

## Protocol for oxalate and total Al and Fe extraction in Soils

### Purpose

This method attempts to estimate concentrations of non-crystalline and crystalline Al and Fe in soils. Non-crystalline forms refer to the more reactive (“amorphous”) minerals that are extracted by ammonium oxalate. The oxalate procedure forms soluble complexes of Al and Fe with oxalate in darkness. The oxalate dissolved both non-crystalline and organically bound forms of Al and Fe, but, with the exception of magnetite, does not dissolve crystalline forms.

The DCB procedure uses a powerful reductant, dithionite, to reduce Fe (III) oxides to Fe(II). Bicarbonate buffers the system (pH 7-8) and sodium citrate is added to prevent the precipitation of dissolved Fe. The DCB procedure dissolves both non-crystalline and crystalline iron oxides; extracts may also include small amount of Fe-bearing silicates. There is no widely used method for estimating crystalline Al in soil. DCB extractions are sometimes used to estimate crystalline Al, but in reality, DCB-extractable Al probably represents Al substituted for Fe in crystalline Fe minerals rather than Al in highly crystalline minerals such as gibbsite. It may include non-crystalline and organically bound Al as well.

### Reagents

- 0.2M ammonium oxalate ( $C_2H_8N_2O_4$ )
  - 142.11g/mol \* 0.2mol/L=28.42g to 1L of DI water.
  - Store in a bottle covered in foil.**
- 0.2M oxalic acid ( $C_2H_2O_4$ )
  - 126.07g/mol \* 0.2mol/L=25.21g to 1L of DI water.
  - Store in a bottle covered in foil.**
- 0.1M sodium hydroxide (NaOH)
  - 40.00g/mol \* 0.1mol/L=4g to 1 L DI water.
- 0.3M sodium citrate ( $Na_3C_6H_5O_7$ )
  - 294.1g/mol \* 0.3mol/L=88.23g to 1 L DI water.
- 1M sodium bicarbonate ( $NaHCO_3$ )
  - 84.01g/mol \* 1.0mol/L=84.01g to 1 L DI water.

### Oxalate-oxalic acid solution

- Mix 100mL of ammonium oxalate (Reagent 1) with 75mL of the oxalic acid (Reagent 2) to whatever total volume is needed for the extraction.
- Test pH. If pH is greater than 3, add oxalic acid until it comes down to 3. If pH is less than 3, add ammonium oxalate until it comes up to 3.

### Citrate-bicarbonate solution

- Make a 4:1 ratio of sodium citrate: sodium bicarbonate. For example, at 40mL a sample: for 160 samples you will need 6.4L of reagent, or 5.12L of sodium citrate and 1.28L of sodium bicarbonate.

## Procedure

### Oxalate extraction for P and non-crystalline Al and Fe

1. Weigh 0.4 g of dry, sieved soil to 50mL centrifuge tube (don't forget to add blanks and reps)
2. Add 40mL of the oxalate reagent to each tube.
3. Cap tubes, cover in tin foil and place in rack.
4. Shake on high for 4 hours.
5. Centrifuge on high for 12 minutes or to clarity.
6. Decant supernatant into nalgene bottle and store until analysis.

### Sodium Hydroxide extraction for crystalline Al

1. After pouring off the oxalate supernatant, add 40mL of 0.1M NaOH reagent to each tube (Reagent 3; you are using the same soil sample as for the previous extraction).
2. Cap tubes and shake on high for 30 minutes.
3. Centrifuge on high for 12 minutes or to clarity.
4. Decant supernatant into nalgene bottle and store until analysis.

### DCB for total Fe (separate extraction) IN THE HOOD

1. Weigh out 0.8g of dry, sieved soil into a 50mL centrifuge tube.
2. Add 0.8g of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (Fisher MSX05301, solid)
3. Add 40mL of the citrate-bicarbonate solution.
4. Cap tubes and shake on high for 16 hours.
5. Centrifuge for 20 minutes or to clarity.
6. Decant supernatant into nalgene bottle and store until analysis.

## Analysis on AA:

### NOTE:

When running your samples, you may notice buildup on the burnerhead that prevents the formation of a clean flame. This is especially true for the DCB samples. If this happens, and your samples are high enough in Fe to be diluted above the detection limit of the AA, dilute your samples at a 1:10 ratio with ultrapure deionized water. For the DCB extracted-samples, it is okay to make up your standards in the citrate-bicarbonate solution only and omit the dithionite.

Also note that a set of standards should be made up in the extraction matrix (or diluted extraction matrix) for each extraction type.

Oxalate-extractable Al range (mmol/kg) = 10-130

Oxalate-extractable Fe (mmol/kg) = 0-120

### Resources:

Darke, A.K. and M.R. Walbridge. 1994. Estimating non-crystalline and crystalline aluminum and iron by selective dissolution in a riparian forest soil. *Communications in Soil Science and Plant Analysis* **25**:2089-2101.

### Calculations:

| Extraction                                 | Descriptor                | Description   |
|--|---------------------------|---|
| 0.2 M ammonium oxalate + 0.2 M oxalic acid | Non-crystalline Fe and Al | Non-crystalline (amorphous) and organically-bound Al and Fe |
| 0.5 M sodium bicarbonate                   | Crystalline Al            | Crystalline aluminum oxides                                 |
| Crystalline + non-crystalline Al           | Total Al                  | Crystalline plus non-crystalline Al                         |

|  |                |                                     |
|--|----------------|-------------------------------------|
| Dithionite + 0.3 M sodium citrate + 1 M sodium bicarbonate | Total Fe       | Crystalline plus non-crystalline Al |
| Total Fe - non-crystalline Fe                              | Crystalline Fe | Crystalline iron oxides             |
|  |                |                                     |