6.6 ALKALINITY AND ACID NEUTRALIZING CAPACITY

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ALKALINITY AND ACID NEUTRALIZING CAPACITY 6.6

Alkalinity and acid neutralizing capacity (ANC) are measures of the ability of a sample to neutralize strong acid. They are determined using identical electrometric procedures involving the acidimetric titration of a sample; the only difference is that the alkalinity sample is filtered, whereas the ANC sample is not filtered (raw, or unfiltered). The terms alkalinity, ANC, and carbonate alkalinity are used in this manual as follows:

- **Alkalinity** is the acid neutralizing capacity of solutes in a water sample, reported in equivalents per liter (or milliequivalents or microequivalents per liter). Alkalinity consists of the sum of titratable carbonate and noncarbonate chemical species in a **filtered water sample** (filter membrane of 0.45-µm pore size or smaller).
- **ANC** is the acid-neutralizing capacity of solutes plus particulates in an **unfiltered water sample**, reported in equivalents per liter (or milliequivalents or microequivalents per liter). ANC is equivalent to alkalinity for samples without titratable particulate matter.
- **Carbonate alkalinity** is the acid-neutralizing capacity attributable to carbonate solutes (bicarbonate and carbonate), reported either in equivalents per liter (or milliequivalents or microequivalents per liter) or in milligrams per liter as a carbonate species, and titrated on a **filtered water sample**. In many aqueous systems, alkalinity is controlled by carbonate chemistry and most commonly is attributable to bicarbonate (HCO_3^-) and less frequently to carbonate (CO_3^{2-}).

Alkalinity: the capacity of solutes in an aqueous system to neutralize acid.

Acid Neutralizing Capacity (ANC): the capacity of solutes plus particulates in an aqueous system to neutralize acid.

Alkalinity is used routinely to check the charge balance of a solution and to gain insights on the evolution of aqueous systems. Alkalinity and ANC provide information on the suitability of water for uses such as irrigation, determining the efficiency of wastewater processes, determining the presence of contamination by anthropogenic wastes, and maintaining ecosystem health.

Any substance in the water sample that reacts with strong acid titrant can contribute to the acid neutralizing capacity.

- Important noncarbonate contributors may include organic ligands (especially acetate and propionate) as well as hydroxide, silicate, borate, and less commonly ammonia and sulfide (Hem, 1985). When found in unusually high concentrations, phosphate and arsenate also may contribute to the acid neutralizing capacity of the sample (Stumm and Morgan, 1981).
- Except for unusual natural waters and waters substantially affected by human activity, noncarbonate ionized contributors generally are not present in large enough quantities to affect alkalinity or ANC determinations.
- Particulate matter can be an important contributor, and must be removed by filtration before titrating the sample for the alkalinity determination.

Alkalinity is determined on a filtered sample.
ANC is determined on an unfiltered sample.

TECHNICAL NOTE: Alkalinity and ANC are measured relative to a solution of carbon dioxide in water; therefore, they are independent of any exchange of carbon dioxide or other common gases between the sample and the atmosphere. However, atmospheric gas exchange can alter the concentrations of individual species, such as bicarbonate. Also, aeration of a sample during filtration can cause mineral precipitation on the filter—this may alter the alkalinity, especially in water systems closed to the atmosphere under ambient conditions.

EQUIPMENT AND SUPPLIES 6.6.1

Equipment and supplies for the electrometric method for determining alkalinity and ANC are listed in table 6.6–1. The equipment must be tested before each field trip and cleaned immediately after each use.

Buret, micrometer buret, and digital titrator

The buret provides good accuracy and precision when used by a trained operator.

- Micrometer burets provide better accuracy and precision than burets—they can deliver acid increments to 0.0001 mL and are available commercially (for example, Gilmont® micrometer burets).
- The digital titrator is not as accurate as a buret, but is popular because it is more convenient and less fragile than a buret and keeps the acid in a virtually closed system. Empty titrant cartridges also are available. (The Hach® brand is used as an example in this document.) **Delivery tubes of clear (instead of red) plastic should be used.**

Volumetric pipet, graduated cylinder, and digital balance

The volumetric pipet is used only for dispensing the correct volume of filtered sample. Selection depends on whether the determination is on an alkalinity (filtered) sample or an ANC (unfiltered) sample.

- Use only class A “TD” pipets. TD is a calibration designation meaning “To Deliver” (TD is distinguished from “TC” or “To Contain” pipets).
- Class A pipets should not be used to aspirate or dispense solutions containing suspended particles—the small bore of this pipet tends to reject particles during aspiration and retain them during delivery (C.J. Patton, U.S. Geological Survey, written commun., 1995).

The graduated cylinder and digital balance are used only for measuring the correct volume of unfiltered (ANC) sample. The digital balance yields higher precision than the graduated cylinder.

Table 6.6–1. Equipment and supplies used for alkalinity or ANC titrations[1]
[mL, milliliters; ANC, acid neutralizing capacity; g, gram; µS/cm, microsiemens per centimeter at 25°Celsius; *N*, normal]

Equipment and supplies needed when using either a digital titrator or a buret

- ✓ pH meter, preferably with automatic temperature compensator (see NFM 6.4 for selection and associated supplies)
- ✓ pH electrode, calibrated, combination or equivalent, and appropriate filling solution, if required
- ✓ Thermometer, calibrated (see NFM 6.1 for selection and calibration criteria)
- ✓ Stirrer, magnetic (battery operated)
- ✓ Stirring bars, Teflon® coated, smallest size (always carry spare bars)
- ✓ Volumetric pipets, class A "TD" (for alkalinity)—25 mL, 50 mL, and 100 mL
- ✓ Graduated cylinder (for ANC). For higher precision, use a digital balance, 0.1-g accuracy, 200-g capacity, pocket-sized (available from Acculab, Inc.)
- ✓ Pipet squeeze bulb or pipet pump
- ✓ Sample bottles, 250 mL, acid rinsed or deionized-water rinsed
- ✓ Beakers, glass—50 mL, 100 mL, and 150 mL
- ✓ Beaker, Berzelius, 300 mL, tall form, spoutless, with two- or three-hole stopper
- ✓ Deionized water (DIW) (maximum conductivity of 1 µS/cm)
- ✓ Dispenser bottle, squeeze, for deionized water
- ✓ Filtration unit, in-line capsule or pressure unit with inert gas (for alkalinity)
- ✓ Sodium carbonate (Na_2CO_3) standard solution
- ✓ Safety gloves, glasses, acid spill kit, and apron
- ✓ Paper tissues, disposable, soft and lint free

Additional equipment and supplies needed when using a digital titrator

- ✓ Digital titrator and mounting assembly
- ✓ Delivery tubes, bent-stem, colorless, transparent
- ✓ Titrant solution: sulfuric acid (H_2SO_4) solution, 0.1600*N* and 1.600*N* (empty or prefilled cartridges are available for use with the Hach® system)

Additional equipment and supplies needed when using a buret

- ✓ Calibrated buret, 25-mL capacity with 0.05-mL graduations and Teflon® stopcock
- ✓ Calibrated buret, 10-mL capacity with 0.02-mL graduations and Teflon® stopcock
- ✓ Micrometer buret (alternative to standard burets, for greater accuracy)
- ✓ Titrant solution: sulfuric acid solution, 0.01639*N*
- ✓ Buret stand and clamp
- ✓ Wire pen cleaner (for cleaning buret tip)
- ✓ Buret cap
- ✓ Buret meniscus reader
- ✓ Acid bottle, pump (for filling buret)

[1]Modify this list to meet the specific needs of the field effort.

Sulfuric acid titrant

Sulfuric acid is the titrant used routinely by the USGS. The normality of sulfuric acid titrant is subject to change with time; proper storage and standardization of the acid titrant is essential.

- 0.1600*N* or 1.600*N* sulfuric acid solutions in prefilled cartridges for the Hach® digital titrator should be obtained by USGS personnel from the USGS One-Stop Shopping. The normality of sulfuric acid in these cartridges is tested by the NWQL prior to distribution. NWQL calculates and reports any correction factors necessary to compensate for cartridge manufacturing anomalies and/or variations in the reported acid normality. Hach Company, as of January 2001, reports a shelf life of 18 months for these cartridges. Expiration dates are printed on each cartridge.
- 0.01639*N* sulfuric acid solution for the buret system is available from a vendor. Alternatively, a sulfuric acid solution of similar normality may be prepared by following the procedure described in section 6.6.2. **Check the normality of this titrant solution each month.**
- Acid solutions of other normality may be needed, depending on the sample chemistry or ionic strength. Prepare the solution under a fume hood. Check the normality monthly.

TECHNICAL NOTE: For samples vulnerable to precipitation reactions, a Berzelius beaker can help minimize gas exchange. Select a size of Berzelius beaker that fits the sample volume and associated titrating equipment and yet minimizes headspace above the sample. Fit the Berzelius beaker with a two- or three-hole stopper to accommodate the electrode(s), the thermometer, and the digital or buret titrator. Another option is to work in a glove box filled with an inert gas atmosphere. Oceanographers use a closed cell with an expanding plunger to avoid gas exchange (Almgren and others, 1977).

CAUTION: Use the safety precautions outlined on the Material Safety Data Sheets (MSDS) when handling chemicals—wear safety glasses, gloves, and protective clothing.

Replacement page 11/18/04.. Note that in the second bullet, the reverence is to a vendor of scientific products.

6.6.1.A MAINTENANCE, CLEANING, AND STORAGE

Proper maintenance, cleaning, and storage of the pH instrument are critical for ensuring the accuracy of alkalinity or ANC determinations; guidance is provided in NFM 6.4.

Clean the volumetric pipets, beakers, bottles, burets, and stirring bars with hot water and nonphosphate detergent. Rinse them copiously with tap water followed by deionized water. If oily or chemical residues are difficult to remove, soak the glassware and nonmetal equipment in a mild (5 percent by volume) hydrochloric acid solution (see Horowitz and others, 1994), and repeat the detergent wash. Store cleaned equipment wrapped or bagged in plastic until ready for use.

