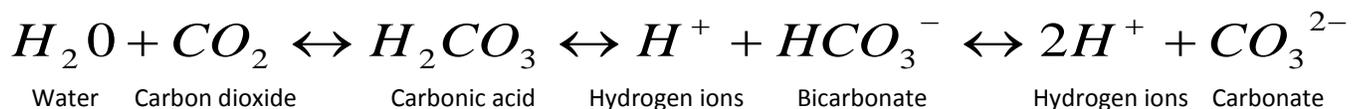


Application Note #97 – Alkalinity and Hardness by Potentiometric Titration Using TRIS Buffer

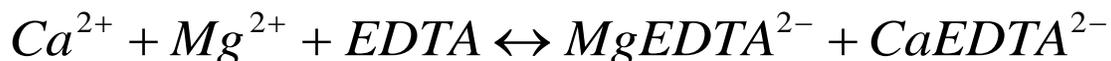
Updated July 2017

Introduction:

Alkalinity refers to the acid-neutralizing or buffering capacity of a solution.¹ The following chemical equilibrium equations represent the bicarbonate buffering system. They depict the relationships between the three forms of alkalinity: carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and hydroxide (OH^-) alkalinity. Hydroxide alkalinity is present in waters with a pH greater than 9.5². Alkalinity analysis involves the titration of samples with a standard 0.02N sulphuric acid (H_2SO_4) titrant to endpoints of pH 8.3 and 4.5³. To perform a manual titration, phenolphthalein or metacresol purple indicator is used for pH of 8.3 (phenolphthalein alkalinity, *palk*) and bromocresol green indicator is used for pH of 4.5 (total alkalinity, *talk*)⁴.



Water high in dissolved minerals, especially calcium and magnesium is described as hard water. Detection of total and speciated hardness by potentiometric titration is an accurate and efficient way to determine the hardness of a sample without the addition of indicators to the sample. This method focuses on the use of a TRIS buffer for hardness analysis. The use of this buffer eliminates the potential for pH electrode shocking, commonly seen with the use of ammonium hydroxide/ammonium chloride buffer, and is an essentially odourless option. Following shocking, a pH electrode may be unable to detect or be slow to respond to changes in pH. A properly responding pH electrode is key in many water analysis tests, including alkalinity, thus the use of this buffer to maintain electrode performance is desirable. The sample is then titrated with EDTA to one or two endpoints and the hardness of the sample is determined. The EDTA complexes with calcium and magnesium in the following way:



Because alkalinity determination decreases the pH to 4.2, and the hardness application requires the pH to be elevated to above 10, it was not known how the hardness of the samples would react to the drastic pH differences. The data in this application note indicates that the drop in pH has no effect on the hardness values of the samples tested. This application note demonstrates that it is possible to run an

alkalinity titration and hardness by potentiometric titration on the same sample aliquot, reducing the sample volume required for the procedure to half of that for the two procedures run on separate aliquots. For additional information about running alkalinity or hardness on separate samples please see the application notes for the individual methods, (Application Note #72 and #126, respectively). Please contact your local MANTECH sales representative to find out how this method can work for you.

Conforms to: Variation of Standard Methods 2340-C and EPA Method 130.1 (Hardness)
EPA, Method No. 310.1 (Alkalinity)
Standard Methods, Method No. 2320 (Alkalinity)
ASTM, Method No. D 1067-92 (Alkalinity)

Sample: All water samples

Concentration Range Tested Between*: 1-1000mg/L (ppm) alkalinity
1.00 to 400mg/L (ppm) total hardness
2.04 to 110mg/L (ppm) Ca²⁺ hardness
0.30 to 30mg/L (ppm) Mg²⁺ hardness

*Total hardness concentrations can be detected greater than 1000ppm with the use of smaller sample volumes, increased titrant concentration, or auto-dilution

Apparatus:

1. TitraSip Module
2. Reagent Addition Pump (for automated TRIS addition)
3. 2x MANTECH Buret
4. Interface Module
5. Calcium electrode
6. pH electrode
7. Detachable electrode cable with BNC connection
8. Autosampler
 - a) AutoMax73, 73 sample locations from a 50mL tube
 - b) AutoMax122, 122 sample locations from a 50mL tube
 - c) AutoMax 197, 197 sample locations from a 50mL tube

Reagents:

1. **0.01 M EDTA (Titrant) Solution**
 - 1.1. Combine 3.723g of EDTA in 1L of DI H₂O.
2. **~50% (v/v) (1 + 1) Hydrochloric Acid Solution**
 - 2.1. In a 500.00mL volumetric flask, add approximately 200mL of DI H₂O(l).
 - 2.2. To this, add 250mL of concentrated HCl_(aq) (Hydrochloric Acid).
 - 2.3. Once solution is at room temperature, bring to volume with DI H₂O(l).

