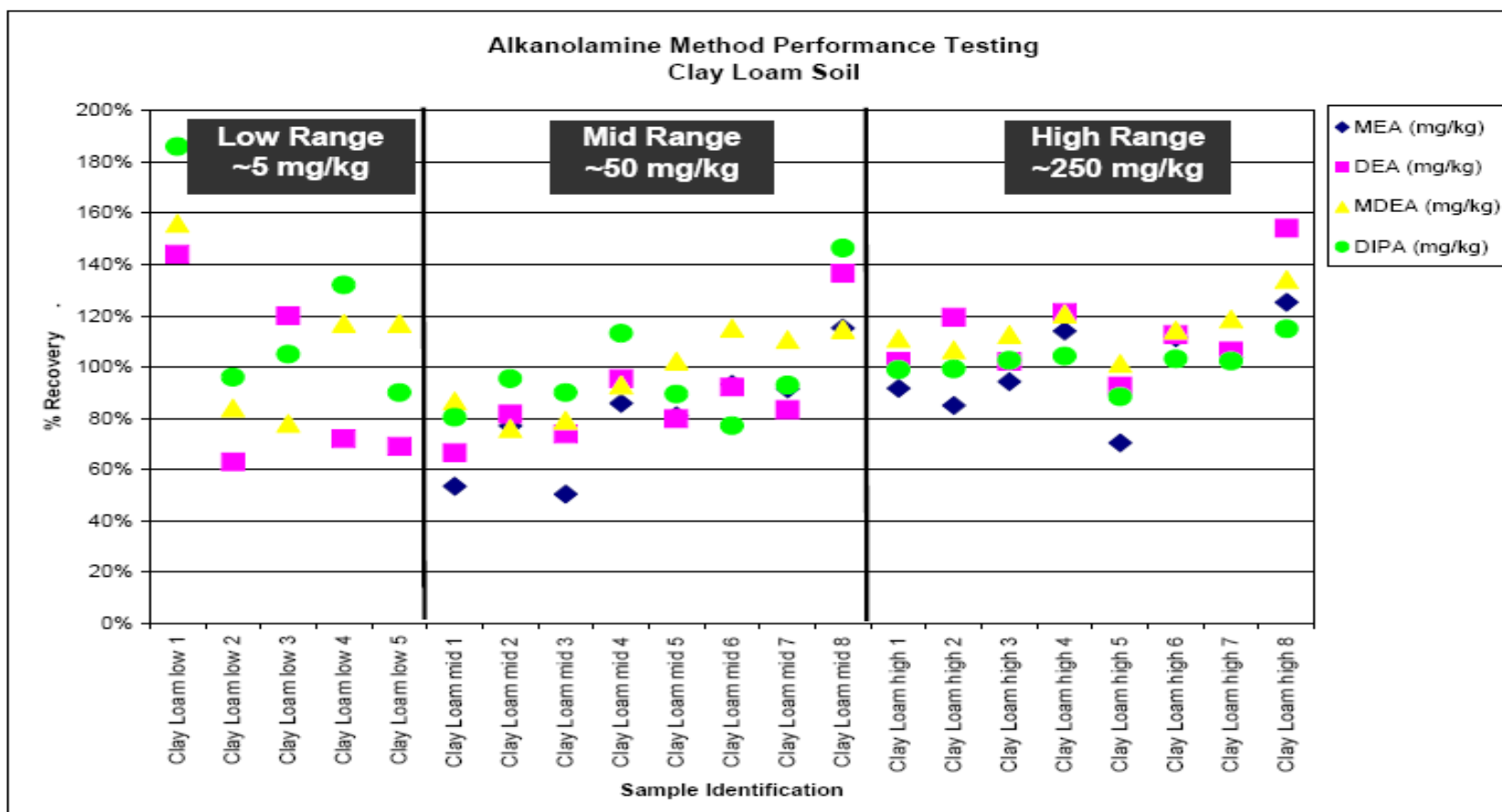
2. Terminology

- 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.

