

6.6 Alkalinity and Acid Neutralizing Capacity

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6.6 Alkalinity and Acid Neutralizing Capacity

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 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-micrometer (μm) pore size or smaller).¹
- ▶ **ANC** is the acid-neutralizing capacity of solutes plus particulates in an **unfiltered water sample**, reported in 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 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 primarily 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 regarding the evolution of aqueous systems. Alkalinity and ANC provide information on the suitability of water for uses such as irrigation, for determining the efficiency of wastewater processes and the presence of contamination by anthropogenic wastes, and for maintaining ecosystem health.

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

- ▶ The primary contributors to alkalinity and ANC typically are bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}).

¹ In standard USGS practice, a filtered sample is operationally defined as having passed through a 0.45- μm pore filter membrane without clogging the filter.

- ▶ 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 ANC of a sample (Stumm and Morgan, 1996).
- ▶ 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 an 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.

6.6.1 Equipment and Supplies

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—acid can be delivered in increments to 0.0001 milliliter (mL) and are available commercially (for example, Gilmont® micrometer burets).
- ▶ The digital titrator 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 for the alkalinity determination.

- ▶ 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 sample for the ANC determination. The digital balance yields higher precision than the graduated cylinder.

Sulfuric acid titrant

Sulfuric acid is the titrant used routinely by the U.S. Geological Survey (USGS). The normality of sulfuric acid titrant is subject to change with time; proper storage and standardization of the acid titrant are essential. Reagents should be stored in a cool (less than 25–30 degrees Celsius (°C)), dry, dark place to ensure maximum shelf life. Check label for expiration date.

- ▶ 0.1600 *Normal (N)* or 1.600*N* sulfuric acid solutions in prefilled cartridges for the Hach® digital titrator should be obtained by USGS personnel from the National Field Supply Services (NFSS) One-Stop Shopping Web site. The National Water Quality Laboratory (NWQL) has calculated a correction factor of 1.01 (see section 6.6.5.A) necessary to compensate for cartridge manufacturing anomalies and (or) variations in the reported acid normality. The Hach Company provides an online certificate of analysis and expiration date for the specific lot number of the prefilled sulfuric acid cartridge. Expiration dates also are printed on each cartridge.
- ▶ 0.01639*N* sulfuric acid solution for the buret system is available from a vendor of scientific products. 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 the 0.01639*N* 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).

Table 6.6–1. Equipment and supplies used for alkalinity or ANC titrations.¹

[TD, to deliver; mL, milliliters; ANC, acid neutralizing capacity; g, gram; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; *N*, normal; NFM, U.S. Geological Survey National Field Manual]

Equipment and supplies needed when using either a digital titrator or a buret
<ul style="list-style-type: none"> ✓ 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, battery operated ✓ 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 $\mu\text{S}/\text{cm}$) ✓ Dispenser bottle, squeeze, for deionized water ✓ Filtration unit, in-line disposable capsule or disc (for the alkalinity sample) ✓ 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
<ul style="list-style-type: none"> ✓ Digital titrator and mounting assembly ✓ Delivery tube, 90 degree or straight with “J”-hook, colorless, transparent ✓ Titrant solution: sulfuric acid (H_2SO_4) solution, 0.1600<i>N</i> and 1.600<i>N</i> (empty or prefilled cartridges are available for use with the Hach[®] system)
Additional equipment and supplies needed when using a buret
<ul style="list-style-type: none"> ✓ 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<i>N</i> ✓ 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.

CAUTION: Use the safety precautions on the Material Safety Data Sheets (MSDS) when handling chemicals.

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 the *National Field Manual* section on pH (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 and should be stored, 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.

If using a digital titrator, perform a calibration check of its accuracy and precision at least annually by using either reference samples or by comparing the results of an alkalinity or ANC measurement with those determined by performing a buret titration on the same sample. If results show an equipment calibration problem, contact the manufacturer for repair or replacement.

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.

6.6.2 Calibration and Standardization

Calibration is required for the pH instrument—follow the 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 must be tested once a 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.

**CAUTION: When diluting concentrated acids, always:
"Do as you 'oughter' and add acid to 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 H₂SO₄ (specific gravity 1.84 grams per milliliter) to approximately 950 mL of fresh deionized water (DIW).
2. Mix thoroughly; dilute with DIW to the 1-liter (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 as described below. 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 (Na₂CO₃):

1. Dry 1.0 gram (g) primary standard Na₂CO₃ at 150 to 160 °C for 2 hours.
2. Cool in a desiccator; weigh out 0.8686 g Na₂CO₃; 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:

$$C_a = \frac{(25 \text{ mL}) \left(\frac{0.8686 \text{ g Na}_2\text{CO}_3}{1.0 \text{ L}} \right) \left(\frac{1 \text{ mole Na}_2\text{CO}_3}{105.989 \text{ g Na}_2\text{CO}_3} \right) \left(\frac{2 \text{ eq}}{1 \text{ mole Na}_2\text{CO}_3} \right)}{V_a} = \frac{(25 \text{ mL}) \left(0.01639 \frac{\text{eq}}{\text{L}} \right)}{V_a}$$

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 acid solution in a tightly sealed 1-L glass bottle. Label the bottle with its contents, normality, date of preparation, expiration date, and the preparer's initials and store it in a cool, dark place.

6.6.3 Collection and Processing

Collect and process the water 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 3 and NFM 4).