3. **~3N Ammonium Hydroxide Solution**

3.1. In a 1.0L volumetric flask, add approximately 97.4mL of concentrated $\text{NH}_4\text{OH}_{(\text{aq})}$ (ammonium hydroxide) and approximately 500mL of DI $\text{H}_2\text{O}_{(\text{l})}$.

3.2. Once solution is at approximately room temperature, bring to volume with DI $\text{H}_2\text{O}_{(\text{l})}$.

4. **Standard Calcium Carbonate Solution**

*must make solutions 2 and 3 prior to making this solution.

4.1. In a 1.000L volumetric flask, dissolve 1.0000g** $\text{CaCO}_{3(\text{s})}$ (Anhydrous Calcium Carbonate) in the 1+1 $\text{HCl}_{(\text{aq})}$, solution (as made in step #2 above).

4.2. To this, add 250mL of DI $\text{H}_2\text{O}_{(\text{s})}$.

4.3. Heat the solution on a hot plate/Bunsen Burner such that it boils for three minutes (this step removes any dissolved $\text{CO}_{2(\text{aq})}$ in the solution).

4.4. Add 10 drops of Methyl Red indicator.

4.5. In a dropwise fashion, add the 3N $\text{NH}_4\text{OH}_{(\text{aq})}$ and the (1+1) $\text{HCl}_{(\text{aq})}$ Solution until the methyl red intermediate orange colour between pH 4.4 and 6.2 is achieved.

4.6. Once at room temperature, bring to volume with DI $\text{H}_2\text{O}_{(\text{l})}$.

**depending on the hydration of your sample, and the conditions in which it is stored, you may need to dry this sample and cool it in a desiccator prior to determining the mass of calcium carbonate (it is vital that the analytical concentration be exact, as this is the primary standard for this method).

5. **TRIS(tris(hydroxymethyl)aminomethane)/Acetylacetone Buffer**

5.1. In a 1.0L bottle, dissolve 19.95g of TRIS in approximately 500mL of DI water.

5.2. To this, add 10.71mL of acetylacetone

6. **Standard sulphuric acid titrant**, 0.02 N: 0.556 mL of concentrated H_2SO_4 in 1L distilled water

7. **Sodium carbonate solution**: 1000 ppm alkalinity= 1.0589 g Na_2CO_3 in 1L distilled water. Dilute as necessary for other concentrations

8. **pH 4, 7, and 10 buffer solutions**

Procedure:

pH Calibration:

1. Place a minimum of 30mL of pH 4, 7, and 10 buffers into the first three positions in the Autosampler rack and run a schedule to calibrate the pH probe. Note that the pH probe may be located on the Autosampler arm or in a TitraSip, depending on system configuration.
2. The sampler will move to the rinse station where the sample transfer line and TitraSip vessel are rinsed with deionized water (if applicable).
3. The sampler will move to the pH 4 buffer position and the sample transfer line will be primed with the pH 4 buffer solution (if applicable).
4. 25mL of buffer solution will be pumped into the TitraSip cell or the sample cup, and the stirrer turned on (if applicable).
5. The pH of the buffer solution is measured and recorded.

6. Steps 2 to 5 will be repeated for the pH 7 and 10 buffer solutions.
7. The calibration curve will be calculated and reported.

*Note the volumes described above will vary by configuration

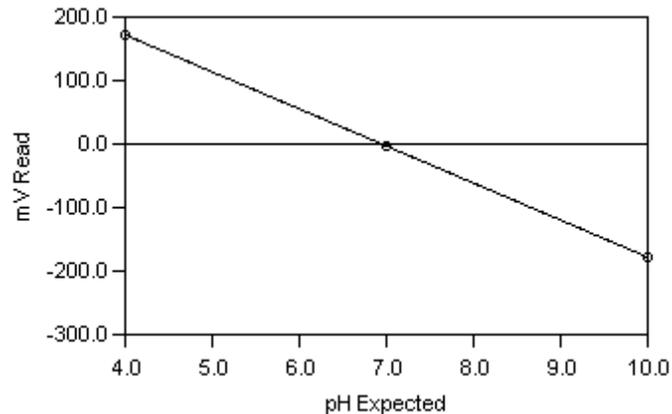


Figure 1: Sample Calibration Curve

Sample Analysis:

1. Place samples in the autosampler rack.
2. The Autosampler will move to the flowing rinse position where the needle and the 85mL TitraSip cell will be rinsed with DI water.
3. The sampler will move to the first sample position where the lines will be primed and the TitraSip cell rinsed with the sample and DI water.
4. 40mL of the sample will be pumped up to the TitraSip cell.
5. The stirrer will be turned on and the initial pH of the sample will be read and recorded.
6. The sample will then be titrated with standard sulphuric acid titrant to pH 4.2. This is done to ensure that information for low-level alkalinity calculations is available when necessary.
7. The alkalinity of the sample will then be calculated and reported.
8. The new pH of the sample will be measured, and 5mL of TRIS buffer is added to the sample to reach a pH of 10.
9. The adjusted pH of the sample will be measured and recorded.
10. The sample will then be titrated with EDTA to the endpoint(s).
11. The final pH of the sample will be measured and recorded, after which the hardness value of the sample will be calculated and reported.
12. Steps 2 to 11 will then be repeated for all of the remaining samples to provide alkalinity and hardness values for the samples.
13. Following completion of the final sample, the needle will take up the appropriate storage solution to store the electrodes until the next run.

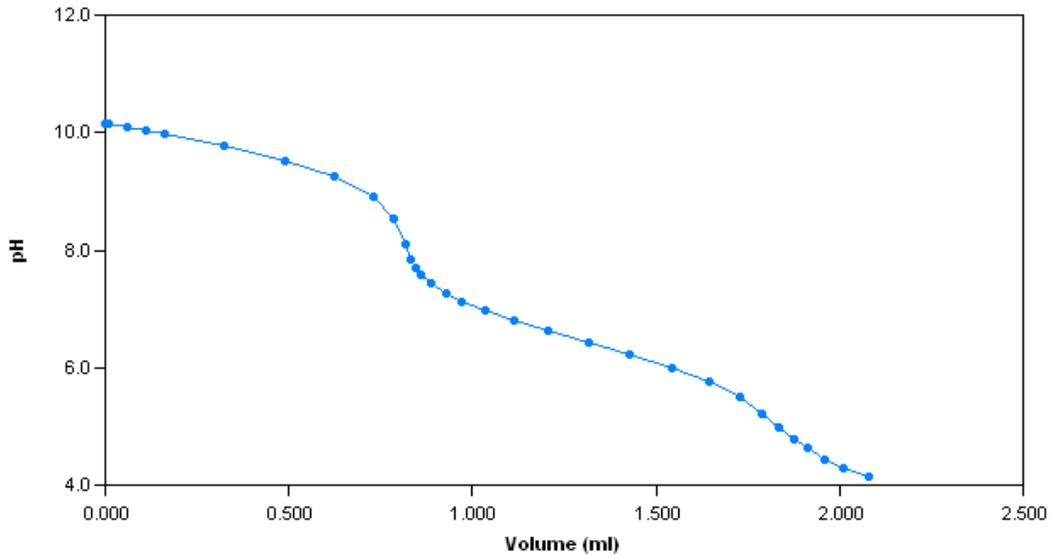


Figure 2: Sample alkalinity titration curve for an approximately 50ppm alkalinity sample

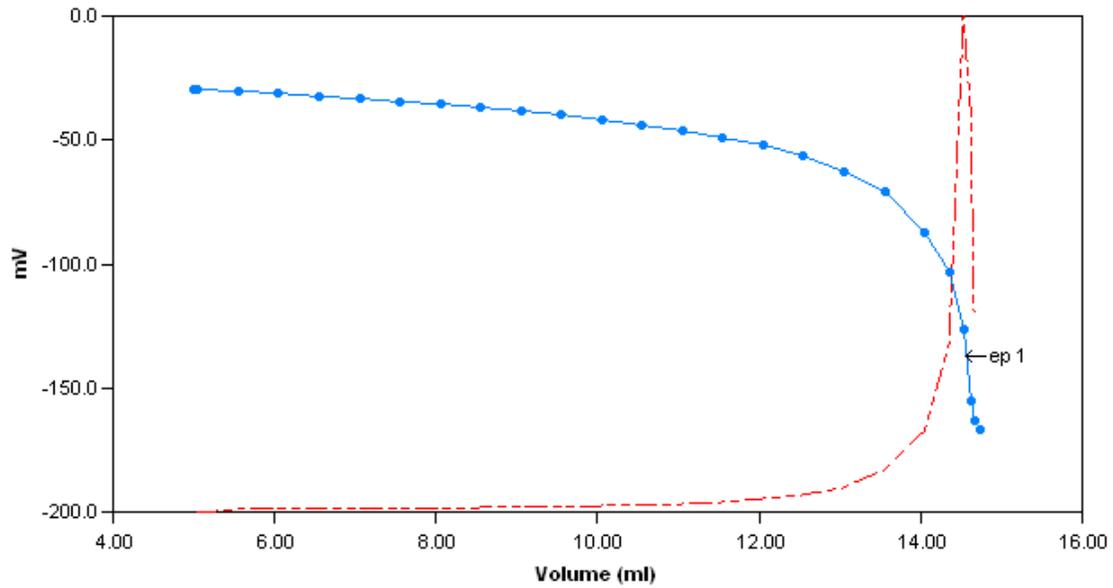


Figure 3: Sample total potentiometric hardness titration curve for a 500 ppm CaCO₃ sample