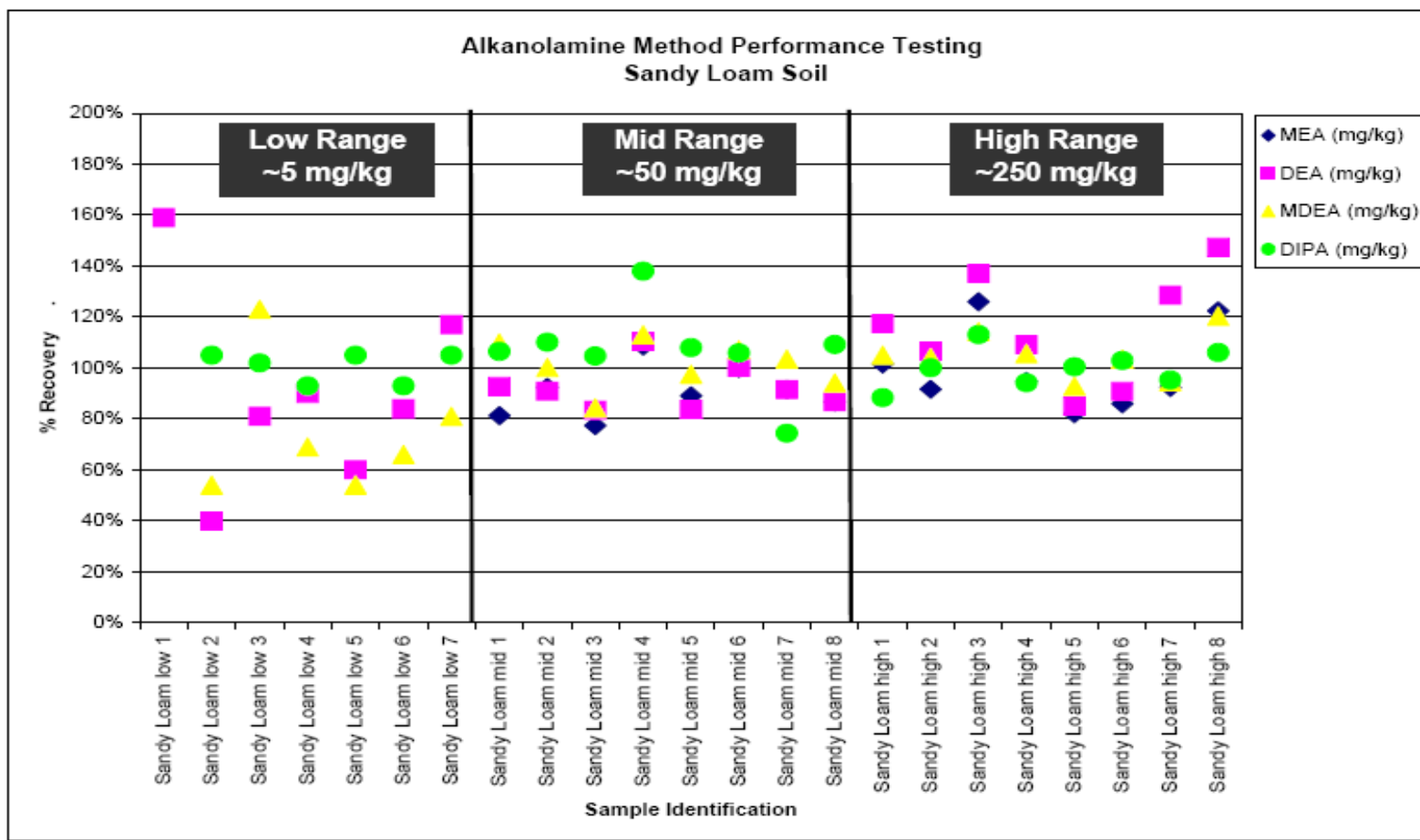
Method Validation

- **Multiple Analysis 3 soil types**
 - High Organic Carbon (most difficult)
 - Clay Loam
 - Sandy Loam
- **Individual 10 g samples**
 - Spiked at 3 levels
 - Spikes allowed to stand minimum 24 hr before extraction
- **Measurement**
 - Randomized design