- In the office laboratory, prerinse the sample bottles with deionized water and store them 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 the water to be sampled (sample filtrate for the alkalinity sample). If the amount of sample is limited or the triple rinse will cause the total field rinse volume to exceed 100 mL, DIW of appropriate quality may be substituted for the first 2 rinses.
- ▶ 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, or addition of CO_2 to 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 under an inert gas atmosphere.

Surface water

Collect and process a representative sample according to USGS-approved methods (see NFM 4.1, 5.0, 5.1, and 5.2).

- ▶ Most USGS water-quality 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 below for groundwater and the procedures for suboxic or anoxic water described in NFM 4.0.2, "Preventing sample contamination."

Groundwater

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 4.0.2, 4.2, 5.0, 5.1, and 5.2 for groundwater sample collection and filtration methods.

- ▶ Purge the well (NFM 4.2) 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.

6.6.4 Measurement

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**, also called the incremental titration 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 and (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 milliequivalents per liter (meq/L) (20 milligrams per liter (mg/L) as CaCO_3), or in which conductivity is less than 100 microsiemens per centimeter ($\mu\text{S}/\text{cm}$), 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 groundwater 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 may 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 using the system requires experience to execute with precision and accuracy.
- ▶ A micrometer buret can achieve accuracy to 0.1 mg/L (determinations are reported to whole numbers if the result is greater than or equal to 100 mg/L as CaCO₃).

The buret system can yield 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 H₂SO₄) 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 CaCO₃). 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; CaCO₃, 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	0.1600
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 or shake 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, as well as the 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 to 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:** Using small increments of acid, titrate carefully to a pH of about 8.0. The data to pH 8.0 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.

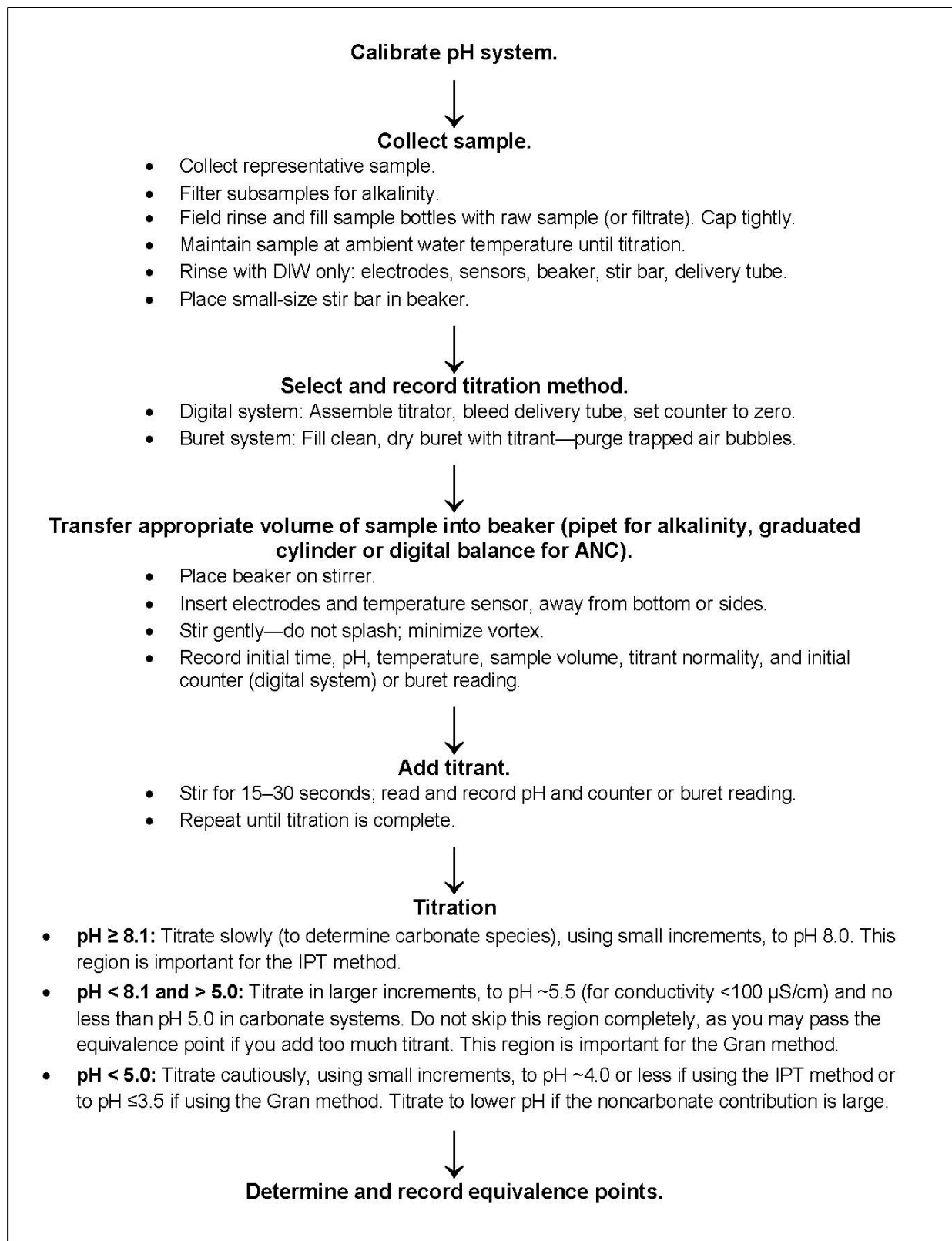


Figure 6.6–1. Summary of alkalinity or ANC titration procedures.

