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September 10, 2012

Office of Water Quality Technical Memorandum 2012.05

Subject: Replacement of the Simple Speciation Method for Computation of Carbonate and Bicarbonate Concentrations from Alkalinity Titrations

This memorandum announces and provides rationale for replacing the “simple speciation method” that commonly is used by the U.S. Geological Survey (USGS) for the computation of carbonate and bicarbonate concentrations from alkalinity titration data with a more accurate and robust method for calculating carbonate species in water samples. Revisions to Chapter 6, Section 6.6 (Alkalinity and Acid Neutralizing Capacity) of the *National Field Manual for the Collection of Water-Quality Data* (NFM) and to all software used by the USGS that computes carbonate and bicarbonate concentrations from alkalinity titration data, will be completed within the timelines given in Table 1, at which point the “advanced” speciation method will become the standard by which carbonate and bicarbonate data are to be determined and reported.

Background

In recent years, two different methods for the computation of carbonate and bicarbonate concentrations from alkalinity titration data have been used by USGS: the “simple speciation method” and the “advanced speciation method.” The simple speciation method is straightforward and provides formulas that are easy to apply with a hand calculator, but the method applies only to samples with a pH of less than about 9.2; significant errors result at sample pH exceeding 9.2. The advanced speciation method applies for any sample pH but uses more complicated equations that require or are facilitated by the use of a computer program.

Change in Policy

In 2009, the Office of Water Quality (OWQ), in consultation with the Water Science Field Team, began examining inquiries about potential discontinuation of the simple speciation method in favor of the advanced speciation method, (a) in consideration that the advanced method is acknowledged as the standard for scientific applications, and (b) to address confusion among project personnel regarding which of the two speciation methods to use. Recognizing that most USGS staff now has access to computers in the field and laboratory that facilitate the use of the advanced speciation method, OWQ made the decision to discontinue the simple speciation method as the standard USGS procedure for calculating aqueous carbonate and bicarbonate concentrations and replace it with the more accurate and more widely applicable advanced speciation method. This decision takes effect immediately and is to be implemented as soon as revisions to the Alkalinity Calculator and the NFM have been completed and made available to Water Science Center personnel (table 1). Note that, although the current version of PCFF includes the option to select either the simple or the advanced method, the simple speciation

option will be removed with the next revision of PCFF and USGS Field Forms (table 1) and personnel are advised to use the advanced speciation method. In addition, field personnel are reminded to document the titration and speciation methods correctly. Method codes appropriate for the advanced speciation method are ASM01 through ASM12; information for when each code should be used is found 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.

The attachment to this memorandum describes in detail the rationale for discontinuing the simple speciation method and using only the advanced speciation method for the computation of carbonate and bicarbonate concentrations from alkalinity titration data.

Table 1. Documents and software slated for revision.

Report, form, or software	Revision deadline	Revised by
NFM, Chapter.6, Section 6.6	9/30/2012	Stewart Rounds
Alkalinity Calculator	9/30/2012	Stewart Rounds
PCFF	3/31/2013	Frank Crenshaw
USGS Field Forms	3/31/2013	Stan Skrobialowski

Contact Information

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This memorandum updates some of the formulas in Quality of Water Branch Technical Memorandum 82.05.

Distribution: All WRD Employees

Attachment: Rationale for Discontinuing the Simple Speciation Method for the Computation of Carbonate and Bicarbonate Concentrations from Alkalinity Titration Data

ATTACHMENT

RATIONALE FOR DISCONTINUING THE SIMPLE SPECIATION METHOD FOR THE COMPUTATION OF CARBONATE AND BICARBONATE CONCENTRATIONS FROM ALKALINITY TITRATION DATA

In recent years, two methods have been available to estimate the concentrations of carbonate and bicarbonate ions in water samples on the basis of titration data for alkalinity or acid neutralizing capacity (ANC). The “simple speciation method” uses relatively simple equations that are easily applied with a hand calculator, but generally can be used without significant errors only for samples with pH values less than about 9.2, or perhaps higher for samples with higher alkalinity. The “advanced speciation method” uses more complicated equations that may require a computer program to apply, but is valid for any sample pH and is more accurate than the simple speciation method.