Reagents must not exceed their shelf life. Store reagents, as appropriate, in a dust-free cabinet, desiccator, or refrigerator. When chemicals to be used for preparation of reagents are received, mark the dates of receipt and expiration on the container. When a reagent is prepared, label the container with the contents, date of preparation, expiration date, and preparer's initials. Store the 0.01639*N* standard sulfuric acid solution and filled Hach® titrant cartridges in a cool, dark place (a storage cabinet or frost-free refrigerator). Seal the filled cartridges in plastic bags to avoid moisture loss or gain.

Some of the recommended procedures for equipment operation may be out of date if the equipment being used is different from that described or if the equipment incorporates more recent technological advances—follow the manufacturer's instructions.

CALIBRATION AND STANDARDIZATION 6.6.2

Calibration is required for the pH instrument—follow instructions in NFM 6.4.

Alkalinity and ANC determinations require the use of an acid titrant with a known concentration. **Accurate standardization of the acid titrant is essential.**

- The normality of locally prepared titrant or 0.01639*N* solution obtained from the OWQRL must be tested once per month. The acid is checked against a fresh standard solution of sodium carbonate, as described below.
- Record on field notes any correction factors necessary to compensate for cartridge manufacturing anomalies and/or variations in the stated acid normality for the lot of prefilled cartridges to be used. This information is available from OWQRL for USGS personnel.

CAUTION: When diluting concentrated acids, always add the acid to the water.

Prepare a sulfuric acid titrant solution:

To prepare your own acid titrant for the buret system, follow the procedure below (adapted from Fishman and Friedman, 1989).

1. Cautiously add 0.5 mL concentrated H_2SO_4 (specific gravity 1.84 g/mL) to approximately 950 mL of fresh deionized water (DIW).
2. Mix thoroughly; dilute with DIW to the 1-L mark.

This recipe results in an acid concentration of roughly 0.018*N*. To determine the actual acid concentration, the solution must be standardized—follow the procedure on the next page. If a concentration of exactly 0.01639*N* is desired, the standardized solution may be diluted with DIW and restandardized.

Prepare the standard solution:

To prepare a fresh standard solution of 0.01639*N* sodium carbonate (Na_2CO_3):

1. Dry 1.0 g primary standard Na_2CO_3 at 150 to 160°C for 2 hours.
2. Cool in a desiccator; weigh out 0.8686 g Na_2CO_3; add to a 1-L volumetric flask.
3. Dilute with DIW to the 1-L mark.

Standardize the sulfuric acid:

1. Calibrate the pH system following instructions in NFM 6.4.
2. Pipet 25 mL of sodium carbonate standard solution into a 100-mL beaker, and titrate with the sulfuric acid solution. Record the pH and volume of titrant added, following the procedure in section 6.6.4.A.
3. Determine the equivalence point of the titration using the inflection point method (section 6.6.4.B). The equivalence point is the point at which the change in pH per volume of titrant added is maximized, and generally will be found near pH 4.5.
4. Determine the normality of the acid as follows:

$$C_a = \frac{(25\ mL)\left(\frac{0.8686\ g\ Na_2CO_3}{1.0\ L}\right)\left(\frac{1\ mole\ Na_2CO_3}{105.989\ g\ Na_2CO_3}\right)\left(\frac{2\ eq}{1\ mole\ Na_2CO_3}\right)}{V_a}$$

$$= \frac{(25 mL)\left(0.01639\frac{eq}{L}\right)}{V_a},$$

where

C_a is acid normality, in equivalents *(eq)* per liter, and
V_a is volume of sulfuric acid added to reach the equivalence point, in milliliters.

5. Store the solution in a tightly sealed 1-L glass bottle.

COLLECTION AND PROCESSING 6.6.3

Collect and process the samples in a manner that ensures that they represent environmental concentrations at the time of collection. Minimize the effects of wind, rain, cold, dust, and sun on the samples. Collect and (or) process the samples in a chamber to protect them from airborne particulates.

Before collecting or processing the sample, clean the samplers, compositing and splitting devices, sample bottles, measurement vessels, and other equipment that contacts the sample (for detailed procedures refer to NFM Chapters 3 and 4).

- Prerinse the sample bottles with deionized water and store in sealable plastic bags until ready for field sampling (acid-rinsed sample bottles are recommended, especially for samples with low alkalinity or ANC). Field rinse the bottle(s) three times with sample (sample filtrate for alkalinity).
- Do not field rinse the measurement vessels. Volumetric pipets and graduated cylinders should be clean and dry before use.

To collect and process the sample:

1. Filter the samples along with other anion samples, if determining alkalinity. The 0.45-µm flowthrough disposable filter capsule is the standard unit used by the USGS. Record on field forms if a different unit or membrane is used, as this can affect the determination.
2. Fill and securely cap two 250-mL sample bottles (instead of one 500-mL bottle) with the sample (filtrate for alkalinity) to ensure that there is sufficient volume to (a) repeat the titration, (b) preserve the integrity of the second aliquot after the first has been opened, and (c) accommodate any losses from spillage.

3. Prevent agitation of the sample or prolonged exposure to air in order to avoid oxidation of hydrogen sulfide, ferrous iron, and manganous manganese, and to prevent precipitation of mineral phases.
   - Loss of carbon dioxide (CO_2) from the sample will not change the alkalinity or ANC determination, but chemical or physical reactions can cause concentrations of bicarbonate and carbonate to change within minutes.
   - Begin the titration as soon as possible, as there is less chance of chemical precipitation once acidification begins. If the titration is delayed, maintain the samples at the temperature of their ambient environment.
   - If there is a tendency for mineral precipitation, collect and process the sample in an inert gas atmosphere.

Surface water

Collect and process a representative sample according to USGS-approved methods (see NFM 4.1, 5.0, and 5.1).

- The USGS NASQAN and BENCHMARK programs require filtration of alkalinity samples through a 0.45-µm membrane.
- To collect and process samples from anoxic lake or reservoir depth intervals, adapt procedures described for ground water.

Ground water

Collect the sample as close to the source as possible, minimize aeration of the sample, and take the precautions described in step 3 above. See NFM 4.2, 5.0, 5.1, and 5.2 for ground-water sample collection and filtration methods.

- Purge the well (NFM 4.2 and 6.0) and connect the filter unit in-line with the pump.
- Flush and fill the sample lines and filter unit with sample water so as to exclude air.

MEASUREMENT 6.6.4

Alkalinity, ANC, and concentrations of bicarbonate, carbonate, and hydroxide species are most commonly determined by analyzing acidimetric-titration data with either the inflection point titration method (section 6.6.4.B) or the Gran function plot method (section 6.6.4.C).

- **The Inflection Point Titration (IPT) method** is adequate for most waters and study needs. Difficulty in identifying the inflection points using the IPT method increases as the ratio of organic acids to carbonate species increases, or as the alkalinity decreases.
- **The Gran function plot (Gran) method** is recommended for water in which the alkalinity or ANC is expected to be less than about 0.4 meq/L (20 mg/L as $CaCO_3$), or in which conductivity is less than 100 µS/cm, or if there are appreciable noncarbonate contributors or measurable concentrations of organic acids.

The Fixed Endpoint method (titration to pH 4.5) rarely is used and is no longer recommended by the USGS for determining alkalinity values because it is less accurate than the IPT and Gran methods. This decrease in accuracy is evident particularly for low concentrations of total carbonate species and for water with significant organic and other noncarbonate contributors to alkalinity or ANC.

Titrate a filtered sample if checking the charge balance or if reporting results as carbonate alkalinity.

6.6.4.A TITRATION SYSTEMS AND PROCEDURES

Titration procedures are identical for surface-water and ground-water determinations on filtered or unfiltered aliquots of fresh to saline water samples. Become familiar with the information and detailed instructions for the buret and digital titration systems and the IPT and Gran methods before proceeding with the titration.

Titration System

Select the titration system to be used.

- The digital titration system is convenient but tends to be less precise and less accurate than the buret system because of mechanical inadequacies. Good technique is necessary to produce acceptable results.
- The buret system can be cumbersome and fragile in the field, and requires experience to execute with precision and accuracy.
- A micrometer buret can achieve accuracy to 0.1 mg/L (routine determinations are reported to whole numbers).

The buret system yields better accuracy than the digital titrator.

Sample volume and acid normality

The methods as presented in this manual require electrometric titration of a sample with incremental additions of a strong acid (commonly H_2SO_4) of known normality. Suggested combinations of titrant normality and sample volume for various ranges of alkalinity or ANC values are given in table 6.6–2. These ranges can overlap at the thresholds indicated and should not be interpreted as absolute. Generally, 1.600*N* acid is too strong for most samples and only is used when alkalinity or ANC is greater than 4.0 meq/L (200 mg/L as $CaCO_3$). A more dilute acid (0.01639*N*) commonly is used with the buret system.

Select the size of the delivery and measurement vessels according to the volume of sample needed. Use a volumetric pipet for an alkalinity sample and a graduated cylinder or digital balance for an ANC sample. When selecting the measurement vessel:

- 50 mL of sample in a 100-mL beaker is typical for most routine work.
- Use 100 mL (or more) of sample in a 150-mL (or larger) beaker for samples with low alkalinity or ANC.
- Use 25 mL or less of a sample in a 50-mL beaker for samples with high alkalinity or ANC. Larger volumes of sample may be used in combination with higher normality titrant.

Table 6.6–2. Suggested sample volume and titrant normality for approximate ranges of alkalinity or ANC

[ANC, acid neutralizing capacity as determined on an unfiltered sample; meq/L, milliequivalents per liter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; mL, milliliter; >, greater than]

ANC or alkalinity (meq/L)	ANC or alkalinity (mg/L as $CaCO_3$)	Sample volume (mL)	Titrant normality
0–1.0	0–50	100 (or larger)	0.1600 (or lower)
1.0-4.0	50-200	50	.1600
4.0-20	200-1,000	100	1.600
>20	>1,000	50	1.600

To achieve greater accuracy, use lower normality titrant, decrease the volume of acid increments, or use a larger sample volume.

To pipet the sample for alkalinity determination:

A small volume of sample will remain in the tip of class A "TD" volumetric pipets—do not blow it out.

