1. **Scope and Application**

   **Matrices:** Aqueous (at least 20% aqueous phase), Soil/Sediment, Solid and Waste
   
   **Definitions:** Refer to Alpha Analytical Quality Manual.
   
   The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.
   
   This method is restricted to use by or under the supervision of analysts experienced in the operation of the pH equipment and in the interpretation of data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.
   
   After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

2. **Summary of Method**

   An aliquot of a water/aqueous sample (analyzed “as is”); soil/sediment or waste sample; is mixed with laboratory reagent water. The pH of the solution is measured electrometrically with a pH meter using a combination electrode.

2.1 **Method Modifications from Reference**

   None.

3. **Reporting Limits**

   There is no reporting limit for this method.

4. **Interferences**

   Samples with very low or very high pH may produce incorrect readings on the meter. For samples with a true pH of > 10, the measured pH may be incorrectly low. This error can be minimized by
using a low-sodium-error electrode. Strong acid solutions, with a true pH of < 1, may give incorrectly high pH measurements.

Temperature fluctuations may cause measurement errors. The use of an automatic temperature compensation probe will minimize temperature errors. If this is not an option, the temperature and pH shall be recorded at the time of the pH reading.

Measurement errors can occur when the electrodes become coated. If an electrode becomes coated with sample material that will not rinse off, perform the following maintenance of the probe. 1) clean the electrode in an ultrasonic bath, or 2) wash the electrode with detergent, rinse several times with reagent water, place in 1:10 HCl solution so that the lower third of the electrode is submerged, and then thoroughly rinse with reagent water.

Solvents should be avoided as they may damage the probe operation.

5. **Health and Safety**

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. **Sample Collection, Preservation, Shipping and Handling**

6.1 **Sample Collection**

The sample should be collected in clean plastic or glass containers. Approximately 20g of soil/sediment sample, and approximately 100mL if aqueous/water sample, is required to allow for sample analysis and/or matrix QC.

6.2 **Sample Preservation**

None.

6.3 **Sample Shipping**

No special shipping requirements are necessary. Refer to Sample Receipt and Login SOP (SOP/01-01).

6.4 **Sample Handling**

Maintain samples at 4°C ± 2°C from sample collection until analysis. Analyze soil/sediment or waste pH samples as soon as possible, and within 24 hours of receipt.

Refer to Sample Receipt and Login SOP (SOP/01-01).

7. **Equipment and Supplies**

7.1 **pH Meter**: Orion Model 720A pH/mV/Temperature meter.

7.2 **Combination pH electrode**: Orion, gel-filled. *Note: The combination electrode has both measuring and reference functions; therefore, a separate reference electrode is not required.*

7.3 **Automatic Temperature Compensation Probe**: Orion

7.4 **Glass Beakers**: 50mL volume
7.5 Magnetic stirrer
7.6 Teflon-coated stir bars
7.7 Analytical balance: Accurate to 0.1g.
7.8 Graduated cylinder: 10mL volume
7.9 Shaker Table: New Brunswick Scientific, Innova 2300

8. Reagents and Standards

8.1 Laboratory Reagent Water: ASTM Type II, deionized (DI) water
8.2 Buffer Solutions: Fisherbrand standard buffer solutions, certified at the following pH concentrations: 4.00, 7.00, 10.00, ~2, ~13. Additionally, a second source of buffer 4.00, 7.00 and 10.00 is required for LCS/ICV and CCV analysis. Buffers are labeled upon receipt and initial opening, and must be used prior to the manufacturer's expiration date. Store buffers at room temperature.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)
Not applicable to this method.

9.2 Laboratory Control Sample (LCS)
A second source pH 7.00 buffer is analyzed immediately following pH meter calibration. Criterion for acceptable recovery is ± 0.05 pH units. Corrective action: If the LCS is outside the acceptable range, re-calibrate the pH meter. Acceptable second source LCS recovery must be obtained prior to the analysis of samples.

9.3 Initial Calibration Verification (ICV)
Refer to Section 9.2.

9.4 Continuing Calibration Verification (CCV)
A CCV is analyzed every 10 samples and at the end of an analytical batch to monitor the accuracy of the calibration during analysis. The CCV is a second source buffer solution (4.00, 7.00, or 10.00) in the appropriate range of the samples. Criterion for acceptable recovery is ± 0.05 pH units. Corrective action: If the CCV is outside of acceptable range, re-calibrate the pH meter and re-analyze all samples since the last acceptable CCV.