Historically, the simplicity of the simple speciation method was an advantage when doing alkalinity titrations in the field because the results could be computed by hand or with a simple hand calculator. Today, it is common for a technician to have a laptop computer or similar computing device in the field or laboratory—wherever they may be performing an alkalinity titration—thus allowing the application of the advanced speciation method to analyze alkalinity titration results without undue burden.

It was suggested in late 2009 that the simple speciation method be discontinued and the advanced speciation method be adopted as the preferred method used by USGS to compute carbonate and bicarbonate concentrations from alkalinity or ANC titration results. This appendix documents the two methods and assesses the errors involved with the simple speciation method.

Carbonate Speciation Assumption

Both the simple and advanced speciation methods rely on one basic assumption—that carbonate and bicarbonate (and hydroxide, for the advanced method) are the only constituents that are neutralized in the alkalinity or ANC titration. Any other constituents in the sample that have acid/base properties and may contribute to sample alkalinity are assumed to be insignificant compared to the contributions by carbonate, bicarbonate, and hydroxide. Of course, many other constituents with acid/base properties (such as ammonia, silicic acid, boric acid, humic and fulvic acids, phosphates, etc.) are present in natural water samples, but their concentrations most often are low enough that they contribute only marginally to alkalinity, have a negligible effect on the shape of the titration curve, and can be safely ignored. If not, then neither speciation method documented here will provide accurate concentrations for carbonate and bicarbonate; the results would only be estimates.

For more information on the contributions of carbonate, bicarbonate, hydroxide, and other acid/base constituents to sample alkalinity, see Hem (1985), Pankow (1991), or Stumm and Morgan (1996). The presence of significant amounts of ammonia or humic acids in a high-pH sample (pH > 9.2) may require more acid titrant to be added during an alkalinity titration to reach the carbonate equivalence point near pH 8.3 than otherwise could be accounted for by carbonate and hydroxide. To test the consistency of a titration dataset against a theoretical titration curve based only on the chemistry of water and carbonic acid, try the theoretical carbonate titration curve analysis method in the Alkalinity Calculator (<http://or.water.usgs.gov/alk/>).

The Simple Speciation Method

In addition to assuming that carbonate and bicarbonate are the only species contributing to sample alkalinity or ANC, the simple speciation method further assumes that only carbonate ions are titrated in the pH range above the carbonate equivalence point, and only bicarbonate ions are titrated in the pH range between the carbonate equivalence point and the bicarbonate equivalence point. The effects of hydroxide (and any other constituents with acid/base properties) are assumed to be negligible.

Using this method, the analyst tries to determine both the carbonate and bicarbonate equivalence points of the titration (see NFM 6.6—Rounds, 2006), and then estimates the concentrations of carbonate and bicarbonate according to the equations in table A1 below.

Table A1. Simple speciation method formulas.

[Abbreviations: meq/L, milliequivalents per liter; mg/L, milligrams per liter]

Constituent	Units	Equation
bicarbonate	meq/L	$1000 (B - 2A) C_a (CF) / V_o$
	mg/L as HCO_3^-	$61017 (B - 2A) C_a (CF) / V_o$
carbonate	meq/L	$2000 (A) C_a (CF) / V_o$
	mg/L as CO_3^{2-}	$60009 (A) C_a (CF) / V_o$

where

- A is the volume of acid titrant needed to reach the carbonate equivalence point near pH 8.3, if present,
- B is the total volume of acid titrant needed to reach the bicarbonate equivalence point near pH 4.5,
- C_a is the normality of the acid titrant in equivalents per liter,
- CF is an acid correction factor (1.00 by default; 1.01 for many Hach digital titrator cartridges—see http://or.water.usgs.gov/alk/cor_factor.html), and
- V_o is the initial volume of the sample being titrated.

Values for A, B, and V_o must be identical; milliliters is convenient. If the titration is performed with a Hach digital titrator, digital counts may be converted to milliliters by dividing the number of counts by 800. If the value of B is determined to be less than zero using Gran's method, the bicarbonate concentration is set to zero. If the initial sample pH is greater than 8.3 and A is not determined, then this method fails and the concentrations of carbonate and bicarbonate are not calculated.