1. Suspend the pipet tip vertically in a beaker, touching neither the walls nor the contents of the receiving vessel.
2. Allow the sample to drain freely until the liquid it contains reaches the bottom of the pipet.
3. Touch the pipet tip to the beaker wall until the flow from the pipet stops—leave the tip in contact with the beaker wall for an additional 10 seconds after the flow stops.

Stirring method

When titrating, stirring helps to establish a uniform mixture of sample and titrant, and an equilibrium between sensors and sample. Select a stirring method and use a consistent technique.

- **If using a magnetic stirrer, stir the sample slowly and continuously**, using a small stir bar; avoid creating a vortex and large streaming potentials. If using a digital titrator, keep the delivery tube immersed throughout the procedure but keep the aperture of the tube away from the stir bar to avoid bleeding acid from the tube to the sample between titrant additions.
- If swirling the sample to mix, make the pH measurement as the sample becomes quiescent, after each addition of titrant.
- Avoid splashing the sample out of the beaker or onto the beaker walls. Droplets on the beaker walls can be rinsed down with deionized water. If you splash the sample out of the beaker, you must start over.
- Allow sufficient time between titrant additions for the pH value displayed on the instrument to equilibrate. Emphasis should be placed on maintaining a consistent technique (titrant additions every 15 - 30 seconds) rather than waiting for the instrument to "lock on" to a particular pH value.

Titration methods

Select and plan your method of titration.

- **IPT method.** Titrate cautiously on both sides of the expected equivalence points (fig. 6.6-1).
  - **If concentrations of contributing carbonate species will be determined and the initial pH is greater than 8.1:** titrate to a pH of about 8.0, carefully using small increments of acid. These data are important in determining the carbonate equivalence point.
  - **If concentrations of contributing carbonate species will not be determined:** titrate rapidly at first, adding relatively large acid increments to bring the pH to about 5.5. Do not skip the pH range above 5.5 completely, or you may pass the equivalence point.
  - **If a pH is below 5.5:** titrate slowly, using small increments of acid. This region is important in determining the bicarbonate equivalence point. Titrate to a pH of 4.0 or lower (3.5 if the sample alkalinity or ANC range is unknown or if the sample contains high concentrations of noncarbonate contributors, such as organic acids).
- **Gran method.** Collect data between and beyond the expected equivalence points (fig. 6.6-1).
  - **If concentrations of contributing carbonate species will be determined:** record titration points throughout the entire pH range of the titration. A good rule of thumb is to collect data along the titration curve roughly every 0.2 to 0.3 pH units. The points on the titration curve that are somewhat removed from the carbonate and bicarbonate equivalence points are used by the Gran method (Pankow, 1991).
  - **If concentrations of contributing carbonate species will not be determined:** it is not necessary to develop incremental titration points above a pH of about 5.5.
  - **Titrate to a pH of 3.5 or lower** (3.0 or less if the sample alkalinity or ANC range is unknown). A sufficient number of titration points beyond the equivalence point are needed to ensure accuracy.

Calibrate pH system.

- Collect representative sample.
- Filter subsamples for alkalinity.

↓

Collect sample.

- Field rinse and fill sample bottles with raw sample (or filtrate). Cap tightly.
- Maintain sample at ambient water temperature until titration.
- Rinse with DIW only: electrodes, sensors, beaker, stir bar, delivery tube.
- Place small-size stir bar in beaker.

↓

Select and record titration method, subsample volume, and titrant normality.

- Digital system: Assemble titrator, bleed delivery tube, set counter to zero.
- Buret system: Fill clean, dry buret with titrant—purge trapped air bubbles.

↓

Transfer appropriate volume of sample into beaker (pipet for alkalinity, graduated cylinder or digital balance for ANC).

- Place beaker on stirrer.
- Insert electrodes and temperature sensor, away from bottom or sides.
- Stir gently—do not splash; minimize vortex.
- Record initial time, pH, temperature, sample volume, titrant normality, and initial counter (digital system) or buret reading.

↓

Add titrant.

- Stir for 15–30 seconds; read and record pH and counter or buret reading.
- Repeat until titration is complete.

↓

- pH ≥ 8.1: Titrate slowly (to determine carbonate species), using small increments, to pH 8.0. This region is important for the IPT method.
- pH <8.1 and > 5.0: Titrate in larger increments, to pH ~5.5 (for conductivity <100 µS/cm) and no less than pH 5.0 in carbonate systems. Do not skip this region completely, as you may pass the equivalence point if you add too much titrant. This region is important for the Gran method.
- pH < 5.0: Titrate cautiously, using small increments, to pH ~4.0 or less if using the IPT method or to pH ~3.5 or less if using the Gran method. Titrate to lower pH if the noncarbonate contribution is large.

↓

Determine and record equivalence points.

Figure 6.6–1. Summary of alkalinity or ANC titration procedures.

Quality-control (QC) procedures

- Verify your accuracy and ability to reproduce the alkalinity or ANC determinations by using reference samples and repeating the titration periodically on duplicate or triplicate samples. The frequency and distribution of QC determinations are established by study requirements.

RULE OF THUMB: QC samples should be collected and titrated no less than every tenth sample. The determination on a filtered sample should be reproducible within ±5 percent when titrating a duplicate aliquot from the same batch of sample filtrate.

- For filtered samples with alkalinity less than 0.4 meq/L (20 mg/L as $CaCO_3$), reproducibility should be between 5 and 10 percent.
- If the alkalinity is about 0.02 meq/L or less, differences between duplicate samples are likely to exceed 10 percent because of rounding errors alone. Such rounding errors may be reduced by using a larger sample volume or a lower normality of titrant.

- **Compare ANC with alkalinity values—**When interferences are absent, titration on an unfiltered sample often results in a determination identical to or within 5 percent of the filtered sample and can be used as the QC check.
  - If filtered and unfiltered values fail the ±5-percent criterion, perform the QC check on the filtered sample.
  - Reproducibility of the ANC determination to within 5 percent on duplicate unfiltered samples can be problematical when the sample has large amounts of particulate matter—extend the quality-assurance criterion to ±10 percent.

To obtain the most accurate results for carbonate species, titrate at the field site without delay.

Digital titrator

Be thoroughly familiar with the operation of the digital titrator before field use. The procedures in this section describe use of the Hach® digital titrator, for which the Hach Company has provided accuracy and precision data. A plunger in the digital titrator forces acid in the titrant cartridge into the delivery tube. The plunger is controlled by a main-drive screw, which in turn is controlled by rotation of the delivery knob. The delivery knob controls the volume of titrant delivered through the delivery tube, as indicated by a digital counter. To minimize errors caused by uncertainty in the volume of titrant dispensed to the sample, titration procedures must account for the accuracy and precision of the titrant-delivery system.

To use the digital titrator:

1. Equilibrate titrant temperature to sample temperature.
2. Assemble the digital titrator.
   - Depress the plunger-release button and retract the plunger.
   - Insert the titrant cartridge into the titrator and twist the cartridge one-quarter turn to lock it into position.
   - Carefully depress the plunger-release button and push the plunger forward until it makes contact with the Teflon® seal inside the cartridge.
3. Remove the vinyl cap from the cartridge (save the cap) and insert the straight end of the delivery tube into the cartridge.
   - Do not push the delivery tube beyond the cartridge tip. Do not alter the delivery tube.
   - Use of a new delivery tube is recommended for each assembly of the titrator. Discard a tube that shows wear.
   - If tubes are reused, store them in separate, clean plastic bags after rinsing with DIW. Do not reuse a tube for a different titrant normality.
4. To ensure that no air bubbles or water are in the delivery tube, hold the titrator with the cartridge tip up and turn the delivery knob to force a few drops of titrant through the end of the delivery tube. Rinse tube exterior with DIW and blot acid or water droplets from the tube before inserting it into the sample.

5. Set the digital counter to zero using the counter-reset knob (taking care not to turn the delivery knob).
6. Transfer the selected volume of the sample (pipet for alkalinity, graduated cylinder or digital balance for ANC) to a clean beaker. If a magnetic stirrer is used, place a clean, dry, small stir bar into the beaker before transferring the sample to the beaker. Do not use a magnetic stirrer for sample conductivity <100 µS/cm. Place beaker on stirrer.
7. Rinse the pH and temperature sensors with DIW. Gently blot with lint-free paper any water droplets adhering to the sensors.
8. Insert the sensors into the beaker.
   - Do not let sensors touch the bottom or wall of the beaker.
   - The amount of sample in the beaker must be sufficient to cover the junction of the reference electrode, the electrode bulb, and the temperature sensor.
9. Measure the initial pH and temperature while gently stirring or after gently swirling the sample.
   - Do not splash sample onto the beaker wall or out of the beaker.
   - Minimize the vortex caused by magnetic stirring, and ensure that the stir bar does not hit the pH electrodes.
   - Record on the field form the pH and temperature values, the initial counter reading (it should read “0000”), the titrant normality, the time, and the sample volume.
10. Immerse the end of the titrant delivery tube in the sample. To prevent bleeding of the titrant from the delivery tube, keep the aperture of the delivery tube away from the stir bar.
11. **Begin titration.** If using a magnetic stirrer, stir the sample slowly and continuously. Measure pH after each addition of titrant, and after the acid and sample are mixed homogeneously. If a magnetic stirrer is not used, swirl to mix the sample and acid after each addition of titrant. Allow 15 to 30 seconds after each addition for equilibration, then record the pH and counter readings.

- **pH ≥ 8.1 —**To determine the carbonate equivalence point using the IPT method, slowly add the titrant in small (but no less than three digital-count) increments until the pH of the sample is less than 8.0. Larger increments can be used for samples containing high carbonate concentrations.
- **pH < 8.1 and ≥ 5.0 —**If using the IPT method, titrate with larger increments to pH ~5.0 (5.5 for sample alkalinity or ANC <0.4 meq/L (<20 mg/L as $CaCO_3$) or sample conductivity <100 µS/cm). Do not skip this pH region entirely; the equivalence point might be passed if too much acid is added. If using the Gran method, collect data points every 0.2 to 0.3 pH units in this region.
- **pH < 5.0 —**To determine the bicarbonate equivalence point with the IPT method, cautiously add the titrant in small (but no less than three digital-count) increments from pH 5.0 to ≤ 4.0. (The most sensitive part of the titration curve is between pH 4.8 and 4.3 for many natural waters.) If using the Gran method, extend the titration to pH ≤ 3.5 (≤ 3.0 for samples high in organic acids or other noncarbonate contributors, or when the alkalinity or ANC range is unknown). The Gran method relies on these low pH points beyond the equivalence point.