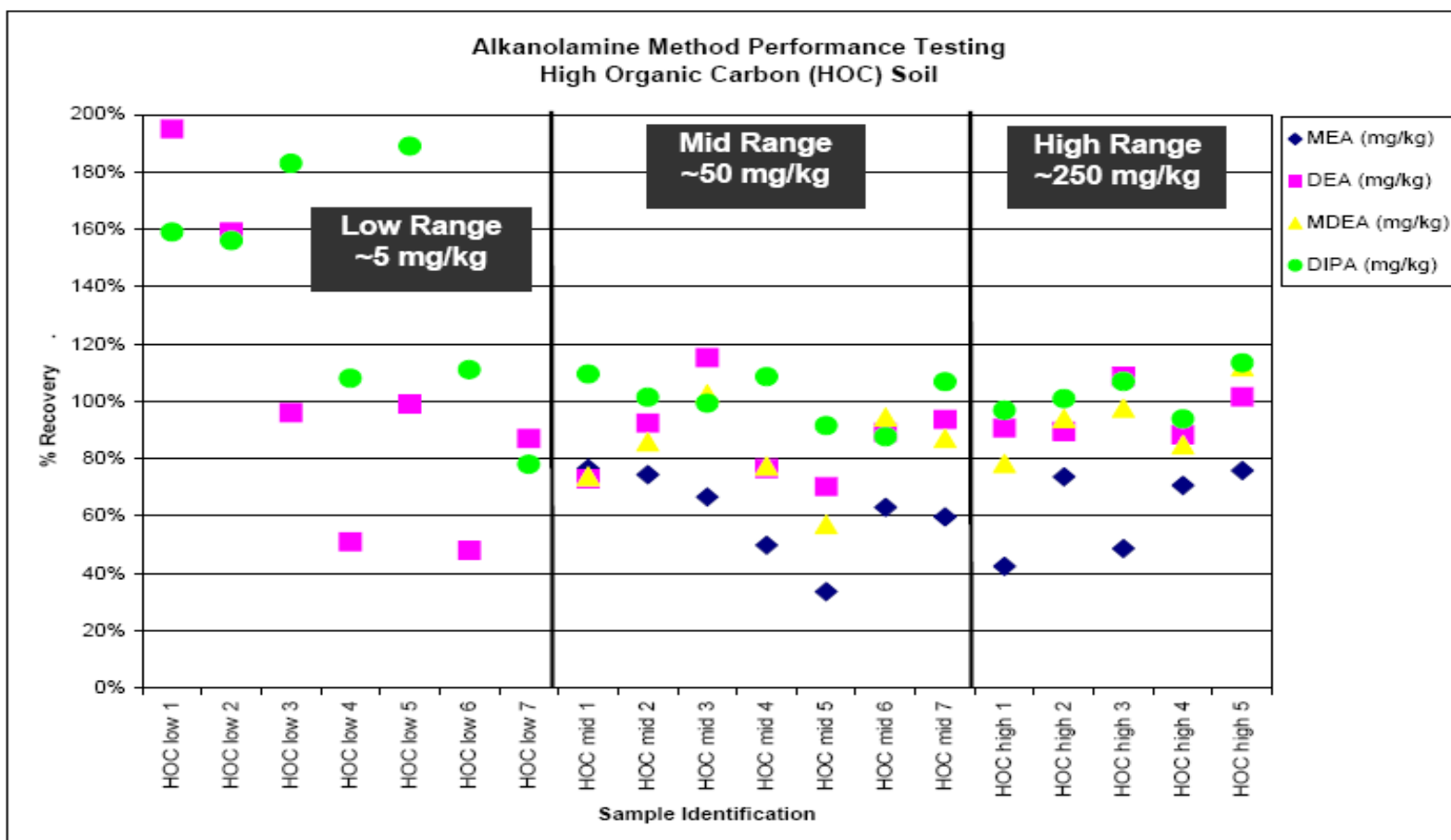
Method Validation



Method Validation



Method Validation



Summary

- **Most challenging amine is MEA, particularly in High Organic Soil with recoveries in the 60%**
- **All others amines have good recoveries > 80% for mid and high range**
- **MDL 1.5 mg/kg for DIPA, MDEA, DEA and 5 mg/kg for MEA**
- **Method has been shared with the private laboratory community via Technical Advisory Group for comment**
- **When new criteria is released, labs are ready with a method that will produce defensible data to support environmental decisions**