The simple speciation method has several problems. First, it does not account for the effects of hydroxide, which become increasingly significant for sample pHs higher than about 9.2, depending on sample alkalinity. Second, the presence of other titratable materials in some samples (generally with sample pH greater than 9.0) can cause the quantity B-2A to be negative, resulting in negative calculated bicarbonate concentrations. Third, the method ignores the fact that small concentrations of carbonate ions exist at pHs below the carbonate equivalence point, assigning those concentrations to bicarbonate. The simple speciation method would report a carbonate ion concentration as zero for any sample without a carbonate equivalence point, lumps

the contribution of hydroxide to sample alkalinity into the carbonate concentration regardless of the fact that hydroxide concentrations can be independently determined from sample pH, and generally has increasing errors as the sample pH increases above about 9.2.

The simple speciation method does provide reasonable estimates for carbonate and bicarbonate concentrations as long as the sample pH is less than about 9.2, or even at slightly higher sample pH if the alkalinity is large. At sample pH values lower than 9.2, the accuracy is quite good and indistinguishable from more complex speciation methods. Using a theoretical titration curve based on the chemistry of carbonic acid in water, tests indicate that errors caused by the use of the simple speciation method are likely to be less than 10 percent for most samples with a pH less than 9.2.

The Advanced Speciation Method

In the advanced speciation method, concentrations of carbonate, bicarbonate, and hydroxide are calculated from sample pH and the measured alkalinity or ANC according to well-known theoretical relations based on the chemistry of water and carbonic acid. 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 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 the value in milliequivalents per liter (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. The concentrations of carbonate, bicarbonate, and hydroxide are constrained to be non-negative.

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 available analysis tools such as the Alkalinity Calculator (<http://or.water.usgs.gov/alk/>) or the PCFF program (<http://water.usgs.gov/usgs/owq/pcff.html>).

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 $K_2 = 10^{-10.33}$. 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 A2.

Table A2. 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

Although the equations used by the advanced speciation method might seem complicated because the K values depend on temperature and because activity corrections, if necessary, depend on ionic strength, the computations can be done quickly and easily using a computer. USGS tools such as the Alkalinity Calculator (<http://or.water.usgs.gov/alk/>) and PCFF (<http://water.usgs.gov/usgs/owq/pcff.html>) have been programmed to use the advanced speciation method to compute carbonate, bicarbonate, and hydroxide concentrations. The Alkalinity Calculator can be used through a web browser with an active Internet connection, or as a stand-alone program. In any case, it is common for a technician to have a laptop computer or similar computing device available in the field or laboratory so that the complexity of the computations is no longer an impediment to using this method.

The advantages of the advanced speciation method are that it is valid for any sample pH, it accounts for the effects of hydroxide, and it accounts for the equilibrium chemistry of the carbonate species rather than assumptions regarding when each constituent is titrated. The method also accounts for the effects of temperature and ionic strength on the chemistry of water and carbonic acid.

Error Analysis

To justify the discontinuation of the simple speciation method, an analysis of the errors associated with that method relative to the advanced speciation method was completed. The advanced speciation method is intrinsically more accurate than the simple speciation method because the advanced method is derived from the known theoretical chemistry of water and carbonic acid; therefore, results from the advanced speciation method are a valid reference for an error analysis.

The sources of error associated with the simple speciation method and included in this analysis are: (1) assigning the effects of hydroxide on alkalinity or ANC to carbonate, and (2) assuming that no carbonate ions exist to be titrated below the carbonate equivalence point. This error analysis does not attempt to assess any errors associated with using either the simple or the advanced speciation method when acid/base constituents other than carbonate, bicarbonate, and hydroxide make significant contributions to sample alkalinity or ANC; that is a separate problem that can be important for some samples and that analysts must try to avoid.

Predictions of carbonate and bicarbonate concentrations from the simple speciation method were compared to predictions from the advanced speciation method for a range of sample alkalinities. At high sample pH, the errors associated with ignoring the effects of hydroxide increase. Near the carbonate equivalence point (near pH 8.3), errors associated with assuming that no carbonate ions are present below that point become more prevalent. Computed errors in the concentrations (mg/L) of carbonate and bicarbonate were normalized to sample alkalinity (mg/L as CaCO₃) and multiplied by 100, producing essentially a percent error relative to sample alkalinity. Results are shown in figures A1 and A2.