To reduce errors in the delivery of acid titrant, add the acid in minimum increments of three digital counts.

12. After completing the titration, remove the digital titrator from the sample; depress the plunger release, retract the plunger, and remove the titrant cartridge. Immediately replace the vinyl cap on the cartridge tip. Rinse the delivery tube with DIW or discard.
13. Analyze the titration data to determine the carbonate and bicarbonate equivalence points using the IPT method (section 6.6.4.B) and/or the Gran method (section 6.6.4.C).
14. Calculate the sample alkalinity or ANC and the concentrations of the carbonate species from the equivalence points, as described in section 6.6.5.

Buret titrator

When using a buret, exercise caution to ensure that the acid does not evaporate or become contaminated with extrinsic matter or moisture. The titrant temperature should be equilibrated to the sample temperature before use. Always empty the buret after each use. Never reuse the titrant solution; dispose of the solution properly.

To titrate with a buret:

1. Fill a clean, dry buret with sulfuric acid titrant (0.01639*N* or other known concentration).
   - Use a 10-mL semimicroburet with 0.05-mL graduations and a Teflon® stopcock for samples with alkalinity or ANC less than 4 meq/L (200 mg/L as $CaCO_3$).
   - Use a 25-mL buret with 0.1-mL graduations and a Teflon® stopcock for samples with alkalinity or ANC of 4 meq/L (200 mg/L as $CaCO_3$) or greater and when the sample pH exceeds 8.1.
   - If greater accuracy is desired, use a Gilmont®-type micrometer buret.
2. Make sure no air bubbles are trapped in the buret or the buret stopcock. Record on field forms the sulfuric acid normality and initial buret reading.
3. Transfer the selected volume of sample (pipet for alkalinity, graduated cylinder or digital balance for ANC) to a clean beaker. **Do not pipet by mouth.**
   - If a magnetic stirrer is used, place a clean, dry, small stir bar into the beaker before transferring the sample to the beaker. Place the beaker on a magnetic stirrer.
   - Do not use a magnetic stirrer if sample conductivity is <100 µS/cm.
4. Rinse the pH and temperature sensors with DIW. Gently blot water droplets adhering to the sensors with lint-free paper (residual DIW will not affect the determination).

5. Insert the sensors into the beaker.
   - Do not let sensors touch the bottom or wall of the beaker.
   - Sample depth in the beaker must be sufficient to cover the junction of the reference electrode, the electrode bulb, and the temperature sensor.
6. Measure the initial pH and temperature while gently stirring or after gently swirling the sample.
   - Do not splash the sample onto the beaker wall or out of the beaker.
   - Minimize the vortex caused by magnetic stirring, and ensure that the stir bar does not hit the pH electrodes.
   - Record on the field form the pH and temperature values, the initial buret reading, the titrant normality, the time, and the sample volume.
7. **Begin titration.** If using a magnetic stirrer, stir the sample slowly and continuously. Measure pH after each addition of titrant, and after the acid and sample are mixed homogeneously. If a magnetic stirrer is not used, swirl to mix the sample and acid after each addition of titrant. Allow 15 to 30 seconds after each addition for equilibration, then record the pH and buret readings.
   - **pH ≥ 8.1 —**To determine the carbonate equivalence point using the IPT method, add the titrant drop by drop in 0.01-mL increments until the pH is less than 8.0. Larger increments can be used for samples containing high carbonate concentrations.
   - **pH < 8.1 and ≥ 5.0 —**If using the IPT method, titrate with larger increments to pH ~5.0 (5.5 for sample with alkalinity or ANC <0.4 meq/L (<20 mg/L as $CaCO_3$) or with sample conductivity <100 µS/cm). Do not skip this pH region entirely; the equivalence point might be passed if too much acid is added. If using the Gran method, collect data points every 0.2 to 0.3 pH units in this region.

- **pH < 5.0 —**To determine the bicarbonate equivalence point with the IPT method, cautiously add the titrant drop by drop in 0.01-mL increments from pH 5.0 to 4.0 or less (the most sensitive part of the titration curve is between pH 4.8 and 4.3 for many natural waters). If using the Gran method, extend the titration to pH 3.5 or less (3.0 or less for samples high in organic acids and other noncarbonate contributors, or when the alkalinity or ANC range is unknown). The Gran method relies on these low pH points beyond the equivalence point.

  TECHNICAL NOTE: 0.01 mL of a standard 0.05-mL drop of titrant tends to remain on the buret tip. To dispense a 0.01-mL titrant drop, quickly rotate the stopcock through 180 degrees (one-half turn) and then rinse the titrant from the buret tip into the beaker with a small quantity of DIW.

8. Analyze the titration data to determine the carbonate and bicarbonate equivalence points using the IPT method (section 6.6.4.B) and/or the Gran method (section 6.6.4.C).
9. Calculate the sample alkalinity or ANC and the concentrations of the carbonate species from the equivalence points, as described in section 6.6.5.

6.6.4.B INFLECTION POINT TITRATION METHOD

The inflection point titration (IPT) method uses the inflection points of the titration curve to determine equivalence points. Whereas for many natural water samples these points are near pH 8.3 and 4.5, it is more accurate to calculate their values from the titration data.

Inflection points are the points of maximum rate of change in pH per volume of titrant added. **Near equivalence points, rapid pH changes occur with small additions of titrant. For this reason, the titration must be performed slowly and cautiously near the expected equivalence points, using small incremental additions of titrant.** The relative error of the determinations can be within ±4 percent if the equivalence point is recognizable within ±0.3 pH unit of the true equivalence point.

To determine the inflection point(s), you can either construct a titration curve by plotting the change in pH divided by the change in titrant volume against the volume of titrant added to the sample, or calculate such values in a table or spreadsheet.

- Graphing the titration curve always is advisable. Such plots are helpful in uncovering typographical errors and spurious maxima that might confuse the detection of the inflection point(s).
- More than one inflection point in close proximity indicates that the true inflection point has been missed. If this occurs, titrate a duplicate sample using smaller acid increments near the inflection point or use a Gran plot. Note that if the acid increments are too small, the location of the inflection points may become masked by noise in the data.
- If the maximum rate of change in pH per volume of titrant occurs at two or more points near an equivalence point (two or more points are “tied” for the maximum value), then determine the location of the equivalence point as the middle of the range where ties were produced. For example, if the maximum rate occurs at digital counts 120, 122, and 126, then the calculated location of the equivalence point is at digital count 123.

- If no clear inflection point(s) can be determined easily, interferences from weak organic acids are likely—use the Gran method.

Example IPT–1A shows the results of an IPT analysis of a typical titration using a digital titrator. Example IPT–1B shows similar results from a buret titration. Both of these titrations have inflection points at both the carbonate and bicarbonate equivalence points. Example IPT–2 uses the IPT method on a sample with low alkalinity; that sample has only one inflection point.

Example IPT–1A: IPT method using the digital titrator

A titration was performed on a natural water sample from the South Diamond Canal inflow to the Donner und Blitzen River, Oregon. The data are plotted in figure 6.6–2 and listed in table 6.6–3. Using the IPT method, the maximum rates of change of pH per volume of titrant added occur at pH 8.27 and 4.50 (at counts 186 and 1014). Because these slopes represent changes between two points, the actual inflection points are located between counts 183 and 186 for the carbonate equivalence point and between 1011 and 1014 for the bicarbonate equivalence point. Thus, the calculated digital-counter values for the inflection points are 184.5 (185) and 1012.5 (1013). The error in using 1014 rather than 1013 typically is insignificant but the larger the increments used, the greater the error. Calculation of the correct inflection point results in reduced errors.

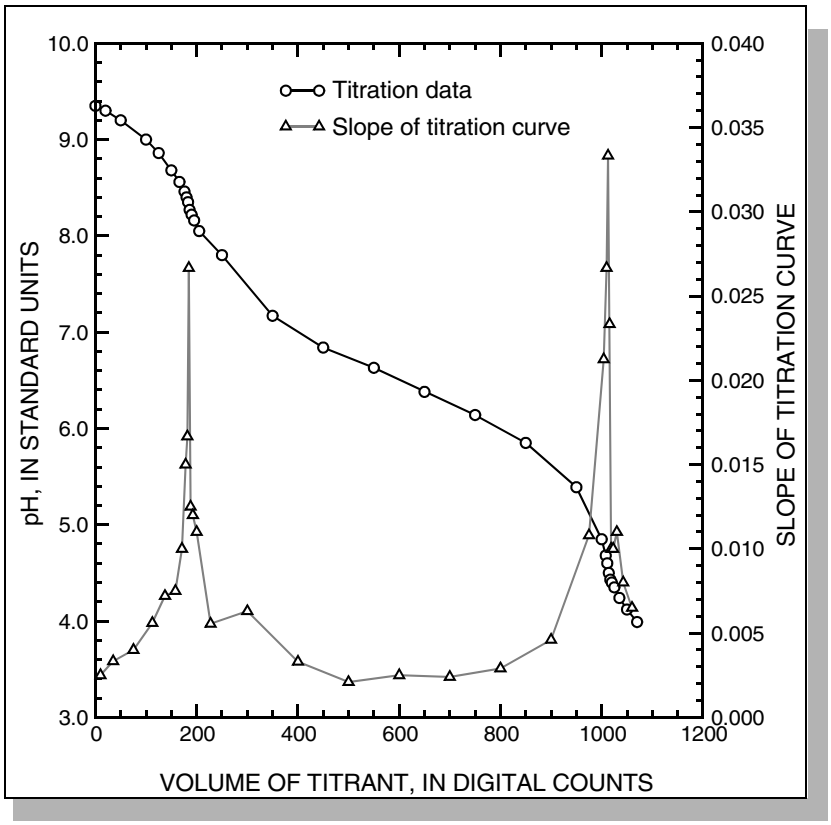

Figure 6.6–2. Plot of data for an inflection point titration using a digital titrator (Example IPT–1A).

