MEASUREMENT 6.6.4

Alkalinity, ANC, and concentrations of bicarbonate, carbonate, and hydroxide species are determined using either the inflection point titration (IPT) method or the Gran function plot (Gran) method to analyze the titration data. Be familiar with the information in 6.6.4.B (IPT method) and 6.6.4.C (Gran method) before selecting the method to be used and before starting the sample titration.

- **The inflection point titration (IPT) method** is adequate for most waters and study needs. Difficulty in identifying the inflection points using an IPT method increases as the ratio of organic acids to carbonate species increases.
- **The 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 IPT and Gran methods require electrometric titration of a sample with incremental additions of H_2SO_4 of specified normality. Suggested combinations of titrant normality and sample volume for various ranges of alkalinity or ANC values are given in table 6.6–2. Generally, 1.600*N* acid is too strong for most samples and is used at alkalinity or ANC greater than 4.0 meq/L (200 mg/L as $CaCO_3$).

Table 6.6–2. Suggested sample volume and titrant normality (*N*) for use with digital titrator or at various ranges of alkalinity or ANC

[meq/L, milliequivalents per liter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; mL, milliliter; >, greater than]

ANC or alkalinity (meq/L)	Alkalinity (mg/L as $CaCO_3$)	Sample volume (mL)	Titrant normality (*N*)
0–1.0	0–50	100	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

Titrate a filtered sample if you will check the charge balance or will report the results as carbonate alkalinity.

6.6.4.A TITRATION 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.

> TECHNICAL NOTE: Fixed endpoint titration to pH 4.5 is no longer used by the USGS for reported alkalinity values because it can be less accurate than the IPT and Gran methods, particularly at small concentrations of total carbonate species and in water with significant organic and other noncarbonate contributors to alkalinity or ANC.

Before beginning titration, select the titration system to be used.

- ► The digital system is convenient but tends to be less precise or accurate than the buret system because of mechanical inadequacies. Good technique is requisite 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 one-tenth of a mg/L (routine determinations are reported to whole numbers).

Select the size of the volumetric pipet (for alkalinity sample) or the graduated cylinder or digital balance (for unfiltered ANC sample) and the measurement vessel, according to the volume of sample needed.

