USGS New York Water Science Center
Soil and Low Ionic Strength Water Quality Laboratory

Electrometric Measurements and Titration

Standard Operating Procedure

1. Scope and Application

1.1 Analytes

Acid Neutralizing Capacity (ANC), pH, and Specific Conductance

1.2 Reporting Limit

None

1.3 Applicable Matrices

This method is used to determine ANC, pH, and specific conductance in precipitation, dilute surface waters and soil waters.

1.4 Dynamic Range

None

2. Summary of Procedure

The analysis of ANC, pH, and specific conductance is performed using an automated titrator equipped with a conductance probe, a pH electrode, and a buret. Initially, the specific conductance probe is lowered into the sample and a measurement is recorded. The sample is subsequently pumped into the titration cell, where the pH is measured and recorded. The ANC is then determined through an open-atmosphere titration using a strong acid that is added three to five increments past the estimated equivalence point. The equivalence point and ANC are then calculated by the method of Gran (1952). The stability of all recorded measurements is evaluated using the instrument software.

3. Safety Issues

3.1 Chemical Hazards

A. Gloves, safety glasses, and lab coats should be worn when preparing and performing this analysis.
B. For proper handling techniques for specific chemicals, consult the appropriate Material Safety Data Sheets (MSDS).

4. Sample Preservation, Containers, Processing and Analysis Times

4.1 Sample Preservation

Samples are stored at 4°C without being filtered or acidified.

4.2 Containers

Samples are stored in 250-mL acid-washed polyethylene bottles.

4.3 Processing and Analysis Times

Sample processing: one week
Lab analysis: two weeks

LIMS entry: one week

5. Reagents and Standards

5.1 General Information

All reagents are commercially purchased and should be stored in the original container. Date the reagent bottles when received and when opened. Note expiration date, if any. No verification of the reagents is necessary.

5.2 Reagents

A. 0.02 N Sulfuric Acid Titrant
   1. Use commercially purchased 0.02 N volumetric sulfuric acid (H_2SO_4).
   2. Replace solution when the expiration date has passed.

B. Reference Electrode Filling Solution
   1. Use commercially purchased Orion Ross electrode filling solution, catalog number 81-00-07.

5.3 Standards

A. 50 µS Potassium Chloride
   1. Use a commercially purchased 50 µS potassium chloride (KCl) specific conductance stock.
   2. Replace stock when the expiration date has passed.

B. Buffers
   1. Use commercially purchased pH 4.00 and pH 7.00 buffers.
   2. Replace buffers when the expiration date has passed.

C. Quality Control (QC) Stock Solution for QC-high Concentration Standard, 0.025M Potassium Phosphate, Monobasic/0.025M Sodium Phosphate, Dibasic Heptahydrate
   1. Dry about 5 g of potassium phosphate, monobasic (KH_2PO_4) at 105°C for about 2 hours and allow to cool in a dessicator.
   2. Add 3.4023 g potassium phosphate, monobasic (KH_2PO_4) and 6.6910 g sodium phosphate, dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$) to a 1,000-mL volumetric flask that contains about 800 mL Milli-Q water.
   3. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
   4. Store in a polyethylene bottle; label and date.
   5. Prepare every 6 months.
   6. To avoid contamination, aliquots of stock solution must not be withdrawn directly from the bottle.

D. Quality Control (QC) Stock Solution for QC-low Concentration Standard, 0.2 N Sulfuric Acid
   1. Use commercially purchased 0.2 N Sulfuric Acid (H_2SO_4).
   2. Replace solution when the expiration date has passed.
   3. To avoid contamination, aliquots of stock solution must not be withdrawn directly from the bottle.

E. QC Samples
   1. Pipet desired amount of QC substock into a 1000-mL volumetric flask.
   2. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
   3. Store in a polyethylene bottles; label and date.
   4. Prepare as needed.