Table 6.6–3. Typical inflection point titration data using a digital titrator (Example IPT–1A)

[—, no data. The shaded rows indicate where the maximum rates of change of pH per digital count occur (at pH 8.27 and 4.50 in this sample)]

pH (standard units)	Change in pH (standard units)	Counter reading (counts)	Change in counter (counts)	Change in pH per change in counter
9.35	—	0	—	—
9.30	0.05	20	20	0.0025
9.20	.10	50	30	.0033
9.00	.20	100	50	.0040
8.86	.14	125	25	.0056
8.68	.18	150	25	.0072
8.56	.12	166	16	.0075
8.46	.10	176	10	.0100
8.40	.06	180	4	.0150
8.35	.05	183	3	.0167
8.27	.08	186	3	.0267
8.22	.05	190	4	.0125
8.16	.06	195	5	.0120
8.05	.11	205	10	.0110
7.80	.25	250	45	.0056
7.17	.63	350	100	.0063
6.84	.33	450	100	.0033
6.63	.21	550	100	.0021
6.38	.25	650	100	.0025
6.14	.24	750	100	.0024
5.85	.29	850	100	.0029
5.39	.46	950	100	.0046
4.85	.54	1000	50	.0108
4.68	.17	1008	8	.0213
4.60	.08	1011	3	.0267
4.50	.10	1014	3	.0333
4.43	.07	1017	3	.0233
4.40	.03	1020	3	.0100
4.35	.05	1025	5	.0100
4.24	.11	1035	10	.0110
4.12	.12	1050	15	.0080
3.99	.13	1070	20	.0065

Example IPT–1B: IPT method using the buret system

If the sample in Example IPT–1A had been titrated with the buret system, the titration data would be similar to that plotted in figure 6.6–3 and given in table 6.6–4. Using the IPT method, the maximum rates of change of pH per volume of titrant added occur at pH 8.27 and 4.50 (at 1.86 and 10.14 mL of acid added). Because these slopes are changes between two points, the actual inflection points are located between 1.83 and 1.86 mL for the carbonate equivalence point, and between 10.11 and 10.14 mL for the bicarbonate equivalence point. The calculated titrant volumes for the inflection points, therefore, are 1.85 and 10.13 mL.

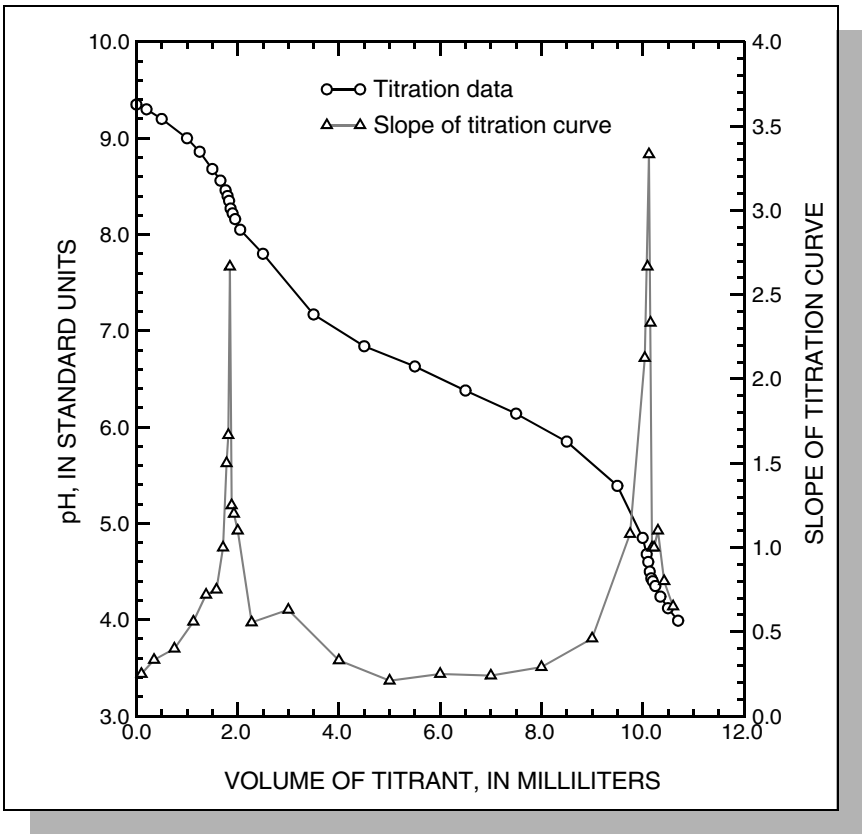

Figure 6.6–3. Plot of data for an inflection point titration using a buret (Example IPT–1B).

Table 6.6–4. Typical inflection point titration data using a buret (Example IPT–1B)
[—, no data. The shaded rows indicate where the maximum rates of change of pH per volume of titrant occur (at pH 8.27 and 4.50 in this sample); mL, milliliter]

pH (standard units)	Change in pH (standard units)	Buret reading (mL)	Titrant volume (mL)	Change in volume (mL)	Change in pH per change in volume
9.35	—	1.20	0.00	—	—
9.30	0.05	1.40	.20	0.20	0.250
9.20	.10	1.70	.50	.30	.333
9.00	.20	2.20	1.00	.50	.400
8.86	.14	2.45	1.25	.25	.560
8.68	.18	2.70	1.50	.25	.720
8.56	.12	2.86	1.66	.16	.750
8.46	.10	2.96	1.76	.10	1.000
8.40	.06	3.00	1.80	.04	1.500
8.35	.05	3.03	1.83	.03	1.667
8.27	.08	3.06	1.86	.03	2.667
8.22	.05	3.10	1.90	.04	1.250
8.16	.06	3.15	1.95	.05	1.200
8.05	.11	3.25	2.05	.10	1.100
7.80	.25	3.70	2.50	.45	.556
7.17	.63	4.70	3.50	1.00	.630
6.84	.33	5.70	4.50	1.00	.330
6.63	.21	6.70	5.50	1.00	.210
6.38	.25	7.70	6.50	1.00	.250
6.14	.24	8.70	7.50	1.00	.240
5.85	.29	9.70	8.50	1.00	.290
5.39	.46	10.70	9.50	1.00	.460
4.85	.54	11.20	10.00	.50	1.080
4.68	.17	11.28	10.08	.08	2.125
4.60	.08	11.31	10.11	.03	2.667
4.50	.10	11.34	10.14	.03	3.333
4.43	.07	11.37	10.17	.03	2.333
4.40	.03	11.40	10.20	.03	1.000
4.35	.05	11.45	10.25	.05	1.000
4.24	.11	11.55	10.35	.10	1.100
4.12	.12	11.70	10.50	.15	.800
3.99	.13	11.90	10.70	.20	.650

Example IPT–2: IPT method for a low alkalinity sample

A water sample collected from Little Abiqua Creek near Scotts Mills, Oregon, provides a good example for a low-alkalinity titration. In this titration, 200 mL of filtered sample were titrated with 0.16*N* titrant and analyzed by the IPT method. The results are shown in figure 6.6–4 and table 6.6–5. The bicarbonate equivalence point was found near a pH of 5.25, between digital counts 134 and 137. The correct digital-counter value at the inflection point, therefore, is 136 (135.5) counts. This results in a calculated alkalinity of 6.8 mg/L as $CaCO_3$.

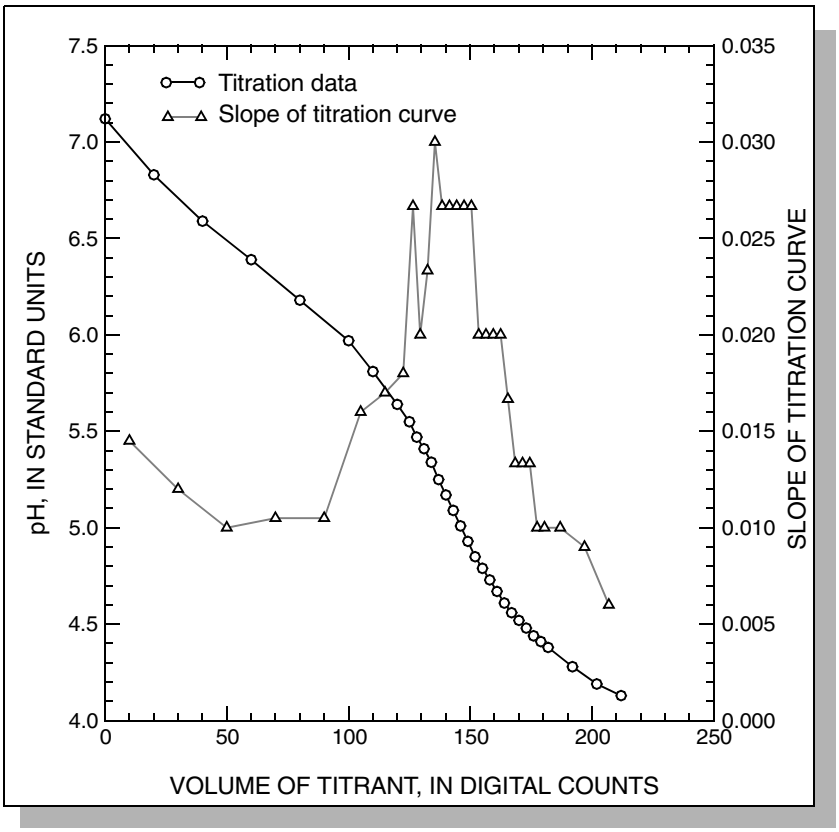

Figure 6.6–4. Plot of data for an inflection point titration of a low-alkalinity sample (Example IPT–2).