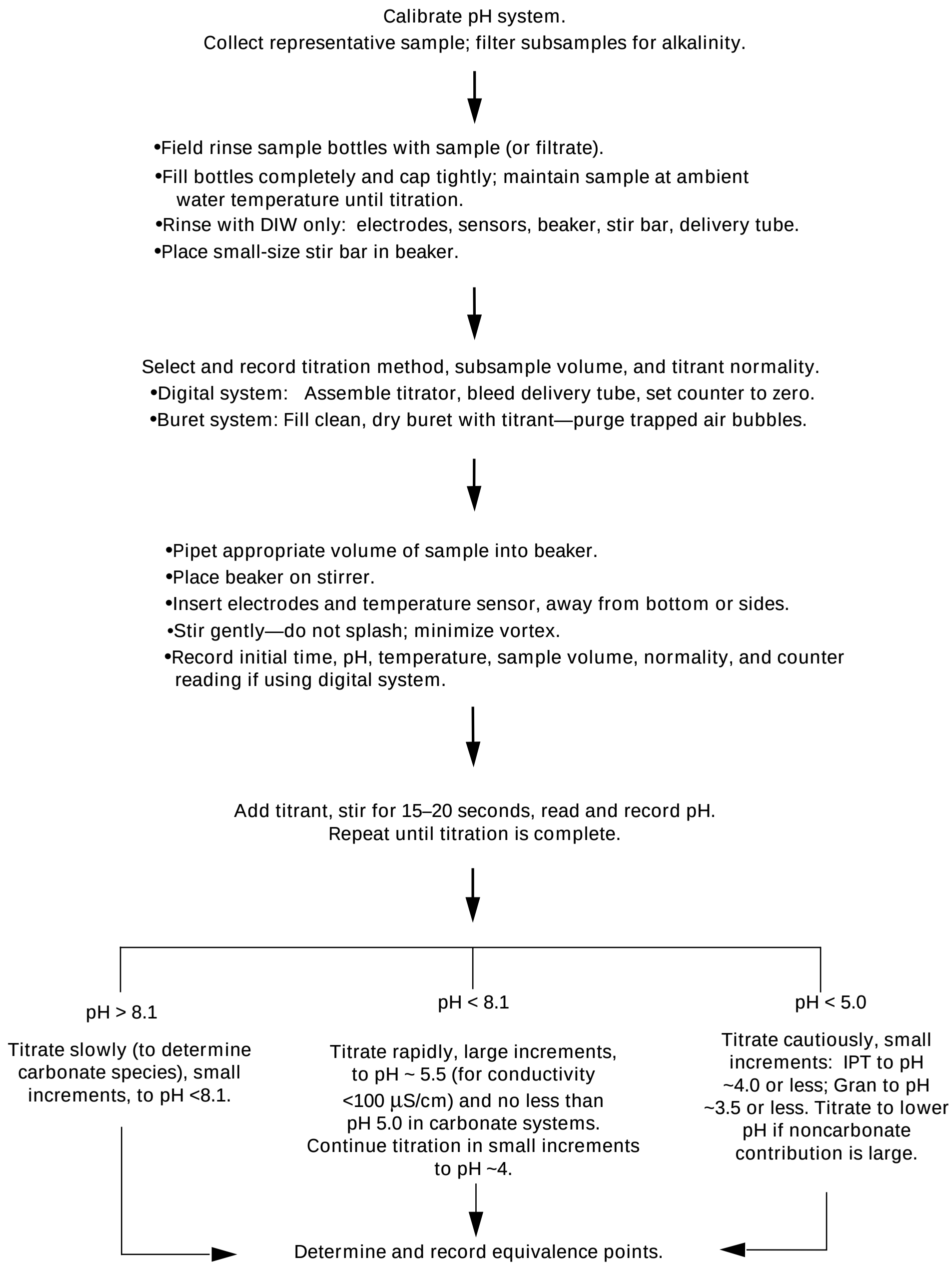
- 50 mL of a sample in a 100-mL beaker is selected for most routine work.
- Use 100 mL of a sample in a 150-mL beaker for low concentration of alkalinity or ANC. If the total sample volume is small, you may need to use a sample volume of 25 mL or less, although concentration is low.
- Use 25 mL or less of a sample and a 50-mL beaker for high concentration of alkalinity or ANC.

To achieve greater accuracy, use lower normality titrant, decrease the volume of acid increments, and increase the number of increments. Figure 6.6–1 provides a general summary of the electrometric titration procedures for alkalinity or ANC.

When pipetting the sample, a small amount of contents remains in the tip of class A "TD" volumetric pipets—do not blow it out, but use the following procedure:

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 bulb.
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.

> The buret system yields better accuracy than the digital titrator.



Calibrate pH system.
Collect representative sample; filter subsamples for alkalinity.

- Field rinse sample bottles with sample (or filtrate).
- Fill bottles completely and 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.

- Pipet appropriate volume of sample into beaker.
- 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, normality, and counter reading if using digital system.

Add titrant, stir for 15–20 seconds, read and record pH.
Repeat until titration is complete.

pH > 8.1

Titrate slowly (to determine carbonate species), small increments, to pH <8.1.

pH < 8.1

Titrate rapidly, large increments, to pH ~ 5.5 (for conductivity <100 µS/cm) and no less than pH 5.0 in carbonate systems. Continue titration in small increments to pH ~4.

pH < 5.0

Titrate cautiously, small increments: IPT to pH ~4.0 or less; Gran to pH ~3.5 or less. Titrate to lower pH if noncarbonate contribution is large.

Determine and record equivalence points.

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

When titrating, stirring helps to establish a uniform mixture of sample and titrant and an equilibrium between sensors and sample.