QC Sample	ANC (μeq/L)	pH (pH units)	Specific Conductance (μS/cm)	QC-low Stock Added (mL)	QC-high Stock Added (mL)	Final Volume (mL)
Low	-39.90	4.44	17.0	0.2	0.0	1000
High	125.0	6.88	39.0	0.0	5.0	1000

6. QC Procedure

A. The pH electrode response is verified by ensuring that the electrode potential for pH 7.00 buffer is $^{+}/_{-}$ 30 mV and the electrode potential for pH 4.00 buffer is about 160 mV greater than for pH 7.00 buffer.
B. The conductivity probe response is verified by ensuring that the conductivity cell constant is approximately 1.00 $^{+}/_{-}$ 0.05.
C. Quality-control samples are analyzed at the start of the run, after every 10 samples during the run, and at the end of the run.
D. For ANC and specific conductance, a quality-control sample is acceptable if the analyzed value is within 10 percent of the QC sample's known value. pH quality-control samples are acceptable if the analyzed value is within 20 percent of the QC-high range known value and 10 percent of the QC-low range known value, when the values are expressed in hydrogen ion concentration.
E. If one of the QC samples fails the acceptance criteria, the run is stopped and the QC sample is re-run. If the QC sample fails again the run is stopped, the QC sample is remade from the substock, and/or the instrument is re-calibrated. Samples associated with the failed QC sample are re-analyzed.

7. Chemical Analysis Procedure

7.1 Instrumentation

Man-Tech PC-Titration Plus automated titrator
PC Titrate software v. 3.0.0.409
Orion Ross 8104-BN combination pH electrode
Jenway conductivity probe

7.2 Start-Up

A. Check the waste container daily and empty if nearing capacity.
B. Check the DI water rinse container daily and fill if close to empty.
C. Check the 0.02 N sulfuric acid titrant and fill if low.

D. Check the level of filling solution in the pH probe and fill to the fill hole level if low.
E. On the computer, double click the **PC-Titrate** icon.
F. If the buret needs to be purged or filled with titrant, click on the **System Prep** auto run button. Click on **Start**.

7.3 Calibration

A. Calibrate the conductance probe weekly or as needed.
B. Remove the conductance probe from the sampler arm and place in a sample tube containing 50 µS conductance standard. Wait for stability. Press the enter key on the conductance meter. Use the up and down arrow keys on the conductance meter to adjust the reading to 50 µS. Press the enter key. Rinse the probe and return to the sampler arm.
C. Note the cell constant (K value) in the instrument notebook.
D. Fill tubes on tray with pH buffers and QC samples in the following order: pH 4.0 buffer, pH 7.0 buffer, DI water, QC samples.
E. In the main menu window, click on the **CALIBRATION:PH** auto run button, or from the template window, load the pH calibration template by clicking on the **Load Template** button and double clicking on the **CALIBRATION:PH** file. Click on **Start**. (Note: Change schedule from "ANC" to "USGS PH- CONDUCTIVITY" if ANC is not being analyzed.)
F. If the calibration is within acceptance criteria, the instrument will analyze the QC samples. If the calibration fails, the run will cease. Refill the buffer tubes and recalibrate. Load the CALIBRATION:PH template by clicking on the **Load Template** button and double clicking on the **CALIBRATION:PH** file. Click on **Start**.
G. If the QC samples fail, rerun QC samples, remake QC samples, and/or recalibrate.
H. To rerun QC samples from this window, load the CALIBRATION:PH template by clicking on the **Load Template** button and double clicking on the **CALIBRATION:PH** file. Delete the first line of the template. Click on **Start**.
I. If the calibration and QC samples pass, set up a sample tray.

7.4 Analysis

A. Take samples out of the refrigerator and let warm to room temperature.
B. Click on the **Load Template** button and double click on the **ANALYZE:ANC** file. (Note: Use the "ANALYZE:PH" template if ANC is not being analyzed.)
C. Enter the sample serial numbers (SSN) into the template under the Sample Name column. Start the tray with a DI water sample. Add 2 QC samples after every 10 environmental samples. Use the click and drag feature to auto increment if the SSNs are consecutive.
D. Fill the autosampler tubes with appropriate samples. The last tube should be filled with pH 7.0 buffer.