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, and whenever the accuracy or precision of the digital titrator is in question. See guidance in 6.6.1.A on maintenance of the digital titrator.

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 CaCO₃), 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 of an unfiltered sample may result in a determination identical to or within 5 percent of the filtered sample and can be used as a QC check.
 - If filtered and unfiltered values fail the ± 5 -percent criterion, perform the QC check on duplicate filtered samples.
 - Reproducibility of the ANC determination to within 5 percent on duplicate unfiltered samples can be problematic 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 while 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 the use of a Hach[®] digital titrator. A plunger in the digital titrator forces acid from the titrant cartridge through 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 (800 counts = 1 mL).

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 a new delivery tube for each assembly of the titrator. Discard the tube after use.
 - Reuse of the delivery tube is not recommended. If reuse becomes necessary: rinse it with DIW; store in a clean sealable plastic bag; only reuse with the same titrant normality; do not reuse if it shows wear.
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 the exterior of the tube 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 if sample conductivity is less than 100 $\mu\text{S}/\text{cm}$. Place the beaker on the 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. If available, record the sample conductivity.

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 a consistent 15 to 30 seconds after each addition for equilibration, then record the pH and counter readings.
 - **pH \geq 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 sample pH is less than 8.0. Larger increments can be used for samples containing high carbonate concentrations.
 - **pH $<$ 8.1 and \geq 5.0** —If using the IPT method, titrate with larger increments to pH \approx 5.0 (5.5 for sample alkalinity or ANC $<$ 0.4 meq/L ($<$ 20 mg/L as CaCO₃) or sample conductivity $<$ 100 μ S/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 \leq 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 \leq 3.5 (\leq 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 CaCO₃).
 - 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 CaCO₃) 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. If available, record the sample conductivity.
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 a consistent 15 to 30 seconds after each addition for equilibration, then record the pH and buret readings.
 - **pH \geq 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 \geq 5.0** —If using the IPT method, titrate with larger increments to pH \approx 5.0 (5.5 for sample with alkalinity or ANC $<$ 0.4 meq/L ($<$ 20 mg/L as CaCO₃) or with sample conductivity $<$ 100 μ S/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 \leq 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 \leq 3.5 (\leq 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.

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, also known as the incremental titration method, uses the inflection points of the titration curve to determine equivalence points. For many natural water samples, these equivalence points are near pHs of 8.3 and 4.5, but it is more accurate to calculate their exact locations 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 construct a titration curve either by (1) plotting the change in pH divided by the change in titrant volume against the volume of titrant added to the sample; (2) calculating such values in a table or spreadsheet; or (3) using a titration-curve analyzer such as the USGS Alkalinity Calculator or PCFF program (see section 6.6.5.C).

- ▶ Graphing the titration curve always is advisable. Such plots are helpful in uncovering data-entry 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.

The example that follows for IPT–1A shows the results of an IPT analysis of a typical titration using a digital titrator. The example for IPT–1B shows similar results using a buret titration. Each of these titrations has inflection points at both the carbonate and bicarbonate equivalence points.

Example IPT–2 shows the results of the IPT method applied to a low alkalinity sample. Note that this 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 smaller errors.

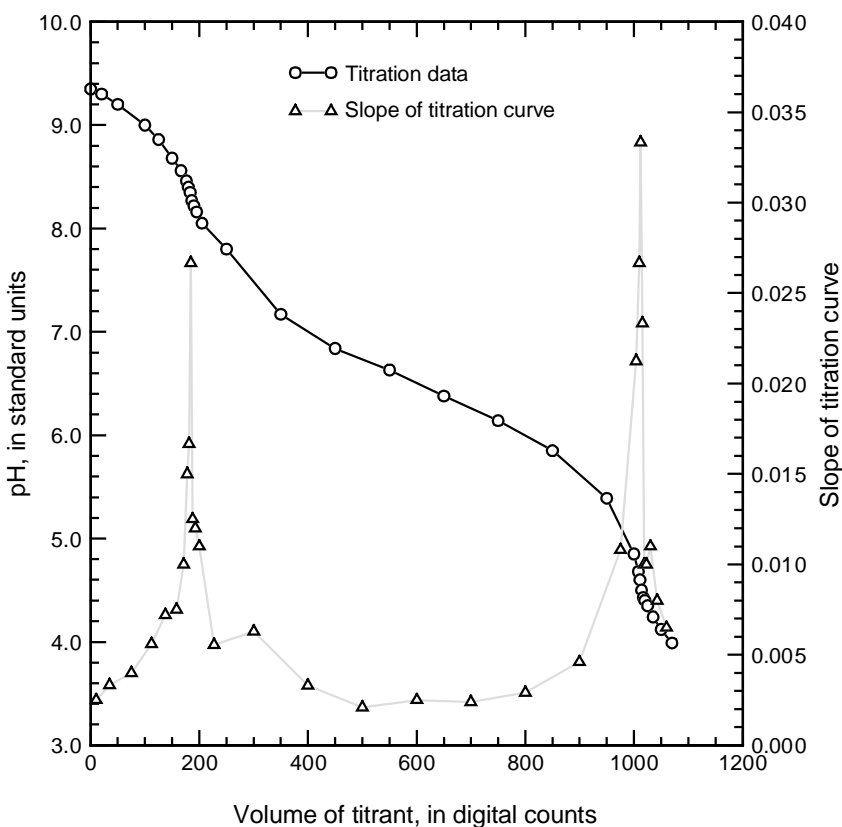


Figure 6.6–2. Plot of data for an inflection point titration using a digital titrator (Example IPT–1A).