- ► **If using a magnetic stirrer, stir the sample slowly and continuously,** using the smallest 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.

If concentrations of contributing carbonate species will be determined—Titrate to pH of about 8.1 carefully, in small increments. If concentrations of contributing carbonate species **will not** be determined—titrate rapidly at first, adding relatively large acid increments to bring pH to about 5.5; then titrate slowly in small increments.

- ► **IPT method.** Titrate to at least pH 4.0 (to pH 3.5 if the alkalinity or ANC range is unknown for the water sampled or if the sample contains high concentrations of noncarbonate contributors, such as organic acids).
  - —Titrate cautiously at andbeyond the expected equivalence points.
  - —Let the pH value stabilize before the next addition of titrant.
- ► Gran method. Titrate to pH 3.5, or to pH 3.0 or less if the alkalinity or ANC range is unknown for the waters sampled.
  - —It is not necessary to develop incremental points above about pH 5.5 for a Gran determination of the bicarbonate equivalence point.
  - —A sufficient number of titration points beyond the equivalence are needed to ensure the accuracy of the calculation.

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

Quality control (QC)—Verify your ability to reproduce the alkalinity or ANC determinations by 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 should be no less than every tenth sample. 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 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 using the standard titration methods because of rounding error alone.

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, repeat the titration on a replicate aliquot of 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.

Calculation

Use the following equation to calculate the alkalinity or ANC in milliequivalents per liter:

$$(meq/L) = \frac{\mathrm{mL}_a \times N\ (meq/mL_{acid}) \times 1{,}000\ (mL/L)}{mL_{sample}}$$

where

mL_a = total volume of the standard acid solution used to reach the equivalence point, in milliliters

N = normality of the standard acid solution used, in milliequivalents per milliliter acid and

mL_{sample} = volume of the sample titrated, in milliliters.

Buret titrator

When using a buret, exercise caution to ensure that the acid does not evaporate or become contaminated by 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.

1. Fill a clean, dry buret with 0.01639*N* sulfuric acid titrant.
   - 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 that no air bubbles are trapped in buret or buret stopcock. Record the sulfuric acid normality and initial buret reading on field forms.
3. Pipet the selected volume of sample 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 pipetting the sample to the beaker. Do not use a magnetic stirrer if sample conductivity is <100 µS/cm. Place beaker on stirrer.
4. Rinse the pH and temperature sensors with DIW. Blot water droplets adhering to the sensors with lint-free paper (residual DIW will not affect the determination).
5. Insert the sensors in the beaker.
   - Do not let the sensors touch the beaker bottom or wall.
   - 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.
- Record on the field form the pH and temperature values, the counter reading (it should read “0000”), the titrant normality, the time, and the sample size.

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 20 seconds after each addition for equilibration, then record pH.
   - **pH ≥ 8.1—**To determine the bicarbonate inflection point, add the titrant drop by drop in 0.01-mL increments with a 25-mL buret until pH is less than 8.0.
   - **pH < 8.1—**Titrate rapidly to pH of about 5.0, using several large acid increments (to pH of 5.5 for sample alkalinity or ANC of 0.4 meq/L (<20 mg/L as $CaCO_3$) or conductivity of sample <100 µS/cm).
   - **pH < 5.0—**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 usually between pH 4.8 and 4.3). Extend titration to pH 3.5 or less if using the Gran method or for a sample high in organic acid concentration.

     TECHNICAL NOTE: 0.01 mL of a standard 0.05-mL drop of titrant tends to remain on the buret tip. To dispense this 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 filtration beaker with a small quantity of DIW (C.J. Patton, U.S. Geological Survey, written commun., 1995).