Table 6.6–5. Inflection point analysis for a low-alkalinity sample (Example IPT–2)

[—, no data. The shaded row indicates where the maximum rate of change of pH per digital count occurs (at pH 5.25 in this sample)]

pH (standard units)	Change in pH (standard units)	Counter reading (counts)	Change in counter (counts)	Change in pH per change in counter
7.12	—	0	—	—
6.83	0.29	20	20	0.0145
6.59	.24	40	20	.0120
6.39	.20	60	20	.0100
6.18	.21	80	20	.0105
5.97	.21	100	20	.0105
5.81	.16	110	10	.0160
5.64	.17	120	10	.0170
5.55	.09	125	5	.0180
5.47	.08	128	3	.0267
5.41	.06	131	3	.0200
5.34	.07	134	3	.0233
5.25	.09	137	3	.0300
5.17	.08	140	3	.0267
5.09	.08	143	3	.0267
5.01	.08	146	3	.0267
4.93	.08	149	3	.0267
4.85	.08	152	3	.0267
4.79	.06	155	3	.0200
4.73	.06	158	3	.0200
4.67	.06	161	3	.0200
4.61	.06	164	3	.0200
4.56	.05	167	3	.0167
4.52	.04	170	3	.0133
4.48	.04	173	3	.0133
4.44	.04	176	3	.0133
4.41	.03	179	3	.0100
4.38	.03	182	3	.0100
4.28	.10	192	10	.0100
4.19	.09	202	10	.0090
4.13	.06	212	10	.0060

6.6.4.C GRAN FUNCTION PLOT METHOD

Gran function plots commonly are used to determine alkalinity and ANC in sea water, low ionic-strength water, water with low carbonate concentrations, and water with measurable concentrations of organic compounds. Gran's method does not rely on the presence of inflection points in the titration curve; therefore, it particularly is useful for waters with low alkalinity.

Using the known chemistry of carbonic acid and some simplifying assumptions, Gran's method linearizes a set of functions that describe parts of the titration curve (Gran, 1952). The linearizing assumptions used by Gran's method are valid only for data that are some distance away from the equivalence points (Pankow, 1991).

- Collect titration points throughout the entire pH range of the titration. A good rule of thumb is to collect data along the titration curve roughly every 0.2 to 0.3 pH unit.
- Titrate to a pH of 3.5 or lower (3.0 or less if the alkalinity or ANC range is unknown for the waters sampled). A sufficient number of titration points beyond the bicarbonate equivalence point are needed to ensure the accuracy of the calculation.

In contrast to the IPT method, the Gran function plot method uses data that are somewhat removed from the equivalence points.

Gran Functions

During an alkalinity titration (carbonate system), the hydrogen ions added convert carbonate to bicarbonate and then bicarbonate to carbonic acid. The titration continues until no more species are reacting. When this process is complete, additional hydrogen ions will be in excess in the solution. **The F_1 Gran function plot identifies the point at which all alkalinity has been titrated and hydrogen ions begin to be in excess.** Beyond the bicarbonate equivalence point, the shape of the curve is determined by hydrogen ions in excess of all hydrogen ion acceptors in the sample. Similar relations are used with the Gran functions in other parts of the titration curve.

Two Gran functions can be calculated for each equivalence point in the titration. Including the equivalence points for hydroxide, carbonate, and bicarbonate, six Gran functions (F_1 through F_6) are useful for analyzing titration data from natural water samples. The functions for the hydroxide equivalence point, however, commonly are not used. Derivations of these Gran functions are available (Stumm and Morgan, 1981).

For an acidimetric titration, the six Gran functions are

$$F_1 = (V_o + V_t)\,(10^{-pH}) / \gamma = (V_t - V_s)\,C_a$$

$$F_2 = (V_s - V_t)\,10^{-pH} = (V_t - V_w)\,K_1'$$

$$F_3 = (V_t - V_w)\,10^{pH} = (V_s - V_t) / K_1'$$

$$F_4 = (V_s - 2V_w + V_t)\,10^{pH} = (V_w - V_t) / K_2'$$

$$F_5 = (V_w - V_t)\,10^{-pH} = (V_t - V_x)\,K_2'$$

$$F_6 = (V_o + V_t)\,10^{pH} = (V_x - V_t)\,C_a / K_w',$$

where

V_o	is	initial volume of the sample;
V_t	is	volume of acid titrant added;
V_s	is	titrant volume at the bicarbonate equivalence point;
V_w	is	titrant volume at the carbonate equivalence point;
V_x	is	titrant volume at the hydroxide equivalence point;
C_a	is	normality of the acid titrant;
γ	is	activity coefficient for H^+;
K_1'	is	first acid dissociation constant for H_2CO_3, corrected for the activity of carbonate species;
K_2'	is	second acid dissociation constant for H_2CO_3, corrected for the activity of carbonate species; and
K_w'	is	acid dissociation constant for water, corrected for the activity of hydroxide.

Note that if these functions are calculated in the correct sequence, the function value on the left side of each equation will consist of known values. By extrapolating these function values to zero, the right side of each equation can be set to zero and can be used to solve for a previously unknown equivalence point.

- The F_1 function, followed by F_2, is the most commonly used Gran function.
- The Gran functions F_1 and F_3 are useful in determining the bicarbonate equivalence point because F_1 and F_3 are zero when $V_t = V_s$. Similarly, F_2 and F_4 are used to determine the carbonate equivalence point ($V_t = V_w$), whereas F_5 and F_6 can be used to determine the hydroxide equivalence point ($V_t = V_x$).

Gran Function Plots

Gran function plots are made by plotting each of the Gran functions against titrant volume and fitting a line through the data points for each function in a particular pH region.

- The F_1 function is valid for the pH range just below the bicarbonate equivalence point. The F_1 data only become linear somewhat beyond the bicarbonate equivalence point; therefore, it is often necessary to titrate the sample down to a pH between 3.5 and 3.0. For systems with measurable concentrations of organic acids, titrate to pH 2.5 (Baedecker and Cozzarelli, 1992).
- Functions F_2 and F_3 are valid in the pH range between the carbonate and bicarbonate endpoints.
- Functions F_4 and F_5 are valid for pH values between the carbonate and hydroxide endpoints.
- Function F_6 is valid for pH values higher than the hydroxide endpoint.

Equivalence points are found by extrapolating each function to where it crosses the x-axis. An idealized Gran analysis would result in a plot such as that shown in figure 6.6–5. The F_1 and F_2 functions are the most commonly used Gran functions.

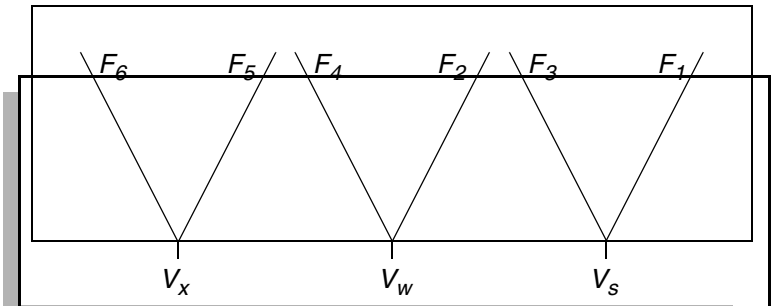

Figure 6.6–5. An idealized Gran function plot, showing six Gran functions

The F_1 function must be calculated first. In order to calculate F_2, one needs to know the location of the bicarbonate equivalence point, V_s, which is obtained from the solution of F_1.

Similarly, the value of V_w from an analysis of F_2 is necessary to plot and analyze F_3. Function F_4 requires both V_s and V_w from the results of F_2 and either F_1 or F_3. Function F_5 requires a value for V_w from the results of either F_2 or F_4.

TECHNICAL NOTE: The Gran functions also can be used to extract useful information from their fitted slopes, such as the values of C_a and the various acid dissociation constants. Further explanation can be found in Stumm and Morgan (1981) and Pankow (1991).

Gran function plots are easy to prepare with a spreadsheet or computer program (see section 6.6.5).

To prepare a Gran function plot:

1. **Bicarbonate equivalence point (Gran function F_1).** Plot $(V_o + V_t)\ 10^{-pH}$ against the titrant volume, V_t. (This formulation ignores activity corrections, setting $\gamma = 1.0$.)
   - When developing this function, V_o and V_t must be in the same units (probably mL).
   - The value of V_t on the x-axis can be in either milliliter or digital counts.
2. Extrapolate a straight line through the data in the region beyond the bicarbonate equivalence point to where it meets the x-axis at $F_1 = (V_o + V_t)\ 10^{-pH} = 0$ or $V_t = V_s$. That point is the bicarbonate equivalence point. See **Example Gran–1** for an illustration of steps 1 and 2.
3. **Carbonate equivalence point (Gran function F_2).** Using the value of V_s from step 2, plot $(V_s - V_t)\ 10^{-pH}$ against the titrant volume, V_t, in the region between the carbonate and bicarbonate equivalence points. Make sure to use the same units for V_t and V_s in developing this function.
4. Extrapolate a straight line through the data in this region to where it meets the x-axis at $F_2 = (V_s - V_t)\ 10^{-pH} = 0$ or $V_t = V_w$. That point is the carbonate equivalence point.

Skip steps 5 and 6 (F_5 and F_6 Gran functions) if the initial sample pH is less than approximately 10.3.

5. **Hydroxide equivalence point (Gran function F_5).** Using the value of V_w from step 4, plot $(V_w - V_t)\ 10^{-pH}$ against the titrant volume, V_t, in the region above the carbonate equivalence point. Use the same units for V_t and V_w in developing this function.
6. Extrapolate a straight line through the data in the region between the carbonate and hydroxide equivalence points to where it meets the x-axis at $F_5 = (V_w - V_t)\ 10^{-pH} = 0$ or $V_t = V_x$. That point is the hydroxide equivalence point.

