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

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

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

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

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

1. Calculate bicarbonate and carbonate species as follows:

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

where

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

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

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

CF is correction factor.

V_s is volume of the sample, in milliliters.

2. Double-check your calculations.

COMPUTER-PROGRAM ANALYSIS OF TITRATION DATA 6.6.5.C

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

PCFF Program

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

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

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

PCFF uses the IPT method to find equivalence points.

Alkalinity Calculator Program

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

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

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

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

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

or can be accessed directly at the following URL:

http://oregon.usgs.gov/alk

Methods used by the Alkalinity Calculator are documented at

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

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

TROUBLESHOOTING 6.6.6

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

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

6.6.7 REPORTING

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

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

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

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

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

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

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

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

Replacement page, 11/2004.