SCOPE

This method measures exchangeable aluminum which is a significant constituent in acidic soils (pH ≤ 5.5).

PRINCIPLE

Aluminum is among the more important and commonly analyzed constituents in natural waters, soils, sediments, geological materials and plant tissues, both because it is an ubiquitous element in soil and geological systems and because, when present in in elevated concentrations, Al can be a powerful toxicant to plants and aquatic organisms.

In acid mineral soils of tropical climate regions, the high aluminum (Al) content, associated to high acidity and low fertility, is one of the main constraints for agricultural production. Traditionally, there have been two primary uses for exchangeable Al values. The first is the formulation of lime requirement for acid soils based on some measure of exchangeable or extractable Al. Second, because of its importance as a predominant cation in acid soils, exchangeable Al is a critical variable in establishing effective cation exchange capacity (ECEC) values which are utilized for soil management and classification purposes, and in evaluating changes in forested soils influenced by acidic deposition and land- use practices.

Soil is leached of exchangeable H and Al with neutral 1 N KCl, and the acid leachate, which is equivalent to the sum of hydrogen and aluminum ions, is titrated with standard alkali.

$$H^+ + OH^- \longrightarrow H_2O$$
$$Al^{+3} + 3\ OH^- \longrightarrow Al(OH)_3$$

The aluminum is the complexed with NaF, releasing an equivalent amount of alkali

$$Al(OH)_3 + NaF \longrightarrow Na_3AlF_6 + 3\ NaOH$$
$$NaOH + HCl \longrightarrow H_20 + NaCl$$

The first titration provides a measure of the total titratable acid displaced from soil, and the second provides a measure of the Al displaced.

The titrimetric method may present inferior sensitivity in relation to the colorimetric methods for the determination of Al, but it is less subject to interferences from ions present in the extract.

TEST PRECAUTIONS

In the titration of KCl extracts, the end point of phenolphthalein is not as abrupt with most acid- base titrations because $Al(OH)_3$ formation during the titration is sluggish. Potentiometric titration method which has been greatly enhanced by the availability of computer controlled automatic titrators and which allow for careful

control of the neutralization reaction and titrations conditions can be conducted on solutions containing dissolved Al such as KCl extracts. The presence of hydronium ion as the hydrolytic product of exchangeable or non-exchangeable sources (or both) will titrate before Al, and this reaction may produce weak non-identifiable end points.

EQUIPMENT

a) Balance, precision of at least 0.001 g
b) Magnetic Stirrer
c) Digital Titrator/Burette

LABORATORY WARE

a) Leaching tubes
b) Volumetric flasks, 50 mL
c) Erlenmeyer flasks, 125 mL
d) Burette, 50 mL
e) Wash bottle
f) Micro pipette, 1-10 mL

CHEMICALS AND REAGENTS

a) KCl, 1M. Dissolve 74.4 g KCl in one liter distilled water. Check if pH is neutral.
b) Standard sodium hydroxide, 0.05 M. Dissolve 2.0 g of NaOH pellets in one liter freshly boiled and cooled distilled water. Cool the solution with with the flask covered to prevent absorption of CO_2. Dilute to the mark when cool. Store protected from atmospheric CO_2. Standardize against potassium acid phthalate (dried at 120°C for 2 hours).
c) Standard hydrochloric acid, 0.05 M. Dilute 4.31 mL of concentrated HCl to one liter with distilled water. Standardize against 0.05M standard NaOH.
d) Sodium fluoride, 1 M. Dissolve 42.0 g of NaF in one liter distilled water.
e) Phenolphthalein, 0.1%. Dissolve 0.1 g of the powder in 100 mL 0f 90% ethanol (Dilute 94.74 ml of 95% ethanol to 100 mL with distilled water).
f) Ethanol, 95%

HEALTH AND SAFETY

Wear proper protective equipment. Use laboratory coat, closed shoes, gas mask or dust mask and chemical gloves when performing analysis to mitigate the harmful effect of exposure on chemicals.

Observe careful and proper handling of chemicals when using strong bases and strong acids. Avoid contact with these corrosive substances that cause irritation to skin, eyes, mucous membranes and breathing passages. The amount of harm caused by chemical burns from acids and bases depends on the concentration of the substance and the duration of exposure.Ensure that eyewash stations and safety showers are proximal to the work-station location. When mixing acids, always pour acid into water. Ethanol is highly flammable in the presence of open flames and sparks, of heat and poses a serious risk of fire. Keep away from sources of heat or ignition.

Avoid mixing incompatible materials to reduce the risks of fire and explosion inside the laboratory.

PROCEDURE *(Dewis and Freitas, 1970)*

Standardization of 0.05 M NaOH with potassium acid phthalate ($KHC_8H_4O_4$)

1. Accurately weigh two 0.35 g portions of potassium hydrogen phthalate (dried at 120°C for two hours) into 250 mL conical flasks and add 40 mL deionized water.
2. Stopper the flasks and shake to dissolve the salt.
3. Titrate each solution with the NaOH solution using phenolphthalein indicator.

$$\text{Molarity (M) NaOH} = \frac{\text{Weight of } KHC_8H_4O_4 \text{, mg}}{204.229 \times \text{mL of NaOH used}}$$

where 204.229 = molecular weight of $KHC_8H_4O_4$, g/mole

Standardization of 0.05 M HCl with 0.05 M NaOH

1. Pipet two 40 mL portions of the standardized NaOH into 250 mL Erlenmeyer Flasks.
2. Titrate each solution with HCl using phenolphthalein indicator.

$$\text{Molarity (M) HCl} = \frac{\text{M of NaOH} \times \text{mL of NaOH}}{\text{mL of HCl}}$$

Extractable Aluminum Determination

1. Place 5.0 g of air- dry sample in the leaching tube.
2. Leach with 10 mL aliquots of KCl (add five portions of 10 mL KCl at 20 minute intervals).
3. Transfer the leachate to a 125 mL Erlenmeyer flask and add 0.40 mL of phenolphthalein indicator. Titrate with standard NaOH, until the solution turns permanently pink (wait for one minute).
4. Destroy the pink color with 0.05 M HCl (Initial Volume of HCl).
5. Add 10 mL of NaF. If the pink color reappears (indicating presence of exchangeable Al), titrate with standard HCl until the solution turns colorless (Final volume of HCl). See if the end point is lasting.