At this point, you can either stop, or try to verify your values of V_s, V_w and V_x by plotting additional Gran functions. To continue plotting, follow these optional steps:

7. In the region between the carbonate and bicarbonate equivalence points, plot $(V_t - V_w)\ 10^{pH}$ against the titrant volume, V_t. This is a plot of the Gran function F_3.
8. Extrapolate a straight line in this region to where it meets the x-axis at $F_3 = (V_t - V_w)\ 10^{pH} = 0$ or $V_t = V_s$ to get another estimate of the bicarbonate equivalence point.
9. In the region between the carbonate and hydroxide equivalence points, plot $(V_s - 2V_w + V_t)\ 10^{pH}$ against the titrant volume, V_t. This is a plot of the Gran function F_4.
10. Extrapolate a straight line in this region to where it meets the x-axis at $F_4 = (V_s - 2V_w + V_t)\ 10^{pH} = 0$ or $V_t = V_w$ to obtain another estimate of the carbonate equivalence point.
11. In the region above the hydroxide equivalence point, plot $(V_o + V_t)\ 10^{pH}$ against the titrant volume, V_t. This is a plot of the Gran function F_6.
12. Extrapolate a straight line in this region to where it meets the x-axis at $F_6 = (V_o + V_t)\ 10^{pH} = 0$ or $V_t = V_x$ to obtain another estimate of the hydroxide equivalence point.

Depending on the number of points used to develop each of the Gran functions, the equivalence points from each pair of functions (F_1 and F_3, F_2 and F_4, F_5 and F_6) may not be identical.

- If both functions appear to fit the data well and use a sufficient number of points, then average the estimates for that equivalence point.
- If one of the functions (F_3, for example) clearly has a poorer fit to the data or uses far fewer points than does its partner (F_1, in this case), then choose the equivalence point calculated from the other Gran function (F_1). Example Gran-1 illustrates the use of Gran function F_1 while Example Gran-2 illustrates use of Gran functions F_1 through F_4.

Example Gran–1: Gran function plot of F_1 only

Gran function plots are useful for samples with low alkalinity. Using the titration data obtained from a sample of Little Abiqua Creek near Scotts Mills, Oregon (from Example IPT–2), a Gran function plot is easily prepared. The necessary calculations are shown in table 6.6-6. The results are plotted in figure 6.6-6. In the region beyond the equivalence point in figure 6.6-6, a straight line results. Extrapolation of this straight line to $(V_o+V_t)10^{-pH} = 0$ locates the equivalence point. The extrapolated straight line intercept at $(V_o+V_t)\ 10^{-pH} = 0$ on figure 6.6-6 is at 139.5 digital counts of titrant added, corresponding to a bicarbonate equivalence point at a pH of approximately 5.18. The calculated alkalinity by this method is 7.0 mg/L as $CaCO_3$, in excellent agreement with the value of 6.8 mg/L as $CaCO_3$ calculated by the IPT method in Example IPT–2.

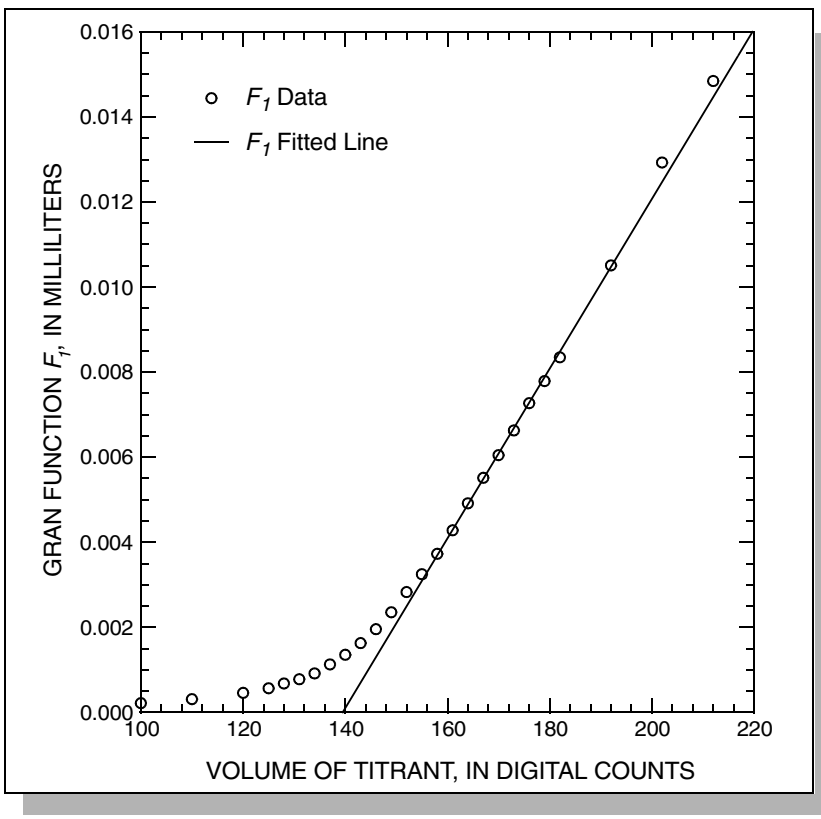

Figure 6.6–6. Example of a Gran function plot using F_1 to determine the bicarbonate equivalence point.

Table 6.6–6. Gran function plot analysis for a low-alkalinity sample—calculation of Gran function F_1 for Example Gran–1.
[V_o, volume of sample; V_t, volume of titrant; mL, milliliters]

pH (standard units)	Counter reading (counts)	Titrant volume, V_t (mL)	V_o+V_t (mL)	10^{-pH}	$(V_o+V_t)10^{-pH}$ (mL)
7.12	0	0.000	200.000	7.586×10^{-08}	1.517×10^{-05}
6.83	20	.025	200.025	1.479×10^{-07}	2.959×10^{-05}
6.59	40	.050	200.050	2.570×10^{-07}	5.142×10^{-05}
6.39	60	.075	200.075	4.074×10^{-07}	8.151×10^{-05}
6.18	80	.100	200.100	6.607×10^{-07}	1.322×10^{-04}
5.97	100	.125	200.125	1.072×10^{-06}	2.144×10^{-04}
5.81	110	.138	200.138	1.549×10^{-06}	3.100×10^{-04}
5.64	120	.150	200.150	2.291×10^{-06}	4.585×10^{-04}
5.55	125	.156	200.156	2.818×10^{-06}	5.641×10^{-04}
5.47	128	.160	200.160	3.388×10^{-06}	6.782×10^{-04}
5.41	131	.164	200.164	3.890×10^{-06}	7.787×10^{-04}
5.34	134	.168	200.168	4.571×10^{-06}	9.149×10^{-04}
5.25	137	.171	200.171	5.623×10^{-06}	1.126×10^{-03}
5.17	140	.175	200.175	6.761×10^{-06}	1.353×10^{-03}
5.09	143	.179	200.179	8.128×10^{-06}	1.627×10^{-03}
5.01	146	.183	200.183	9.772×10^{-06}	1.956×10^{-03}
4.93	149	.186	200.186	1.175×10^{-05}	2.352×10^{-03}
4.85	152	.190	200.190	1.413×10^{-05}	2.828×10^{-03}
4.79	155	.194	200.194	1.622×10^{-05}	3.247×10^{-03}
4.73	158	.198	200.198	1.862×10^{-05}	3.728×10^{-03}
4.67	161	.201	200.201	2.138×10^{-05}	4.280×10^{-03}
4.61	164	.205	200.205	2.455×10^{-05}	4.914×10^{-03}
4.56	167	.209	200.209	2.754×10^{-05}	5.514×10^{-03}
4.52	170	.213	200.213	3.020×10^{-05}	6.046×10^{-03}
4.48	173	.216	200.216	3.311×10^{-05}	6.630×10^{-03}
4.44	176	.220	200.220	3.631×10^{-05}	7.270×10^{-03}
4.41	179	.224	200.224	3.890×10^{-05}	7.790×10^{-03}
4.38	182	.228	200.228	4.169×10^{-05}	8.347×10^{-03}
4.28	192	.240	200.240	5.248×10^{-05}	1.051×10^{-02}
4.19	202	.253	200.253	6.457×10^{-05}	1.293×10^{-02}
4.13	212	.265	200.265	7.413×10^{-05}	1.485×10^{-02}

Example Gran–2: Gran function plot using F_1 through F_4

In this example, the same titration data that were used in Example IPT–1A in section 6.6.4.B are analyzed using the Gran method. The sample pH (9.35) was not high enough to justify the use of Gran functions F_5 and F_6, so only functions F_1 through F_4 are used.

The results are shown in figure 6.6–7, and indicate a bicarbonate equivalence point at 1005 counts (from F_3, only 2 data points could be used for F_1), and a carbonate equivalence point at about 209 counts (F_2 estimated the equivalence point at 214, F_4 at 204). Although this is not an ideal data set for Gran function analysis (the titration did not extend to pH values lower than about 4.0), the Gran method was able to provide reasonable estimates of the equivalence points.

Using a bicarbonate equivalence point of 1005 counts as determined by the Gran method, an acid titrant normality of 0.16*N*, and a sample volume of 100 mL, the calculated alkalinity of this sample is 100.5 mg/L as $CaCO_3$ (see section 6.6.5). Using an equivalence point of 1013 counts for this sample from the analysis in Example IPT–1A (inflection point method), the calculated alkalinity would be 101.3 mg/L as $CaCO_3$. The agreement between these two methods is very good, producing a discrepancy of less than 1 percent. Results from either method would be reported as 101 mg/L as $CaCO_3$.