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.

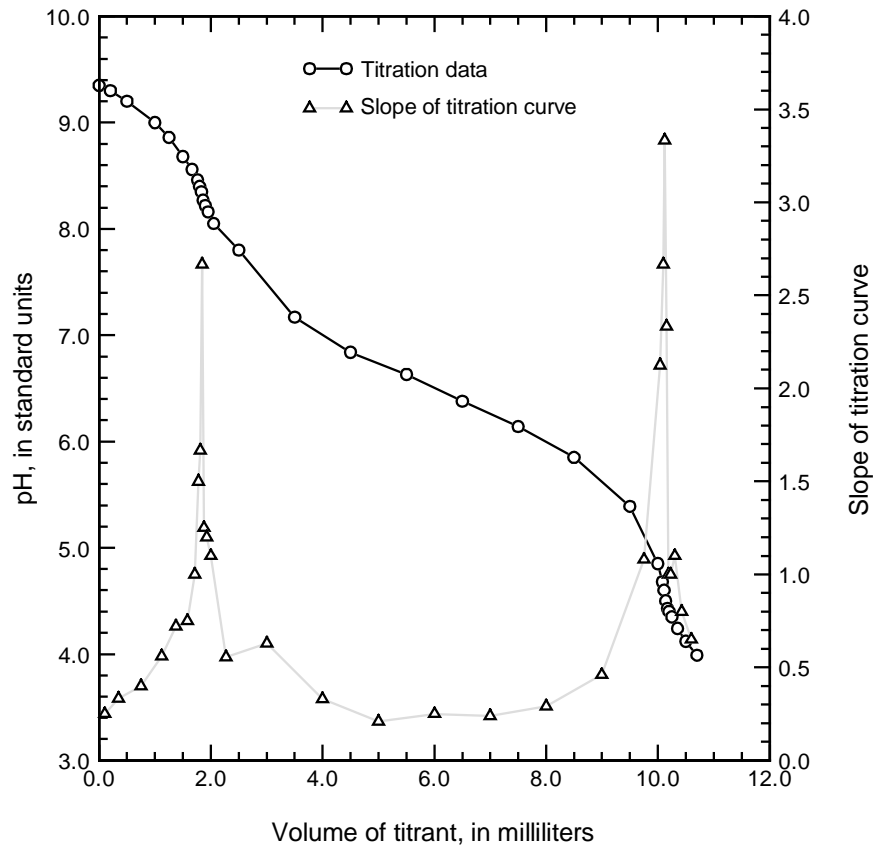


Figure 6.6-3. Plot of data for an inflection point titration using a buret (Example IPT-1B).

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 0.16N 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 .

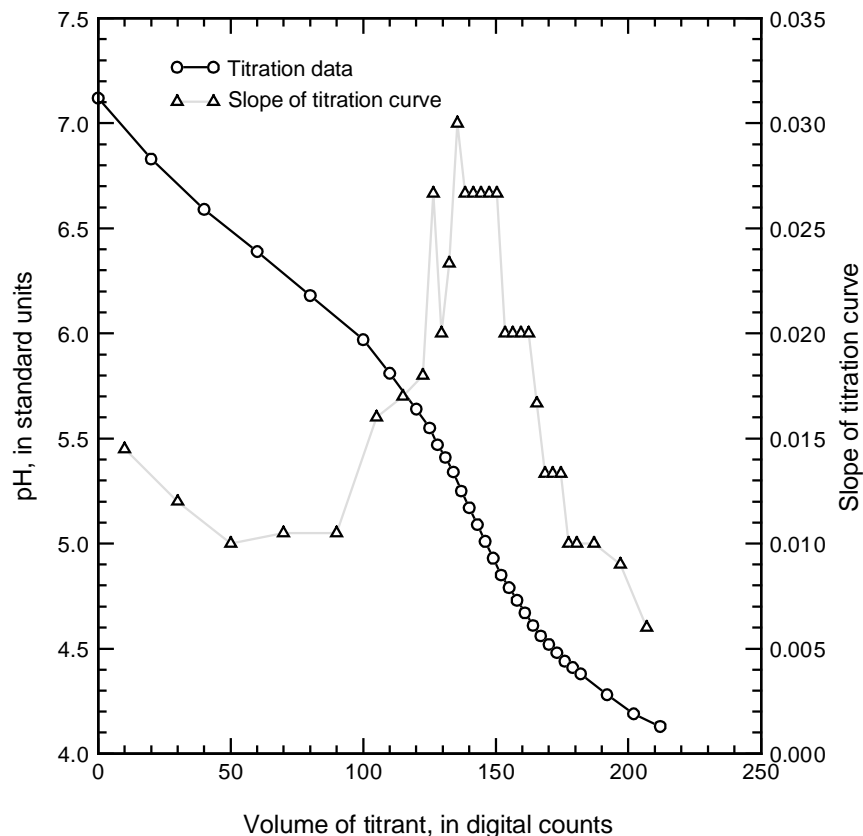


Figure 6.6–4. Plot of data for an inflection point titration of a low-alkalinity sample (Example IPT–2).

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 low ionic-strength water, water with low carbonate concentrations, and water with measurable concentrations of titratable 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, 1996).

