1. SCOPE

This method is used to determine alkalinity, pH, conductivity and acidity in aqueous, soil and sludge samples by automated titrimetric analysis. It is appropriate for natural and treated water sources including drinking water, industrial and biosolid wastes and all types of soil.

2. DERIVATION

This method is derived from:

Standard Methods for the Examination of Water and Wastewater, methods 2310 B (Acidity), 2320 B (Alkalinity), 2510 B (Conductivity) and 4500-H B (pH).

Environmental Protection Agency (EPA) method 9045D for pH and conductivity in soil samples.

Samples which fall under PALA accreditation are analyzed by methods derived from Centre d’expertise en analyse environnementale du Québec, methods MA.315-Alk-Aci and MA. 303 – pH-con-tur, current versions.

3. PRINCIPAL OF THE METHOD

The alkalinity of waters and waste waters is the capacity of that water to accept protons. Carbonate (CO_3^{2}), bicarbonate (HCO_3^-) and hydroxide (OH^-) are the major contributors to the alkalinity of water. Borates, phosphates, ammonia, amines, silicates, organic carboxylates and phenates (in humus), as well as other basic anions, may also contribute. The alkalinity is determined by titration with a known standard solution (H_2SO_4) to successive bicarbonate and carbonic acid equivalence points as indicated electrometrically.

The alkalinity titration results in the determination of total alkalinity (talk) and phenolphalein alkalinity (palk). Using the palk and talk the three principal forms of alkalinity, bicarbonate, carbonate and hydroxide, can be determined using stoichiometric relationships. These calculations assume the absence of other acids such as boric, phosphoric and silicic acids.

The acidity of waters and waste waters is the ability of that water to react with a strong base to a designated pH. Acidity is caused by weak organic acids, such as acetic and tannic acids, and strong mineral acids including sulfuric and hydrochloric acids. The acidity is determined by the titration of the sample with a known standard solution of sulfuric acid to an end point pH of 3.9 to determine mineral activity, and an end point pH of 8.3 with sodium hydroxide to determine total acidity.

The pH of waters and waste waters is based upon the hydrogen ion activity. It is determined electrometrically using a glass electrode. A change of 1 pH unit produces an electrical change of 59.1 mV at 25°C. At a given temperature, the acidic or basic characteristic of a solution is indicated by the pH.

The conductance of waters and waste waters yields a measure of its capacity to convey an electric current. This is related to the total concentration of the ionized substances in water and the temperature at which the measurement is made. A submersible platinum conductance electrode is used to measure the conductance of samples and a potassium chloride solution with a known conductance at the same temperature.

4. INTERFERENCES

- Large amounts of the salts of weak organic and inorganic acids may cause interferences with the electrometric pH measurement which can in turn affect the pH and alkalinity values.
- Oil and grease and high suspended solids contained in sludge samples may interfere by coating the pH electrode and causing a sluggish response. These samples must be analyzed on the beaker titration system for Conductivity, Alkalinity, and pH analysis. Sludge samples for alkalinity analysis must be centrifuged and diluted to reduce interference from high- suspended solid content and work within the maximum range of the beaker systems.
- The alkalinity, acidity, pH, and conductivity of samples must be determined as soon as possible after collection, as sample preservation is not possible.
- Refrigerate aqueous samples at 5°C +/-3°C until the time of analysis to minimize microbiological decomposition of solids. Allow samples to warm to room temperature prior to analysis.
- For vial autotitrators highly visual suspended solids should be allowed to settle prior to analysis as they have the potential to clog the sipper.
- Dissolved gasses (including CO2, hydrogen sulfide, or ammonia) contributing to acidity or alkalinity results may be lost or gained during storage or titration. This can be minimized by analyzing to the endpoint promptly after opening the sample container, avoiding vigorous shaking or mixing.
- Conductivity blanks less than 10 µS/cm may be difficult to measure with usual measurement electronics and cell capacitance.
- Acidity blank acceptance criteria corresponds with the natural acidity levels of the laboratory deionized water.

5. SAMPLE REQUIREMENTS

Sampling information and concerns:	Representative sample must be taken.

Containers to be used:	Plastic or glass
Sample size:	Optimum aqueous sample volume 500mL Minimum aqueous sample volume 100mL Optimum solid sample size 50g Minimum solid sample size 20g for pH and conductivity Minimum solid sample size 2g for alkalinity
Preservation required:	None
Temperature requirements for storage:	Refrigerate solutions and Reg 153 soils at 5°C +/- 3°C. All other soil samples are stored at room temperature.
pH requirements:	None
Pre-treatment:	None
Holding time (from time of collection to start of analysis):	Alkalinity 14 days Acidity 14 days Conductivity 28 days pH solutions 7 days pH and conductivity soils 30 days pH (PALA accredited samples) 48 hours
Disposal of samples:	Refer to WI-CA-[ENV]AD-LAK-AD-014

6. REFERENCES

American Public Health Association, American Water Works Association, Water Environment Federation Current Edition. Standard Methods for the Examination of Water and Wastewater; Washington, D.C.

Mantech PC Titrate operational manual.

Ministry of Environment, Conservation and Parks, Laboratory Services Branch, E3218 - The Determination of Conductivity, pH And Alkalinity In Water And Effluents By Potentiometry, current version

Centre d’expertise en analyse environnementale du Québec. *Determination of Alkalinity and Acidity by Titration*, MA.315 – Alk-Aci current verison, Centre d’expertise en analyse environnementale du Québec (DGCSCEAEQ) du ministère de l’Environnement, de la Lutte contre les changements climatiques, de la Faune et des Parcs (MELCCFP). Elle a été produite par la Direction des communications du MELCCFP.

Centre d’expertise en analyse environnementale du Québec. Determination of pH, Conductivity, and Turbidity in Water with an Robotic Titrator, MA.303 – pH-con-tur, current verison, Centre d’expertise en analyse environnementale du Québec

(DGCSCEAEQ) du ministère de l’Environnement, de la Lutte contre les changements climatiques, de la Faune et des Parcs (MELCCFP). Elle a été produite par la Direction des communications du MELCCFP.

Practices for the Collection and Handling of Drinking Water Samples, Version 2.0, Laboratory Services Branch, Ministry of the Environment. April 1, 2009.

Environmental Protection Agency, United States, 2004, Method 9045. Current version Soil and Waste pH.

Laboratory Services Branch Ministry of the Environment, Conservation and Parks, , Protocol for Analytical Methods Used in the Assessment of Properties under Part XV.1 of the *Environmental Protection* Act and Excess Soil Quality*, February 19, 2021 Version 3.1*

Water Management – Policies Guidelines Provincial Water Quality Objectives of the Ministry of Environment and Energy, July 1994, reprinted 1999 Ontario. PIBS3303E