Calculation

Use the following equations to calculate alkalinity or ANC and carbonate species from inflection points with 0.01639*N* sulfuric acid:

$$\text{Alkalinity or ANC (meq/L)} = \frac{mL_a \times N\ (meq/mL_{acid}) \times 1000(mL/L)}{mL_{sample}}$$

$$\text{Alkalinity (mg/L as } CaCO_3) = 1000/mL_s \times (0.8202 \times mL_a) \times CF$$

$$\text{Bicarbonate (mg/L as } HCO_3^-) = 1000/mL_s \times [(mL_a \text{ from ip near pH 8.3 to ip near pH 4.5}) - (mL_a \text{ to ip near pH 8.3})] \times CF$$

$$\text{Carbonate (mg/L as } CO_3^{2-}) = 1000/mL_s \times [(mL_a \text{ at ip near pH 8.3}) \times 0.9835] - (mg/L\ OH^- \times 3.527) \times CF$$

$$\text{Hydroxide (mg/L as } OH^-) = 1000/mL_s \times [(mL_a \text{ to ip near pH 8.3}) - (mL_a \text{ from ip near pH 8.3 to ip near pH 4.5})] \times 0.2788 \times CF$$

where:

mL_{sample} or mL_s = volume of sample, in milliliters

mL_a = volume of H_2SO_4 added, in milliliters

ip = inflection point

CF = correction factor for H_2SO_4 normality (to be used if normality of H_2SO_4 is not exactly 0.01639*N*; CF is determined by dividing the actual normality of the H_2SO_4 by 0.01639)

N = normality of acid solution used.

The presence of hydroxide is indicated when the carbonate titrant volume exceeds the bicarbonate titrant volume.

Digital titrator

It is necessary to be thoroughly familiar with the operation of the digital titrator before field use. 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.

1. Record the sample volume to be titrated and the titrant normality. Equilibrate titrant temperature to sample temperature.
2. Assemble the digital titrator.
    a. Depress the plunger-release button and retract the plunger.
    b. Insert the titrant cartridge into the titrator and twist the cartridge one-quarter turn to lock it into position.
    c. 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.
    - Tag the delivery tube to avoid cross contamination. Do not interchange delivery tubes between cartridges with different titrant normality.
4. Purge the titrant through the delivery tube to ensure that no air bubbles or water are in the tube by holding the titrator with the cartridge tip up and turning the delivery knob to force a few drops of titrant through the end of the delivery tube. Rinse tube exterior with DIW and blot off acid or water droplets 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. Pipet the selected volume of the sample to a clean beaker. If a magnetic stirrer is used, place a clean, dry, small stir bar into the beaker before pipetting the sample to the beaker. Do not use a magnetic stirrer for sample conductivity <100 μS/cm.

7. Insert sensors into the beaker.
   - Rinse the pH and temperature sensors with DIW. Blot off water droplets adhering to the sensors.
   - 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.

8. Measure the initial pH and temperature while gently stirring or after gently swirling the sample.
   - Do not splash sample onto beaker wall or out of the beaker.
   - Minimize the vortex caused by magnetic stirring.
   - Record the pH and temperature values, the counter reading (it should read “0000”), the titrant normality, the time, and the sample size on field forms.

9. 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.

10. **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 the titrant. Allow 15 to 20 seconds after each addition for equilibration, then record pH.
    - **pH $\geq$ 8.1—**Slowly add the titrant in replicate increments no greater than two to three digital counts until pH of the sample is about 8.0, to determine the carbonate inflection point. Record the pH and digital counter reading after each addition of the titrant. Larger increments can be used for samples containing high carbonate concentrations.
    - **pH <8.1—**Titrate rapidly with several large acid increments to pH of about 5.0 (to pH 5.5 for sample alkalinity at 0.4 meq/L (<20 mg/L as $CaCO_3$) or sample conductivity <100 µS/cm).
    - **pH <5.0—**Add titrant cautiously, in increments of one to three digital counts, 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 and to pH 3.0 or less for samples high in organic acids and other noncarbonate contributors, or when the alkalinity or ANC range is unknown.

11. After completing the titration, depress the plunger release, retract the plunger, and remove the titrant cartridge. Immediately replace the vinyl cap on the cartridge tip. Discard the delivery tube after each use.