For an acidimetric titration, the six Gran functions are

$$\begin{aligned}
 F_1 &= (V_o + V_t)(10^{-pH})/\gamma = (V_t - V_s)C_a \\
 F_2 &= (V_s - V_t)10^{-pH} = (V_t - V_w)K_1' \\
 F_3 &= (V_t - V_w)10^{pH} = (V_s - V_t)/K_1' \\
 F_4 &= (V_s - 2V_w + V_t)10^{pH} = (V_w - V_t)/K_2' \\
 F_5 &= (V_w - V_t)10^{-pH} = (V_t - V_x)K_2' \\
 F_6 &= (V_o + V_t)10^{pH} = (V_x - V_t)C_a/K_w'
 \end{aligned}$$

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 the normality of the acid titrant;
- γ is the activity coefficient for H^+ ;
- K_1' is the first acid dissociation constant for H_2CO_3 , corrected for the activity of carbonate species;
- K_2' is the second acid dissociation constant for H_2CO_3 , corrected for the activity of carbonate species; and
- K_w' is the 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 (V_t) 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.

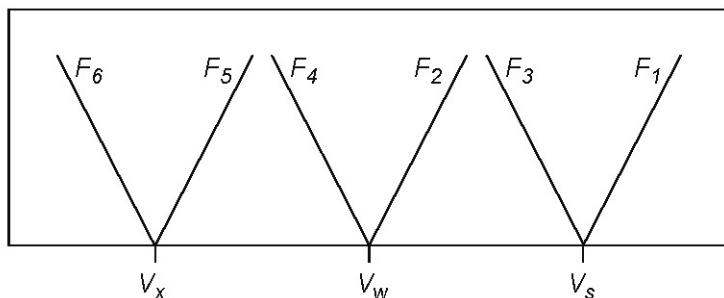


Figure 6.6–5. An idealized Gran function plot, showing six Gran functions.

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 acid-titrant concentration (C_a) and the various acid dissociation constants. Further explanation can be found in Stumm and Morgan (1996) and Pankow (1991).

To prepare a Gran function plot:

1. **Bicarbonate equivalence point (Gran function F_1).** Plot $(V_o + V_t) 10^{-\text{pH}}$ 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 $F_1 = (V_o + V_t) 10^{-\text{pH}} = 0$ 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 $(V_s - V_t) 10^{-\text{pH}}$ 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 $F_2 = (V_s - V_t) 10^{-\text{pH}} = 0$ 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 $(V_w - V_t) 10^{-\text{pH}}$ 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 $F_5 = (V_w - V_t) 10^{-\text{pH}} = 0$ 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 $(V_t - V_w) 10^{\text{pH}}$ 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 $F_3 = (V_t - V_w) 10^{\text{pH}} = 0$ 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 $(V_s - 2V_w + V_t) 10^{\text{pH}}$ 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 $F_4 = (V_s - 2V_w + V_t) 10^{\text{pH}} = 0$ or $V_t = V_w$ to obtain another estimate of the carbonate equivalence point.
11. In the region above the hydroxide equivalence point, plot $(V_o + V_t) 10^{\text{pH}}$ 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 $F_6 = (V_o + V_t) 10^{\text{pH}} = 0$ 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 .

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

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 $(V_o+V_t)10^{-\text{pH}} = 0$ locates the equivalence point. The extrapolated straight line intercept at $(V_o+V_t) 10^{-\text{pH}} = 0$ 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.

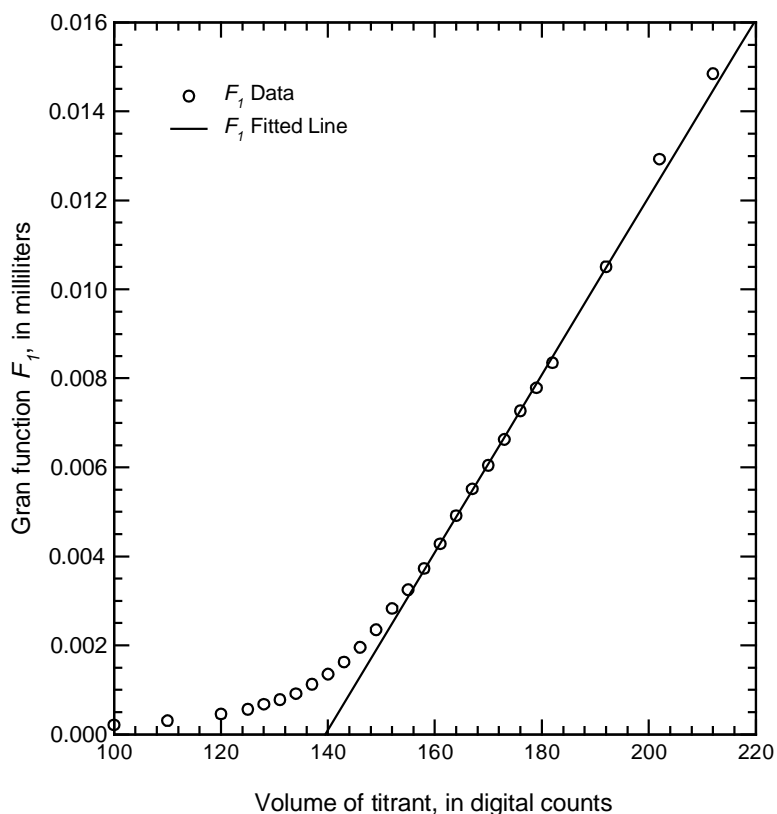


Figure 6.6-6. Example of a Gran function plot using F_1 to determine the bicarbonate equivalence point.