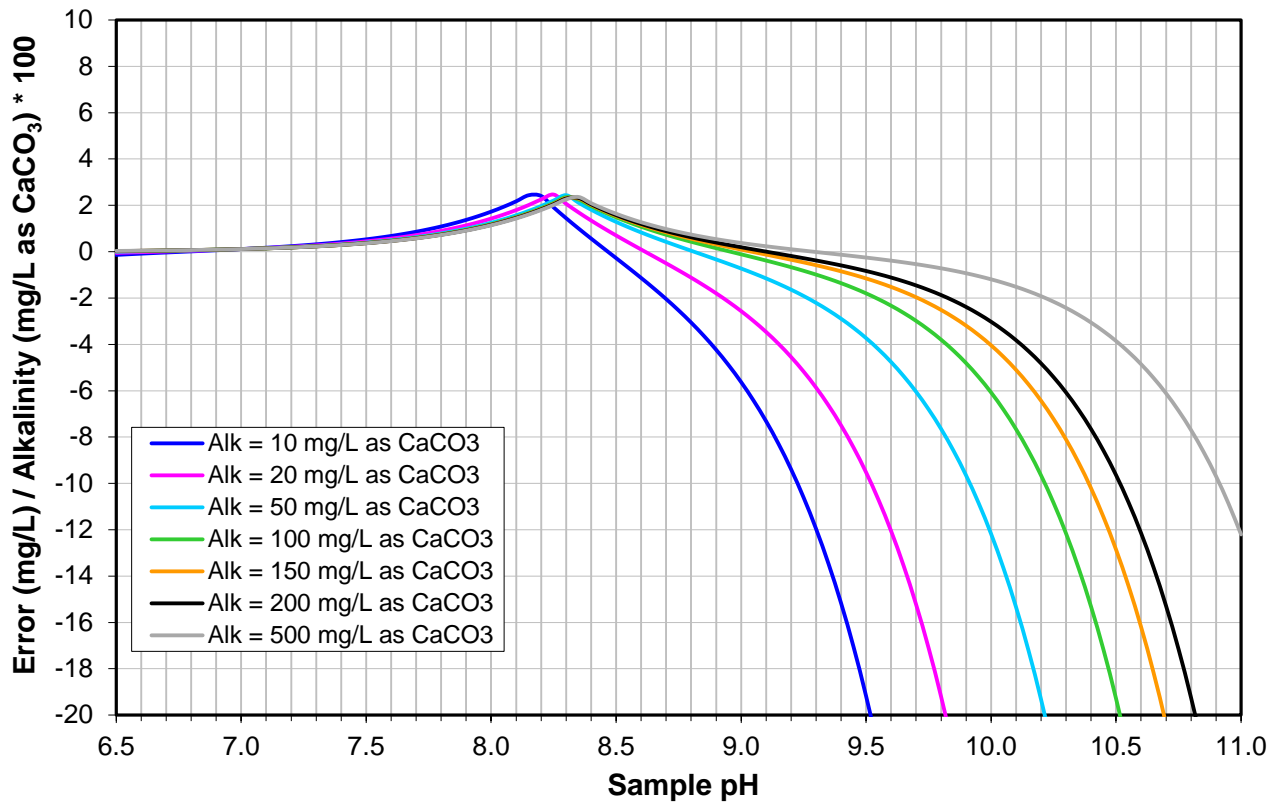


Figure A1. Graph showing the normalized error in the **bicarbonate** concentration prediction from the simple speciation method. The error quantified on the Y axis is essentially a percent error relative to sample alkalinity; to find the absolute concentration error, divide a plotted value by 100 and multiply by sample alkalinity. The larger errors toward higher pH values are due to neglecting the contribution of hydroxide, while errors in the vicinity of the carbonate equivalence point near pH 8.3 are due to assuming that no carbonate ions exist below that equivalence point.