9.5 Matrix Spike
Not applicable to this method.

9.6 Laboratory Duplicate
Samples are analyzed in duplicate at a frequency of 10% or 1 per batch of 10 samples or less, whichever is more frequent. Relative percent difference (RPD) between sample duplicate
results must be ≤ 15%. **Corrective action:** If RPD does not meet criteria, determine if the cause is matrix related or lab related. If matrix related, include a narrative with the client report explaining the matrix effect on the imprecision of the pH result. If error was lab related, repeat the analysis.

\[
\text{RPD} = \frac{(R1 - R2)}{(R1 + R2)} \times 100
\]

9.7 **Method-specific Quality Control Samples**

None.

9.8 **Method Sequence**

- pH Meter calibration
- LCS / ICV
- Samples 1-9
- Laboratory Duplicate
- CCV

10. **Procedure**

10.1 **Equipment Set-up**

Turn on pH meter and allow to warm up.

10.2 **Initial Calibration**

The pH meter/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples. Calibrate using pH buffer 7 and 4 for neutral or acidic samples. Calibrate using pH buffer 7 and 10 for basic samples. For extremely acidic or basic samples use the ~2 or ~13 buffers in place of the 4 or 10 buffers, respectively.

10.2.1 Immerse the clean probe in a fresh 25 - 50mL aliquot of pH buffer 7.00, add a magnetic stir bar and place the beaker on a magnetic stirring plate. Using the front knob, adjust the digital read-out to 7.00.

10.2.2 Rinse the probe and transfer to a fresh 25 - 50mL aliquot of 4.00 or 10.00 buffer solution, as appropriate. Place the beaker on a magnetic stirring plate. While stirring, use the rear knob to adjust the digital read-out to 4.00, or 10.00, as appropriate for the buffer solution being used for calibration of the meter.

10.2.3 To verify that the calibration remains correct after the adjustment for the second buffer, rinse the probe in reagent water and immerse in the second source pH buffer 7.00. If the reading is 7.00 ± 0.05 pH units, proceed with sample analysis. **Corrective Action:** If the pH reading is not within the defined limits, repeat Sections 10.2.1 through 10.2.3.

10.3 **Equipment Operation and Sample Processing**

Standardize the meter and electrode system as outlined above. Meter must be set to “PH” during all sample analyses.
Weigh 20g of soil/sediment or waste in a 50mL beaker. Add 20mL reagent water and continuously stir the soil/water slurry on a magnetic stir plate for 5 minutes. NOTE: The analyst may use 10g soil and 10mL reagent water, dependent upon the sample, provided the soil/water ratio is 1:1. For sediments with high organic content: Weigh 10g to 20g in 125mL plastic bottle with a 1/1 ratio of DI water. Shake sample for 30 minutes on a Shaker Table. Allow to settle and then shake again for 5 minutes and let settle again.

Let a soil/water slurry suspension stand for about 1 hour to allow most of the suspended particles to settle out. Let a waste/water slurry suspension stand for about 15 minutes to settle particles.

Place the pH electrode in the beaker and adjust the level of the electrode such that it is just below the suspension.

Allow probe to stabilize before recording the pH reading.

For water/aqueous samples, use 25-50mL of the sample provided. Analyze “as is” and DO NOT MIX with any additional DI water. Transfer the sample aliquot to a 50mL beaker, and read the pH as above for soil/sediment/waste samples.

Rinse electrode thoroughly between samples.

10.4 Continuing Calibration
To verify that the calibration remains accurate throughout the batch sequence, after every 10 samples or less and at the end of the batch sequence rinse the probe in reagent water and immerse in the second source pH buffer 7.00. The pH reading must be 7.00 ± 0.05 pH units. Corrective Action: If the pH reading is not within the defined limits, repeat Sections 10.2.1 through 10.2.4 and reanalyze any samples since the last acceptable CCV.

10.5 Preventive Maintenance
The electrode is rinsed with DI and gently dried with a KimWipe between sample readings.

11. Data Evaluation, Calculations and Reporting
The pH meter reads directly in pH units. Report pH of the soil/sediment sample, as measured in water, to the nearest 0.1 pH unit. Report “pH as soil/waste pH measured in water at [room temperature]°C”, where the temperature of the measurement is reported as room temperature, 25°C. Results are reported as pH units between 1 and 12.

Very acid (low) pH samples are reported as <1 pH units, and very basic (high) pH samples are reported as >12 pH units.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data
Section 9 includes Corrective Actions for data that is out of tolerance.
13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha’s Chemical Hygiene Plan the Hazardous Waste and Disposal SOP (G-006) for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan
SOP/08-05 MDL Generation
SOP/08-12 IDC Generation
Hazardous Waste and Disposal SOP (G-006)
Sample Receipt and Login SOP (SOP/01-01)

16. Attachments

None.