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)	$10^{-\text{pH}}$	$(V_o+V_t)10^{-\text{pH}}$ (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 0.16N, 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 .

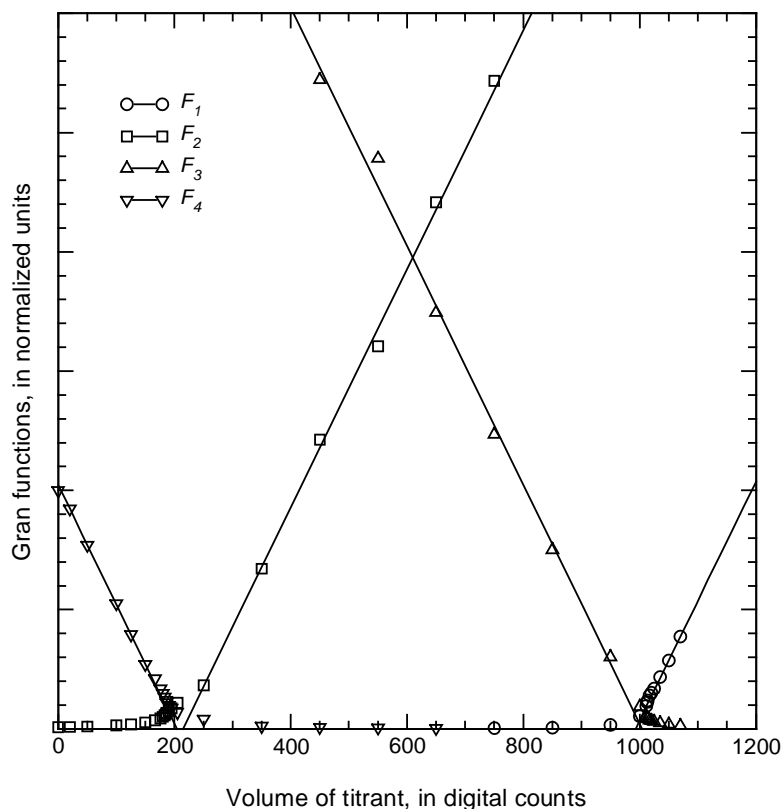


Figure 6.6-7. Example of a Gran function plot using F_1 , F_2 , F_3 , and F_4 to determine carbonate and bicarbonate equivalence points.

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 to the bicarbonate equivalence point:

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

and

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

where

- Alk* is the alkalinity or ANC of the sample.
- B* is the 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 the concentration of acid titrant, in milliequivalents (*meq*) per milliliter (same as equivalents per liter, or normality *N*).
- CF* is a correction factor (see below).
- V_s* is the volume of sample, in milliliters.
- mmol* is millimoles, in this case for calcium carbonate.

The correction factor *CF* is equal to 1.01 when using the Hach digital titrator cartridges, as determined by the NWQL and resulting from a bias caused by the configuration of those cartridges. For other titration methods, *CF* is equal to 1.0.

6.6.5.B Carbonate-Speciation Equations

For samples in which the alkalinity or ANC is due primarily to bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and hydroxide (OH^-), the concentrations of those constituents in the sample can be determined directly from the sample's pH and alkalinity or ANC with the following equations:

$$[\text{HCO}_3^-] \left(\frac{\text{meq}}{\text{L}} \right) = \left(\frac{\text{Alk} - K'_w \times 10^{\text{pH}} + \frac{10^{-\text{pH}}}{\gamma}}{1 + 2K'_2 \times 10^{\text{pH}}} \right) \times \left(\frac{1000 \text{ meq}}{1 \text{ mol}} \right)$$

$$[\text{CO}_3^{2-}] \left(\frac{\text{meq}}{\text{L}} \right) = \left(\frac{\text{Alk} - K'_w \times 10^{\text{pH}} + \frac{10^{-\text{pH}}}{\gamma}}{2 + \frac{10^{-\text{pH}}}{K'_2}} \right) \times \left(\frac{2000 \text{ meq}}{1 \text{ mol}} \right)$$

$$[\text{OH}^-] \left(\frac{\text{meq}}{\text{L}} \right) = (K'_w \times 10^{\text{pH}}) \times \left(\frac{1000 \text{ meq}}{1 \text{ mol}} \right)$$

where

- Alk* is the computed sample alkalinity or ANC in equivalents per liter (eq/L)—divide value in meq/L by 1000 to obtain eq/L;
- pH* is the initial sample pH;
- K'_w is the acid dissociation constant for water, corrected for the activity of hydroxide;
- K'_2 is the second acid dissociation constant for H_2CO_3 , corrected for the activity of carbonate species; and
- γ is the activity coefficient for H^+ .

To convert concentrations in meq/L to mg/L, multiply the bicarbonate result by 61.0171, the carbonate result by 30.0046, and the hydroxide result by 17.0073.

These equations are valid for any sample pH and account for activity corrections—deviations from ideal chemical behavior typically caused by the presence of other ions. The calculation and application of activity coefficients is an advanced topic that is not covered here, but is addressed by some of the tools described in section 6.6.5.C.