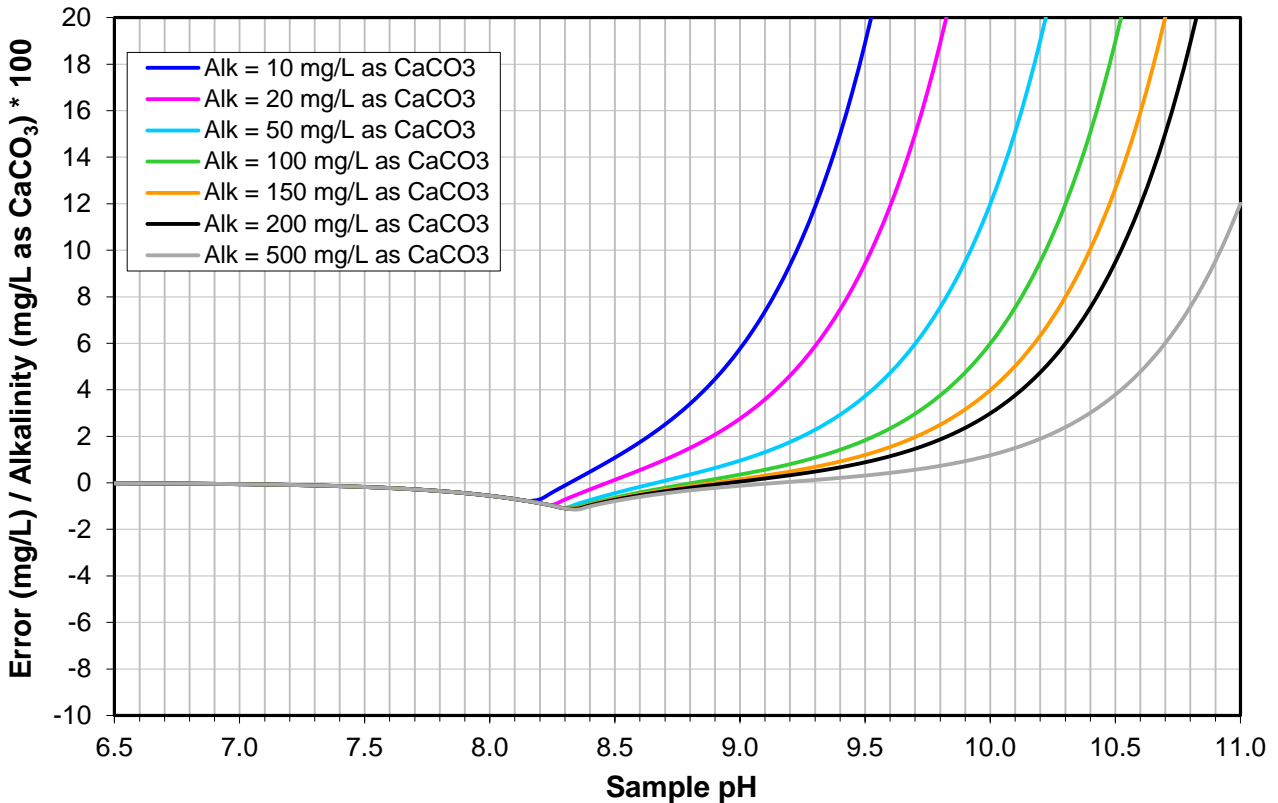


Figure A2. Graph showing the normalized error in the **carbonate** concentration prediction from the simple speciation method. The error quantified on the Y axis is essentially a percent error relative to sample alkalinity; to find the absolute concentration error, divide a plotted value by 100 and multiply by sample alkalinity. The larger errors toward higher pH values are due to neglecting the contribution of hydroxide, while errors in the vicinity of the carbonate equivalence point near pH 8.3 are due to assuming that no carbonate ions exist below that equivalence point.

An examination of the error computations indicates that errors produced by the simple speciation method due to ignoring the effects of hydroxide and assigning its alkalinity contributions to carbonate can be limited to 10 percent or less of the sample alkalinity by limiting the ratio of the hydroxide concentration (moles/L) to the sample alkalinity (eq/L) to less than about 0.08. An equation that provides this constraint in the form of a pH limit is as follows:

$$\text{pH} < \log_{10} \left(\frac{0.08 \times \text{Alk} \left(\frac{\text{mg}}{\text{L}} \text{ as } \text{CaCO}_3 \right)}{50043.6} \right) = \log_{10} \left((1.599 \times 10^8) \times \text{Alk} \left(\frac{\text{mg}}{\text{L}} \text{ as } \text{CaCO}_3 \right) \right)$$

According to this equation, the error in the carbonate and bicarbonate concentrations (mg/L) caused by ignoring the contributions of hydroxide would be limited to less than 10 percent of sample alkalinity (mg/L as CaCO₃) by applying the simple speciation method to samples with a pH no higher than 9.2 for an alkalinity of 10 mg/L as CaCO₃, or a pH no higher than 10.9 for a sample with an alkalinity of 500 mg/L as CaCO₃. Table A3 shows more example results from this equation.