12. **Calculate alkalinity/ANC in the field—**

$$\text{Alkalinity or ANC (meq/L)} = \frac{mL_a \times \mathbf{N}(meq/mL_{acid}) \times 1000\ (mL/L)}{mL_{sample}}$$

- To determine carbonate alkalinity concentrations and concentrations of contributing species, plot change in pH divided by change in digital counts against digital counts of the titrant or tabulate change in pH divided by change in digital counts.
- Refer to table 6.6–3 for digital titration factors.
- The factors and equations used for the 0.1600*N* or 1.600*N* titrant cartridges are as follows (these calculations are based on the same equations described under the buret titration procedures, except that milliliters of acid used is shown as digital counts for the Hach™ titrator; 800 counts = 1 mL):

$$\text{Alkalinity or ANC (meq/L)} = B(D3)(C_a)/mL_s$$

$$\text{Carbonate (mg/L as } CO_3^{2-}) = A(D1)/mL_s$$

$$\text{Bicarbonate (mg/L as } HCO_3^{-}) = (B-2A)(D2)/mL_s$$

$$\text{Hydroxide (mg/L as } OH^{-}) = (A-C)(D4)/mL_s$$

$$\text{Alkalinity (mg/L as } CaCO_3) = B(D3)/mL_s$$

where:

mL_s = volume of the sample, in milliliters

A = digital count from the initial pH to the inflection point near 8.3

B = digital count from the initial pH to the inflection point near 4.5

C = digital count from the inflection point near 8.3 to the inflection point near 4.5

D = digital titration factor

C_a = concentration of acid.

Table 6.6–3. Digital titration factors

[*N*, acid normality]

Factors	**0.01600*N* titrant**	**0.1600*N* titrant**	**1.600*N* titrant**
D1	1.20	12.0	120
D2	1.22	12.2	122
D3	1.00	10.0	100
D4	.34	3.4	34

INFLECTION POINT TITRATION METHOD 6.6.4.B

The IPT method uses the inflection points of plotted values to select equivalence points instead of assuming equivalence points to be at pH 8.3 and 4.5 (as in the fixed endpoint method). Inflection points are 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, titration as you near and pass the expected equivalence points must be slow and cautious, using small incremental additions of titrant.** 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.

Use either the buret or digital titrator. To determine the inflection point, you can either construct a titration curve by plotting the change in pH divided by the change in titrant volume against the incremental volumes of the titrant added to the sample, or tabulate a titration. Figures 6.6–2 and 6.6–3 represent the titration of a sample that has both a carbonate and a bicarbonate inflection point, whereas tables 6.6–4 and 6.6–5 represent a titration that resulted only in a bicarbonate inflection point.

- ► 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.
- ► If no clear point or points can be determined easily, interferences from weak organic acids are likely—use the Gran method.

EXAMPLES:

IPT method using the buret system. Referring to table 6.6–4, pH 4.51 at a titrant volume of 8.95 mL is the point of maximum rate of change of pH per volume titrant. The actual inflection point is before the titrant volume corresponding to the maximum change in pH per unit volume of acid added; therefore, the correct value lies between 8.95 mL and the previous value, 8.90 mL. In this example, the calculated titrant volume 8.93 mL would be the correct inflection point.

IPT method using the digital titrator. Referring to table 6.6–5, pH 4.51 is the point of maximum rate of change of pH per volume of titrant. The actual inflection point, however, is between the digital-counter value (454) representing the maximum change in pH per unit volume of acid added and the previous digital-counter value (452). The correct (calculated) digital-counter value for the inflection point would be 453. The error in computing concentration from the digital-counter value 454 instead of the digital-counter value 453 is considered insignificant. Note, however, that the larger the increments used, the greater the significance of the error. Calculation of the correct inflection point is recommended.