In dilute freshwater systems, activity corrections may be neglected, allowing the activity coefficients (γ) to be set to 1.0 and the “infinite-dilution” acid dissociation constants (K_w , K_1 , K_2) to be used in place of values that include activity corrections (K_w' , K_1' , K_2'). The nominal values of these constants in dilute freshwater at 25 °C are $K_w = 10^{-14.0}$, $K_1 = 10^{-6.35}$, and $K_2 = 10^{-10.3}$. Values at other temperatures can be computed with the following equation:

$$\log_{10}(K) = a_1 + a_2T + \frac{a_3}{T} + a_4 \log_{10}(T) + \frac{a_5}{T^2}$$

where T is the absolute water temperature in Kelvin ($T = t(^{\circ}\text{C}) + 273.15$) and the coefficients are given in Table 6.6–7.

Table 6.6–7. Coefficients to compute the temperature dependence of acid dissociation constants for water and carbonic acid, as tabulated by Stumm and Morgan (1996).

Acid Dissociation Constant	Coefficient				
	a_1	a_2	a_3	a_4	a_5
K_w	-283.971	-0.05069842	13323.0	102.24447	-1119669.0
K_1	-356.3094	-0.06091964	21834.37	126.8339	-1684915
K_2	-107.8871	-0.03252849	5151.79	38.92561	-563713.9

TECHNICAL NOTE: Prior to 2012, NFM included equations for the calculation of bicarbonate and carbonate concentrations based on the volumes of titrant required to reach the carbonate and bicarbonate equivalence points. That “simple speciation” method assumed that only carbonate ions were titrated in the pH range above the carbonate equivalence point, and only bicarbonate ions were titrated in the pH range below the carbonate equivalence point. The result was a set of equations that were easy to apply but suffered from two problems.

First, the method did not account for the effects of hydroxide, which resulted in significant errors for samples with pH values higher than 9.2. Second, the method ignored the fact that small concentrations of bicarbonate ions exist at pHs above the carbonate equivalence point, and small concentrations of carbonate ions exist at pHs below the carbonate equivalence point. Because of these limitations and the availability of a more general and accurate method (included in this version of NFM), the older “simple speciation” method has been discontinued.

Important points to remember:

- ▶ The equations to compute concentrations of bicarbonate, carbonate, and hydroxide shown above are valid for any sample pH, but the equations for bicarbonate and carbonate are only valid if these three species are the only significant contributors to the sample alkalinity or ANC.
- ▶ If the sample contains other titratable species such as ammonia, borate, silicic acid, or humic and fulvic acids that contribute significantly to alkalinity or ANC, then the equations for bicarbonate and carbonate shown here no longer apply, and use of a full geochemical model such as PHREEQC (Parkhurst and Appelo, 1999) is recommended.² Versions of PHREEQC may be obtained at no cost from the USGS at <http://water.usgs.gov/software>.
- ▶ Double-check your calculations!

6.6.5.C Computer-Program Analysis of Titration Data

USGS computer programs are available to simplify alkalinity or ANC plotting and calculation tasks. Two such tools are described here:

Alkalinity Calculator

The Web-based or stand-alone **Alkalinity Calculator** is a publically available tool that helps to analyze titration data and determine alkalinity or ANC using several different methods, including:

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

The Calculator's methods are valid for the full range of pH measured in natural waters and provide a simple means for performing the alkalinity and carbonate-speciation calculations described in sections 6.6.5.A and 6.6.5.B, including activity corrections and temperature adjustments.

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

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 bicarbonate, carbonate, and hydroxide were titrated in the sample. An excellent fit with this method is evidence that the titration curve is dominated by bicarbonate and carbonate, providing useful feedback for reporting and using the results.

A link to the Alkalinity Calculator is available at <http://water.usgs.gov/owq/methods.html>³ or can be accessed directly at <http://or.water.usgs.gov/alk>.³

The methods used by the Alkalinity Calculator are documented at <http://or.water.usgs.gov/alk/methods.html>.³

Personal Computer Field Form (PCFF)

The PCFF software provides another means for USGS users to analyze titration data in the field using the methods described in this manual. This software can determine alkalinity or ANC from titration data using the IPT or Gran function plot methods, and applies the carbonate-speciation calculations as shown in section 6.6.5.B. More information about PCFF can be obtained by USGS users only from <http://water.usgs.gov/usgs/owq/pcff.html>.³

6.6.6 Troubleshooting

The major difficulties with equipment used to measure 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.

³ The URLs shown were accessed on 8/24/2012.

6.6.7 Reporting

Report and publish results from filtered samples 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 (typically mg/L as CaCO₃). For measurements made using section 6.6.4 procedures, when calculating ANC, alkalinity, bicarbonate, or carbonate in milligram units, report:

- ▶ Less than (<) 1,000 mg/L and equal to (=) or greater than (>) 100 mg/L to whole numbers; however, to the tenths place if <100 mg/L.
- ▶ 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.
- ▶ Do not report hydroxide, carbonate, or bicarbonate concentration as 0.0 mg/L; instead, report values less than 0.1 mg/L as <0.1 mg/L.
- ▶ Hydroxide, carbonate, and bicarbonate concentration values cannot be negative.
- ▶ Alkalinity and ANC values may be negative; report negative values with the same number of significant figures that would be used if the values were positive.
- ▶ Be sure that the titration method and speciation methods are documented correctly in the data base.
 - The carbonate speciation equations in section 6.6.5.B are collectively called the “advanced speciation method.” Appropriate method codes for the advanced speciation method are ASM01 through ASM12. Information on when each code should be used is provided at <http://or.water.usgs.gov/alk/reporting.html>.
 - Parameter and method codes for field measurements are available at http://water.usgs.gov/usgs/owq/Forms/Fieldmeasurement_parametersmethods.doc.⁴

⁴ For turbidity, parameter and method codes can be accessed at http://water.usgs.gov/owq/turbidity_codes.xls.