Table A3. Maximum acceptable sample pH to avoid more than a 10 percent error, relative to sample alkalinity or ANC, in the concentrations (mg/L) of carbonate and bicarbonate computed from the simple speciation method.

Sample alkalinity (mg/L as CaCO ₃)	Maximum sample pH to keep hydroxide errors less than 10 percent
10	9.2
20	9.5
50	9.9
100	10.2
150	10.4
200	10.5
500	10.9
1000	11.2
2000	11.5

Note that even though the errors (in mg/L) may be constrained to less than 10 percent relative to sample alkalinity, the absolute magnitude of the concentration error may be substantial for a sample with a large alkalinity. A 10 percent error for a sample with an alkalinity of 500 mg/L as CaCO₃ means that the carbonate and bicarbonate concentrations could have errors as large as 50 mg/L. **By limiting the application of the simple speciation method to samples with a pH of less than 9.2 (the current guidance), the absolute concentration errors in mg/L also are limited to less than about 1 mg/L for a sample of any alkalinity.**

Errors associated with the incorrect assumption that the carbonate concentration is zero below the carbonate equivalence point also can be problematic for predictions from the simple speciation method. These errors are somewhat limited, however, compared to the potential errors discussed above for neglecting the effect of hydroxide. For example, errors in the predicted concentration of bicarbonate are limited to no more than about 2.5 percent (relative to sample alkalinity) in the vicinity of the carbonate equivalence near pH 8.3 (figure A1). For an alkalinity of 10 mg/L as CaCO₃, this error is only 0.25 mg/L; for an alkalinity of 500 mg/L as CaCO₃, the error is as much as 12.5 mg/L. For carbonate, the potential errors are slightly smaller, on the order of up to 1.1 percent (relative to sample alkalinity).

Recommendation and Implications

Because of greater accuracy and applicability over a wide range of sample pH, the OWQ has determined that the advanced speciation method should be used in preference to the simple speciation method for the calculation of carbonate and bicarbonate concentrations from alkalinity titration data, and that the simple speciation method should be discontinued. The main advantage of the simple speciation method (ease of calculation) no longer outweighs its disadvantages (limited pH range of applicability and assumptions that are inconsistent with the chemistry of carbonic acid). The greater computational burden of the advanced speciation method is offset by the availability of easy-to-use programs such as the Alkalinity Calculator and PCFF.

No significant implications for historical data should arise as a result of this change in the recommended method. The simple speciation method and the advanced speciation method typically produce nearly identical results for samples with a pH of less than 9.2, with no

significant difference at lower pHs. As long as the simple speciation method was being applied only to samples with a pH less than 9.2, few problems should exist in NWIS. The simple speciation method probably was being applied to samples with pH greater than 9.2, however, and the advanced speciation method was not generally available until June of 2001.

The magnitude of the errors produced by the simple speciation method depends on the alkalinity and the pH of the sample. For higher alkalinity samples, higher sample pH values can be analyzed with the simple speciation method and still suffer small percent errors, but perhaps significant absolute errors.

Personnel should remember to document the titration and speciation methods correctly. Method codes appropriate for the advanced speciation method are ASM01 through ASM12; information for when each code should be used is found 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.

More Information

Much more information on the chemistry of carbonic acid, alkalinity titrations, and the estimation of carbonate and bicarbonate concentrations from titration data is available from Hem (1985), Pankow (1991), Stumm and Morgan (1996), and Section 6.6 of the USGS National Field Manual (Rounds, 2006). An update to Section 6.6 of the NFM will include much of the information presented here on the advanced speciation method. Additional details may be found on the methods page for the Alkalinity Calculator at <http://or.water.usgs.gov/alk/methods.html>.

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