E. Click on **Start**.
F. As the run progresses, monitor the QC samples by viewing the results under the Equation Results tab. The run will proceed until the template is finished.
G. If a QC sample fails, the run must be stopped manually by clicking on the **Stop** button. Load new QC samples onto the tray position and analyze QC's again.
H. Click on **Start**.
I. If the QC sample fails again, remake QC samples from substock and/or recalibrate.
J. At the end of the run, click the **Print** button on the Equation Results Tab.
K. Note the run date and any samples that require re-runs on the printout.

7.5 Shut Down

A. The autosampler will fill the titration cell with pH 7.0 buffer for pH probe storage at the end of the run.
B. Close the Shazam report window. The autosampler will move to the home position.
C. Click **Okay** to exit to the main menu. Exit PC-Titrate.

7.6 Maintenance

A. Rinse any salt deposits off of the pH electrode before use.
B. Cover the fill hole and store the pH electrode in pH 7.00 buffer when not in use.
C. Do not let the pH bulb reference junction dry out. As the internal fill solution level drops toward the junction, add fill solution until it reaches the fill hole level.
D. For long-term storage, rinse and fill the buret with Milli-Q water.
E. Sample tubes are rinsed, soaked in DI water overnight, and oven dried at 60°C between uses.
F. The pump tube should be replaced as it becomes worn or stretched; the frequency depends upon the number of samples analyzed. The sample and rinse tubes should be changed as they become discolored or clogged. Note dates in instrument notebook.
G. Buildup and clogging in the waste lines may require periodic replacement of the lines; note in instrument notebook.

7.7 Data Processing and LIMS Entry

A. In the **PC-Titrate** main menu window, click on the **Historical Data Report** auto run button. Click on **Start**.
B. In the Shazam report window, click on the **Define Search** tab.
C. Click on the white **New Report** icon.
D. Click on the yellow **Open Report** icon.
E. Double click on **ph.srw**.
F. Change the date filter by double clicking on the date box. Enter the appropriate run date. Click **Okay**.

G. Click on the **Preview Report** tab.
H. Under **File**, choose **Export**.
I. From the menu, pick **ASCII delimited file (*.txt)** as the file type.
J. Type in the file name as phMMDDYYYY.
K. Click **Okay**; click **Okay**.
L. Repeat steps 7.7.D to 7.7.K for ANC and conductance using the file names: anc.srw and ancMMDDYYYY, cond.srw and condMMDDYYYY respectively.
M. In Microsoft Excel, open all files for the run date. They are stored in C:\Program Files\Hinterland\PC Titrate\Reports. All files are in a comma delimited text format.
N. Edit files as needed, keeping the three constituents in separate files.
O. Save as a comma delimited file (.csv file extension).
P. Print a copy, note the filename on the copy, and close the file.
Q. Double click **Watershed LIMS** icon.
R. Click **Custom**, then **Import Data**.
S. Under the Import drop down, choose **pH or Cond or ANC**.
T. Choose and open the desired file.
U. Choose **Client**, **Analysis**, **Units**, type in **Test Date**, and choose **Analyst**.
V. Exclude and/or edit any data necessary.
W. Click **Client ID to Sample No**.
X. Click **Set Data**.
Y. Investigate problems for data that did not transfer or are duplicated.

8. Archiving

8.1 Data

Data files are backed-up daily by an automatic back-up program. Hard copies of the runs are filed and kept indefinitely. The laboratory LIMS system is backed up daily by automatic back-up program.

8.2 Samples

Samples are stored at room temperature until data can be verified. Sample bottles are cleaned and reused for new samples.

9. References

Orion Research Incorporated, 1990, Ross pH electrode instruction manual: Boston, Orion Research, Laboratory Products Groups, 21 p.

Gran, G., 1952, Determination of the equivalence point in potentiometric titrations – Part II: Analyst, v. 77, p. 661-671.

Metcalf, R.C., and Peck, D.V., 1991, Dilute, neutral pH standard of known conductivity and acid-neutralizing capacity: Analyst, v. 116, p. 221-231.

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies – laboratory analysis for surface water chemistry:

Washington, D.C., U.S. Environmental Protection Agency, EPA 600/4-87/026 (variously paged).

10. Key Words

Specific conductance, pH, acid neutralizing capacity, ANC, titration, electrometric measurements, water, soil water.