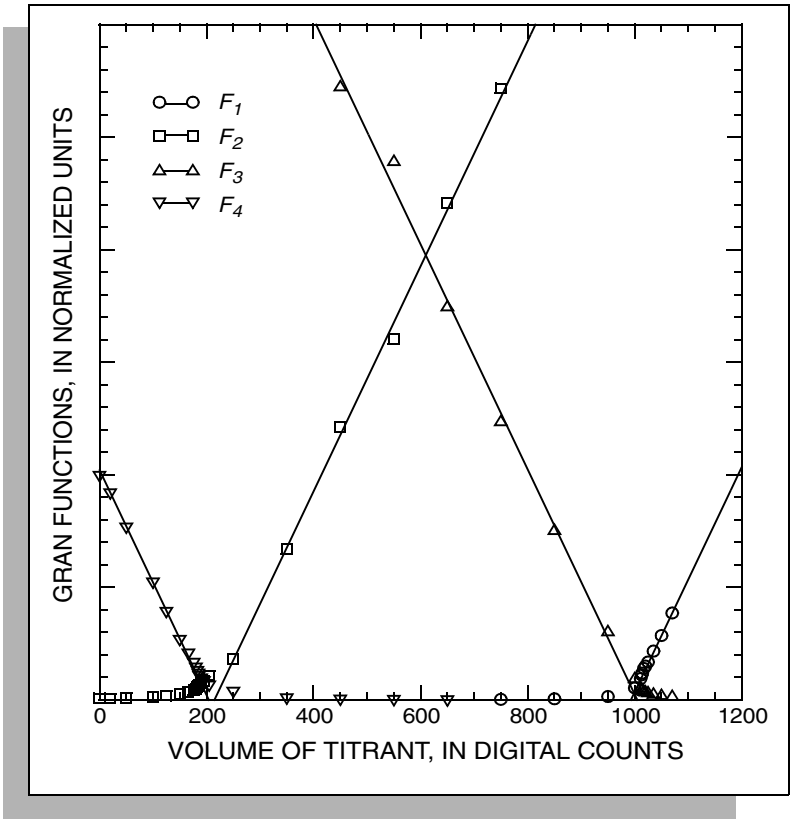

Figure 6.6–7. Example of a Gran function plot using F_1, F_2, F_3, and F_4 to determine carbonate and bicarbonate equivalence points.

6.6.5 CALCULATIONS

Concentrations of alkalinity or ANC and carbonate species can be calculated by hand, or in a spreadsheet (sections 6.6.5.A and 6.6.5.B), or by using a computer program (section 6.6.5.C). For hand calculations, first determine the equivalence points using the IPT (section 6.6.4.B) or Gran function (section 6.6.4.C) method. The equations below are valid for buret or digital titration equipment, and any acid concentration and sample volume.

6.6.5.A ALKALINITY OR ANC

Calculation of alkalinity or ANC is a simple accounting of the amount of acid used to neutralize the sample:

$$Alk\left(\frac{meq}{L}\right) = \left[\frac{B\ (mL) \times C_a\left(\frac{meq}{mL}\right) \times CF}{V_s\ (mL) \times \left(\frac{1\ L}{1000\ mL}\right)}\right] = 1000(B)(C_a)(CF)/V_s$$

and

$$Alk\left(\frac{mg}{L}\text{ as } CaCO_3\right) = Alk\left(\frac{meq}{L}\right) \times \left(\frac{1\ mmol\ CaCO_3}{2\ meq}\right) \times \left(\frac{100.087\ mg\ CaCO_3}{1\ mmol\ CaCO_3}\right)$$
$$= 50044(B)(C_a)(CF)/V_s$$

where

Alk is alkalinity or ANC of the sample.
B is volume of acid titrant added from the initial pH to the bicarbonate equivalence point (near pH 4.5), in milliliters.
To convert from digital counts to milliliters, divide by 800 (1.00 mL = 800 counts).
C_a is concentration of acid titrant, in milliequivalents (*meq*) per milliliter (same as equivalents per liter, or *N*).
CF is correction factor (see below).
V_s is volume of the sample, in milliliters.
mmol is millimoles of calcium carbonate.

The correction factor *CF* is equal to 1.01 as determined by the NWQL, resulting from a bias caused by the configuration of Hach digital titrator cartridges.

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CARBONATE-SPECIATION EQUATIONS FOR SAMPLES WITH pH ≤ 9.2 6.6.5.B

- **To calculate bicarbonate and carbonate species using the equations below, the following assumptions must apply:**
  - Bicarbonate and carbonate are the only species providing significant contributions to alkalinity or ANC. (If the sample contains other titratable species in significant amounts, the calculated bicarbonate and carbonate concentrations will be in error.)
  - The sample pH is ≤ 9.2.
- If sample pH is > 9.2, calculations are more complex and use of the Alkalinity Calculator computer program (section 6.6.5.C) is recommended.
- If the sample contains other titratable species such as ammonia, borate, or silicic acid that contribute significantly to alkalinity or ANC, use of a full geochemical model such as PHREEQC (Parkhurst and Appelo, 1999) is recommended.[2]

TECHNICAL NOTE: The equations provided below for bicarbonate and carbonate only apply for samples with a pH of 9.2 or less because the effects of hydroxide were neglected. The equations remain useful, however, because they still apply to a wide range of natural water samples. The error in using these equations should be less than 10 percent and/or less than 1 mg/L. Speciation equations for samples with a pH greater than 9.2 that account for the presence of hydroxide and the equilibrium chemistry of carbonic acid can be found at http://oregon.usgs.gov/alk/methods.html (refer to the documentation for the Alkalinity Calculator Program, section 6.6.5.C).

[2]A description of such geochemical models is beyond the scope of this manual.

1. Calculate bicarbonate and carbonate species as follows:

Constituent	Formula
Bicarbonate (meq/L)	$1000(B-2A)(C_a)(CF) / V_s$
Bicarbonate (mg/L as HCO_3^-)	$61017(B-2A)(C_a)(CF) / V_s$
Carbonate (meq/L)	$2000(A)(C_a)(CF) / V_s$
Carbonate (mg/L as CO_3^{2-})	$60009(A)(C_a)(CF) / V_s$

where

A is volume of acid titrant added from the initial pH to the carbonate equivalence point (near pH 8.3), in milliliters.
To convert from digital counts to milliliters, divide by 800 (1.00 mL = 800 counts).

B is volume of acid titrant added from the initial pH to the bicarbonate equivalence point (near pH 4.5), in milliliters.
To convert from digital counts to milliliters, divide by 800 (1.00 mL = 800 counts).

C_a is concentration of acid titrant, in milliequivalents per milliliter (same as equivalents per liter, or *N*).

CF is correction factor.

V_s is volume of the sample, in milliliters.

2. Double-check your calculations.

COMPUTER-PROGRAM ANALYSIS OF TITRATION DATA 6.6.5.C

Two USGS computer programs that are available to simplify alkalinity or ANC plotting and calculation tasks include the Personal Computer Field Form (**PCFF)** program and the Web-based **Alkalinity Calculator**. These cover the full range of pH measured in natural waters and are useful for performing the complex calculations needed for samples with pH > 9.2.

PCFF Program

The PCFF program is a Windows-based tool that allows users to enter field-derived sample collection data into standard USGS field forms electronically.

The PCFF can be accessed at the following FTP address:
ftp://disftp.er.usgs.gov/pub/NWIS/PCFF

- PCFF minimizes the manual input of information, helps eliminate transcription errors, and saves the user time.
- PCFF can perform some common field calculations, such as the analysis of titration data to determine alkalinity or ANC.
- PCFF uses the inflection point titration method (section 6.6.4.B) to find equivalence points in the titration data.

PCFF uses the IPT method to find equivalence points.

Alkalinity Calculator Program

The Alkalinity Calculator is a Web-based program that allows users to analyze titration data and determine alkalinity or ANC with several different methods. The current version of the Alkalinity Calculator provides a choice of the following recommended methods:

- The inflection point (IPT) method
- The Gran function plot method
- A theoretical carbonate titration curve method.

The IPT and Gran methods implemented by the Alkalinity Calculator are as described in this manual. The carbonate titration curve method attempts to fit the titration data with a theoretical titration curve derived solely from the chemistry of carbonic acid. This method shows the user whether the chemistry of carbonic acid alone can account for the shape of the entire titration curve. If the fit is poor, it is likely that more than just hydroxide, carbonate, and bicarbonate were titrated in the sample. An excellent fit with this method is evidence that the titration curve is dominated by carbonate and bicarbonate.

The Alkalinity Calculator can be found on the Internet from a link that can be accessed at the following URL:

http://water.usgs.gov/owq/methods.html

or can be accessed directly at the following URL:

http://oregon.usgs.gov/alk

Methods used by the Alkalinity Calculator are documented at

http://oregon.usgs.gov/alk/methods.html

The Alkalinity Calculator Program allows the user to choose among the IPT, Gran, and other methods of finding equivalence points.

TROUBLESHOOTING 6.6.6

The major difficulties with equipment used to measure for alkalinity or ANC are the same as for pH measurement—refer to NFM 6.4. Particulate materials, including algae or other biota, can interfere with the stability and reproducibility of pH readings. Such difficulties normally are eliminated by filtering the sample.

When the sample has low ionic strength, or when dissolved organic compounds or noncarbonate inorganic species are present that can interfere with the titration (note color, odor, or previous chemical analysis), the Gran function determination is recommended to avoid some of these problems.

6.6.7 REPORTING

Report alkalinity and ANC to three significant figures. Only the value from filtered samples is to be published as alkalinity. Titration values from unfiltered samples are to be entered and published as ANC.

Alkalinity and ANC should be reported in milliequivalents per liter (or microequivalents per liter), if possible. If this option is not available in the data base, calculate alkalinity and ANC in milligrams per liter, assigning all neutralizing capacity to the carbonate system.

If calculating ANC, alkalinity, bicarbonate, or carbonate in milligram units, then report:

- Less than 1,000 mg/L, to whole numbers;
- 1,000 mg/L and above, to three significant figures.
- Carbonate alkalinity usually is reported in the data base in milligrams per liter as calcium carbonate.

Conversion factors listed below are taken from Hem (1985).

Multiply	By	To obtain
Alkalinity (mg/L as HCO_3^-)	0.8202	Alkalinity (mg/L as $CaCO_3$)
Alkalinity (mg/L as HCO_3^-)	0.4917	Alkalinity (mg/L as CO_3^{2-})
Alkalinity (mg/L as $CaCO_3$)	0.01998	Alkalinity (meq/L)
Bicarbonate (mg/L as HCO_3^-)	0.01639	Bicarbonate (meq/L)
Bicarbonate (mg/L as HCO_3^-)	16.389	Bicarbonate (µeq/L)
Carbonate (mg/L as CO_3^{2-})	0.03333	Carbonate (meq/L)
Hydroxide (mg/L as OH^-)	0.05880	Hydroxide (meq/L)

Report the average value for duplicate samples or the median when more than two replicate samples are used for quality control and the value falls within the appropriate quality-assurance criterion for variability.

Use the correct parameter code to indicate (1) the method of titration or calculation and (2) a filtered or unfiltered sample.

Replacement page, 11/2004.