Table 6.6–4. Results of typical inflection point titration using a buret
[mL, milliliter]

pH	Change in pH	Titrant volume (mL)	Change in volume	Change in pH per change in volume
7.28	—	0.00	—	—
7.00	0.28	2.00	2.00	0.140
6.70	.30	4.00	2.00	.150
6.33	.37	6.00	2.00	.185
5.73	.60	8.00	2.00	.300
5.24	.49	8.50	.50	.980
4.93	.31	8.70	.20	1.55
4.81	.12	8.80	.10	1.20
4.72	.09	8.85	.05	1.80
4.62	.10	8.90	.05	2.00
4.51[a]	**.11**	**8.95**	**.05**	**2.20**
4.42	.09	9.00	.05	1.80
4.34	.08	9.05	.05	1.60
4.22	.12	9.12	.07	1.71
3.92	.30	9.22	.20	1.50
3.62	.30	9.32	.20	1.50

[a] pH 4.51 is the point at which the maximum rate of change of pH per volume of titrant occurs.

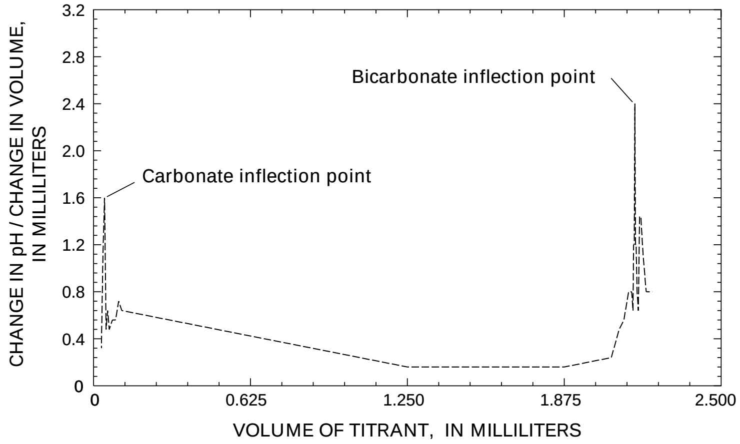


Figure 6.6–2. Example of an inflection point titration using a buret.

Table 6.6–5. Results of typical inflection point titration using a digital titrator

pH	Change in pH	Counter reading (mL)	Change in counter	Change in pH per change in counter
7.28	—	0	—	—
7.00	0.28	100	100	0.0028
6.70	.30	200	100	.0030
6.33	.37	300	100	.0037
5.73	.60	400	100	.0060
5.24	.49	435	35	.0140
4.93	.31	445	10	.0310
4.81	.12	448	3	.0400
4.72	.09	450	2	.0450
4.62	.10	452	2	.0500
4.51[a]	**.11**	**454**	**2**	**.0550**
4.42	.09	456	2	.0450
4.34	.08	458	2	.0400
4.22	.12	461	3	.0400
3.92	.30	471	10	.0300
3.62	.30	481	10	.0300

[a] pH 4.51 is the point of maximum rate of change of pH per digital count.

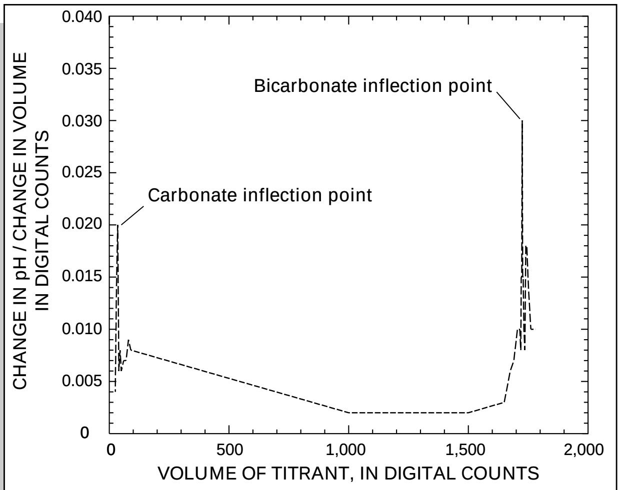


Figure 6.6–3. Example of inflection point titration using a digital titrator.

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. The Gran function plot method also is used for calculations of the base neutralizing capacity in waters of low ionic strength such as atmospheric deposition.

