How to Calculate Alkalinity and Its Components

Generally, the calculation of alkalinity and its component members of Bicarbonate (HCO$_3^-$), Carbonate (CO$_3^{2-}$), and Hydroxide (OH) are explained in a manner meant to impress the reader with the author’s command of chemistry. Whilst somewhat interesting, most analysts simply want to know how to do the calculation so they can get on with their job. Hopefully, the following information will be clear.

### Step 1 – Titrate the sample to pH 8.3 (if initial pH > 8.3)

**Phenolphthalein Alkalinity also known as P alkalinity Calculation**

\[
\text{mg P Alkalinity as CaCO}_3/\text{L} = [\text{ml to pH 8.3}] \times [\text{Normality}] \times 50,000 \text{ / ml sample}
\]

**Example:**

\[
(2.02 \times 0.0198 \times 50,000 / 50 \text{ ml} = 40.04
\]

----------- NOTE ---------------------------------
The constant of 50,000 used in this equation is derived from:

1. Multiplying the equation X 1000 to put the units in Liters
2. Multiplying the equation X 50 (1 equivalent weight of CaCO$_3$) to get the number into units of CaCO$_3$ from meq.

### Step 2 – Titrate the sample to pH 4.3

**Total Alkalinity Calculation**

Total Alkalinity is always reported as mg/L as CaCO$_3$
The calculation is:

\[
[\text{ml to pH 4.5}] \times [\text{Normality}] \times [50,000 / \text{ ml of sample}]
\]

**Example :**

Total Alk as mg CaCO$_3$/L = 3.56 X 0.0198 X 50,000 / 50 ml = 70.49

----------- NOTE ---------------------------------
The constant of 50,000 used in this equation is derived from:

1. Multiplying the equation X 1000 to put the units in Liters
2. Multiplying the equation X 50 (1 equivalent weight of CaCO$_3$) to get the number into units of CaCO$_3$ from meq.
### Step 3 – Calculate the Components (HCO₃, CO₃, OH)

<table>
<thead>
<tr>
<th>Result of titration</th>
<th>Hydroxide Alkalinity as CaCO₃</th>
<th>Carbonate Alkalinity as CaCO₃</th>
<th>Bicarbonate Conc. as CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>P = 0</td>
<td>0</td>
<td>0</td>
<td>T</td>
</tr>
<tr>
<td>P &lt; 1/2T</td>
<td>0</td>
<td>2P</td>
<td>T – 2P</td>
</tr>
<tr>
<td>P = 1/2T</td>
<td>0</td>
<td>2P</td>
<td>0</td>
</tr>
<tr>
<td>P &gt; 1/2T</td>
<td>2P – T</td>
<td>2(T – P)</td>
<td>0</td>
</tr>
<tr>
<td>P = T</td>
<td>T</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

where P = phenolphthalein alkalinity; T = total alkalinity

In the example data from steps 1 and 2, we know that our P Alkalinity = 40.04
In the example data from steps 1 and 2, we know that our T Alkalinity = 70.49

Now we need to use the Alkalinity relationship chart to determine how our components actually exist in the water sample. Find the expression in the first column that is true.

Using our example data, where P = 40.04 mg/L and T = 70.49 mg/L, we find that we would use line 4 of the chart above to calculate our components since 40.04 is > 35.25 and is the only true statement when calculated from the column equations.

Therefore we use the equations from line 4:

\[
\begin{align*}
\text{Milligrams OH Alkalinity as CaCO}_3 &= (2 \times 40.04) - 70.49 = 9.59 \\
\text{Milligrams CO}_3 \text{ Alkalinity as CaCO}_3 &= 2(70.49 - 40.04) = 60.9 \\
\text{Milligrams HCO}_3 \text{ Alkalinity as CaCO}_3 &= 0
\end{align*}
\]

---------------------NOTE--------------------------------------------------------------------
The values calculated above are still in units of alkalinity. We report Bicarbonate (et. al.) as mg HCO₃ as CaCO₃/L not mg HCO₃ Alkalinity as CaCO₃/L.
To change the Component Alkalinity to the equivalent weight of HCO$_3^-$, CO$_3^{2-}$ and OH, we need to calculate a factor to change the weight of the Alkalinity to the weight of the component (HCO$_3^-$, etc.). This is done using “equivalents.”

To calculate the equivalent factors for the three components, do the following:

**Step 1. Calculate the molecular wt. of the compound and note its valance.**
- Equivalent weight of CaCO$_3$ = 100 mg, Valence = 2 = 50 mg/eqv
- Equivalent weight of HCO$_3^-$ = 61 mg, Valence = 1 = 61 mg/eqv
- Equivalent weight of CO$_3^{2-}$ = 60 mg, Valence = 2 = 30 mg/eqv
- Equivalent weight of OH = 17 mg, Valence = 1 = 17 mg/eqv

(Valence values are absolute numbers)

**Step 2. Calculate the equivalent wt factor of the component by dividing its equivalent wt by the equivalent weight of CaCO$_3$ and then dividing by the valance.**

- Factor for HCO$_3^-$ = \[\frac{61 \text{ mg}}{50 \text{ mg}}\] / 1 = 1.219
- Factor for CO$_3^{2-}$ = \[\frac{30 \text{ mg}}{50 \text{ mg}}\] / 2 = 0.5996
- Factor for OH = \[\frac{17 \text{ mg}}{50 \text{ mg}}\] / 1 = 0.3398

**Step 3. Multiply the component alkalinity concentration by the corresponding equivalent weight factor**

To report out the above constituents, you multiply the value obtained from the chart by the equivalent wt. factor.

For example
- mg/L HCO$_3^-$ as CaCO$_3$ = [mg HCO$_3^-$ Alk/L] X 1.219
- mg/L CO$_3^{2-}$ as CaCO$_3$ = [mg CO$_3^{2-}$ Alk/L] X 0.5996
- mg/L OH as CaCO$_3$ = [mg OH Alk / L] X 0.3398

(From the calculated results in step 2)
- mg/L HCO$_3^-$ as CaCO$_3$ = 0 X 1.219 = 0
- mg/L CO$_3^{2-}$ as CaCO$_3$ = [60.9] X 0.5996 = 36.51
- mg/L OH as CaCO$_3$ = [9.59] X 0.3398 = 3.25

These are the values that are reported.
Additional Notes

*************NOTE********************
HCO₃ alkalinity will always be a greater number than the Total Alkalinity because it weighs less. In other words, it takes more HCO₃ by weight to neutralize 1 ml of acid than it would CaCO₃ by weight. Another way to look at it is that it takes 1.219 times as many mg of HCO₃ to react with the same amount of acid as compared to mg of CaCO₃.

*************NOTE********************
If you wanted to calculate the Total Alkalinity as meq/L you may, but it isn’t usually done. The calculation is:

Meq CaCO₃/L = [ml to pH 4.5] X [Normality] X 1,000 / ml of sample

The constant of 1,000 used in this equation is derived from:
1. Multiplying the equation X 1000 to put the units in Liters