Conversion factors listed below are taken from Hem (1985) and were verified independently by the author of this document.

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 ($\mu\text{eq/L}$)
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.

USGS data entry into the National Water Information System: use the correct parameter code to indicate (1) the method of titration or calculation and (2) a filtered or unfiltered sample. A summary of parameter and method codes for alkalinity titration results is available at <http://or.water.usgs.gov/alk/reporting.html>.

Selected References

- Almgren, T.D., Dyrssen, David, and Strandberg, Mats, 1977, Computerized high-precision titrations of some major constituents of seawater on board the R.V. Dmitry Mendeleev: Deep-Sea Research, v. 24, p. 345–364. (Available online at [http://dx.doi.org/10.1016/0146-6291\(77\)95000-7](http://dx.doi.org/10.1016/0146-6291(77)95000-7); accessed 8/24/2012)
- American Public Health Association, American Water Works Association, and Water Environment Federation, 2005, Standard methods for the examination of water and wastewater (21st ed.): Washington, D.C., American Public Health Association, p. 2–27 to 2–29.
- American Society for Testing and Materials, 1977, Standard test methods for acidity or alkalinity of water, No. D 1067: Philadelphia, American Society for Testing and Materials, p. 129–137.
- Baedecker, M.J., and Cozzarelli, I.M., 1992, The determination and fate of unstable constituents of contaminated groundwater, in Lesage, Suzanne, and Jackson, R.E., eds., Groundwater contamination and analysis at hazardous waste sites: New York, Marcel Dekker, p. 425–461.
- Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535–H, 17 p. (Also available at <http://pubs.er.usgs.gov/publication/wsp1535H>; accessed 8/24/2012.)

- Charlton, S.R., and Parkhurst, D.L., 2002, PHREEQCI—A graphical user interface to the geochemical model PHREEQC: U.S. Geological Survey Fact Sheet FS-031-02, 2 p. (Also available at <http://pubs.er.usgs.gov/publication/fs03102>; accessed 8/24/2012.)
- Drever, J.I., 1988, *The geochemistry of natural waters* (2d ed.): Englewood Cliffs, N.J., Prentice-Hall, p. 48–58.
- Edmond, J.M., 1970, High precision determination of titration alkalinity and total carbon dioxide content of sea water by potentiometric titration: *Deep Sea Research*, v. 17, p. 737–750.
- Fishman, M.J., and Friedman, L.C., eds., 1989, *Methods for determination of inorganic substances in water and fluvial sediments*: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p. (Also available at <http://pubs.er.usgs.gov/publication/twri05A1>; accessed 8/24/2012.)
- Gran, G., 1952, Determination of the equivalence point in potentiometric titrations: *Analyst*, v. 77, no. 920, p. 661–671.
- Hansson, Ingemar, and Jagner, Daniel, 1973, Evaluation of the accuracy of Gran plots by means of computer calculations—application to the potentiometric titration of the total alkalinity and carbonate content in sea water: Amsterdam, Elsevier Scientific Publishing Co., 12 p.
- Hem, J.D., 1985, *Study and interpretation of the chemical characteristics of natural water* (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, p. 105–111. (Also available at <http://pubs.er.usgs.gov/publication/wsp2254>; accessed 8/24/2012.)
- Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94–539, 57 p. (Also available at <http://pubs.er.usgs.gov/publication/ofr94539>; accessed 8/24/2012.)
- Pankow, J.F., 1991, *Aquatic chemistry concepts*: Chelsea, Michigan, Lewis Publishers, 673 p.
- Parkhurst, D.L., and Appelo, C.A.J., 1999, Users guide to PHREEQC (version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, accessed August 3, 2012, at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html.
- Roberson, C.E., Feth, J.H., Seaber, P.R., and Anderson, Peter, 1963, Differences between field and laboratory determinations of pH, alkalinity, and specific conductance of natural water: U.S. Geological Survey Professional Paper 475–C, p. C212–C215. (Also available at <http://pubs.er.usgs.gov/publication/pp475C>; accessed 8/24/2012.)
- Stumm, Werner, and Morgan, J.J., 1996, *Aquatic chemistry—chemical equilibria and rates in natural waters* (3d ed.): New York, John Wiley & Sons, p. 148–191.
- Wagner, R.J., Boulger, R.W., Jr., Oblinger, C.J., and Smith, B.A., 2006, Guidelines and standard procedures for continuous water-quality monitors—Station operation, record computation, and data reporting: U.S. Geological Survey Techniques and Methods 1-D3, available online only at <http://pubs.water.usgs.gov/tm1D3>.
- Wells, F.C., Gibbons, W.J., and Dorsey, M.E., 1990, Guidelines for collection and field analysis of water-quality samples from streams in Texas: U.S. Geological Survey Open-File Report 90–127, 79 p. (Also available at <http://pubs.er.usgs.gov/publication/ofr90127>; accessed 8/24/2012.)

- Wood, W.W., 1981, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, p. 15–18. (Also available at <http://pubs.er.usgs.gov/publication/twri01D2>; accessed 8/24/2012.)
- Yurewicz, M.C., 1981, Incremental field titration of bicarbonate: Water Resources Division Bulletin, October 1981–December 1982: U.S. Geological Survey Open-File Report 81-1017, p. 8–13.

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