The Gran function plot method uses functions that linearize titration curves, making it possible to determine alkalinity or ANC with a few points rather than relying on the inflection point from an entire titration curve (Baedecker and Cozzarelli, 1992). Four Gran functions can be calculated over the entire titration curve. The F_1 function, described below, is the most commonly applicable Gran function.

► The F_1 function requires titration data beyond the equivalence point, usually to pH between 3.0 and 3.5. For systems with measurable concentrations of organic acids, titrate to pH 2.5 (Baedecker and Cozzarelli, 1992).

► The buret titration system is recommended to achieve the accuracy desired when using the Gran method: substitute the equivalence points determined by the Gran function plot into the equations given in the discussion of the buret system. The digital titration system also is used under some circumstances (illustrated on table 6.6–6 and fig. 6.6–4): refer to table 6.6–3 to calculate concentrations.

To construct a Gran function plot:

1. Titrate incrementally to about pH 3.5. It is not necessary to develop incremental points above about pH 5.5 for a Gran determination of the bicarbonate equivalence point.

2. Plot $(V_o + V_t)\ 10^{-pH}$ against the titrant volume (fig. 6.6–4 and table 6.6–6) using the F_1 function for the bicarbonate equivalence point,

   where:

   V_o = volume of the sample
   V_t = volume of the titrant added
   V_s = volume of the titrant needed to reach the bicarbonate equivalence point
   V_w = volume of the titrant needed to reach the carbonate equivalence point.

3. Extrapolate the straight line in the region beyond the equivalence point to $(V_o+V_t)\ 10^{-pH}=0$ or $V_t=V_s$.

- ► **Carbonate equivalence point.** Plot $(V_t-V_s)\ 10^{-pH}$ against the titrant volume (in mL or digital counts). To locate the equivalence point, extrapolate the straight line in the region beyond the equivalence point to $(V_t-V_s)\ 10^{-pH}=0$ or $V_t=V_w$.

- ► **Hydroxide equivalence point.** Plot $(V_o-2V_w+V_t)\ 10^{-pH}$ against the titrant volume (in mL or digital counts). To locate the equivalence point, extrapolate the straight line in the region beyond the equivalence point to $(V_o+V_t)\ 10^{-pH}=0$ or $V_t=V_w$.

TECHNICAL NOTE: During 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 Gran function plot identifies the point at which all alkalinity has been titrated and hydrogen ions begin to be in excess. Beyond the equivalence point, the shape of the curve is determined by hydrogen ions in excess of all hydronium ion acceptors in the sample. The curvature results from the logarithmic relation between pH and hydrogen-ion activity.

EXAMPLE:

Gran function plot method using the digital titrator. Refer to figure 6.6-4 and table 6.6-6. In the region beyond the equivalence point in figure 6.6-4, a straight line results. Extrapolation of this straight line to $(V_o=V_t)10^{-pH}=0$ or $V_t=V_s$ locates the equivalence point. The extrapolated straight line intercept at $(V_o+V_t)\ 10^{-pH}=0$ on figure 6.6-4 is 0.566 mL of titrant added and corresponds to an equivalence point at approximately pH of 4.58.

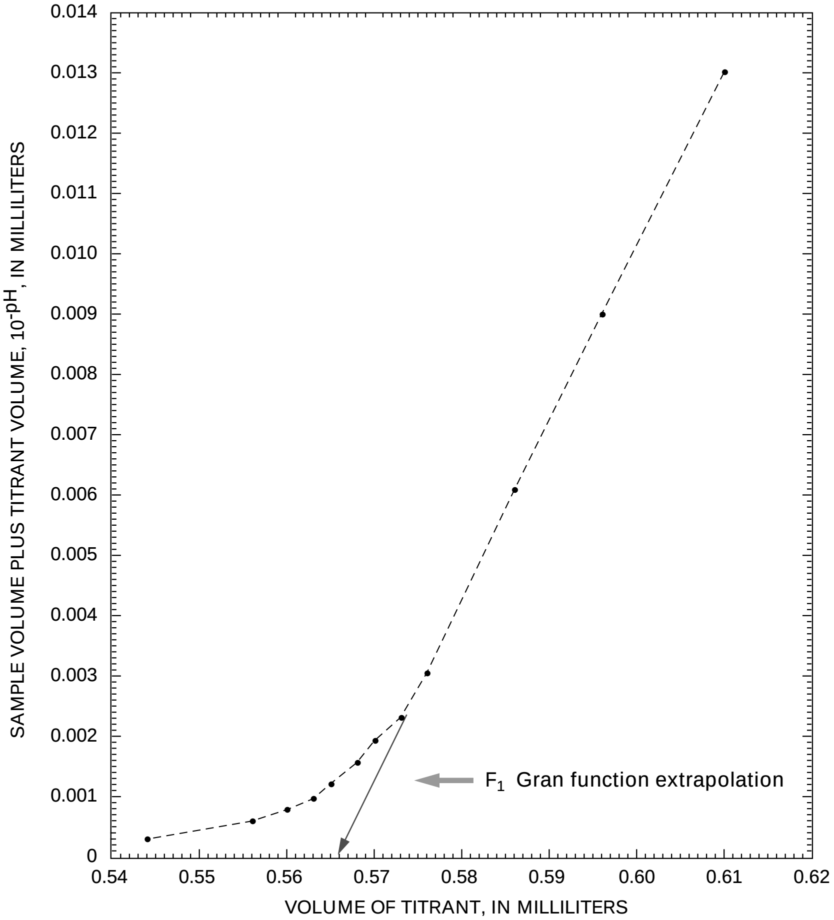


Figure 6.6–4. Example of Gran function plot of a bicarbonate titration using a digital titrator.

Table 6.6–6. Example of information needed for a Gran function plot

[Data shown in columns 1, 2, 6, and 7 are results of an incremental titration using a digital titrator—remaining columns show calculations used for the Gran function plot (fig. 6.6–4); V, volume of sample; v, volume of titrant; mL, milliliters; cts, digital counts; e– , base 10 logarithm to the negative exponent]

pH	Change in pH	10^{-pH}	(V+v) in mL	(V+v) 10^{-pH} in mL	Counter reading cts/mL	Change in counter	Change in pH/ change in counter
7.28	0.00	5.248e–8	50.000	2.624e– 6	0/0.00	0	0
7.00	.28	1.000e– 7	50.125	5.012e– 6	100/.125	100	.0028
6.70	.30	1.995e– 7	50.250	1.003e– 5	200/.250	100	.0030
6.33	.37	4.677e– 7	50.375	2.356e– 5	300/.375	100	.0037
5.73	.60	1.862e– 6	50.500	9.404e– 5	400/.500	100	.0060
5.24	.49	5.754e– 6	50.544	2.908e– 4	435/.544	35	.0140
4.93	.31	1.175e– 5	50.556	5.940e– 4	445/.556	10	.0310
4.81	.12	1.549e– 5	50.560	7.831e– 4	448/.560	3	.0400
4.72	.09	1.906e– 5	50.563	9.635e– 4	450/.563	2	.0450
4.62	.10	2.399e– 5	50.565	1.213e– 3	452/.565	2	.0500
4.51	.11	3.090e– 5	50.568	1.563e– 3	454/.568	2	.0550
4.42	.09	3.802e– 5	50.570	1.923e– 3	456/.570	2	.0450
4.34	.08	4.571e– 5	50.573	2.312e– 3	458/.573	2	.0400
4.22	.12	6.026e– 5	50.576	3.048e– 3	461/.575	3	.0400
3.92	.30	1.202e– 4	50.589	6.082e– 3	471/.586	10	.0300
3.75	.17	2.399e– 4	50.601	8.998e– 2	477/.596	6	.0280
3.59	.16	2.399e– 4	50.610	1.301e– 2	487/.610	10	.0160