Calculations:
Alkalinity calculation for phenolphthalein alkalinity (palk)

Function	Expression	Result
palk (P)	$= \frac{xvol(8.3) * tcon * 50\ 000}{svol}$	mg CaCO ₃ / L

xvol(8.3)= volume of standard acid titrant used to titrate to pH 8.3
 tcon= normality of titrant (N)
 50 000= equivalent weight of CaCO₃ as defined in the methods⁸
 svol= volume of sample titrated (mL)

Alkalinity calculation for total alkalinity (talk)

Function	Expression	Result
talk (T)	$= \frac{xvol(4.5) * tcon * 50\ 000}{svol}$	mg CaCO ₃ / L

xvol(4.5)= volume of standard acid titrant used to titrate to pH 4.5
 tcon= normality of titrant (N)
 50 000= equivalent weight of CaCO₃ as defined in the methods⁸
 svol= volume of sample titrated (mL)

*Alkalinity calculation for potentiometric titration using low-level method**

Function	Expression	Result
talk (T)	$= \frac{[2 * xvol(4.5) - xvol(4.2)] * tcon * 50\ 000}{svol}$	mg CaCO ₃ / L

xvol(4.5)= volume of standard acid titrant used to titrate to pH 4.5
 xvol(4.2)= volume of standard acid titrant used to titrate to pH 4.2
 tcon= normality of titrant (N)
 50 000= equivalent weight of CaCO₃ as defined in the methods⁸
 svol= volume of sample titrated (mL)

*Low-level alkalinity method is only used for samples with alkalinity values calculated at less than 20ppm⁸.

Results for P and T alkalinity offer a means for stoichiometric classification of the hydroxide, carbonate, and bicarbonate forms of alkalinity.

- Hydroxide (OH⁻) alkalinity is present if *palk* is more than half the *talk*
- Carbonate (CO₃²⁻) alkalinity is present when *palk* is not zero but is less than *talk*
- Bicarbonate (HCO₃⁻) ions are present if *palk* is less than half the *talk*

Table 1: Alkalinity Calculations

Result of Titration	Hydroxide (OH ⁻) Alkalinity as CaCO ₃	Carbonate (CO ₃ ²⁻) Alkalinity as CaCO ₃	Bicarbonate (HCO ₃ ⁻) Alkalinity as CaCO ₃
P = 0	0	0	T
P < 1/2T	0	2P	T – 2P
P = 1/2T	0	2P	0
P > 1/2T	2P – T	2(T – P)	0
P = T	T	0	0

Hardness calculations

$$\text{ppm Ca}^{2+} = \frac{(\text{tcon}) \cdot 40.078 \cdot 1000 \cdot (\text{Ve1})}{\text{svol}}$$

$$\text{ppm Mg}^{2+} = \frac{(\text{tcon}) \cdot 24.305 \cdot 1000 \cdot (\text{Ve2} - \text{Ve1})}{\text{svol}}$$

$$\text{ppm CaCO}_3 = \frac{(\text{tcon}) \cdot 1000 \cdot 100.087 \cdot (\text{Ve2})}{\text{svol}}$$

- tcon = titrant concentration (N)
- Ve1 = first inflection point (mL)
- Ve2 = second inflection point (mL)
- svol = sample volume (mL)

To calculate the $[\text{Ca}^{2+}]_{\text{actual}}$ from the CaCO₃ standard,

$$\frac{\text{Mass CaCO}_3 \text{ (g)}}{100.087 \text{ g/mol}} \div \text{Volume of Volumetric Flask} = [\text{Ca}^{2+}]$$

To convert from ppm Magnesium and ppm Calcium to ppm Calcium carbonate,

$$\frac{\text{ppm Mg}^{2+} \text{ (mg/L)}}{24.3050 \text{ g/mol}} \times \frac{\text{ppm Ca}^{2+} \text{ (mg/L)}}{40.078 \text{ g/mol}} \times 100.078 \text{ g/mol} = \text{ppm CaCO}_3 \text{ (mg/L)}$$

N.B.

100.087 g/mol = Molar Mass of Calcium Carbonate (anhydrous)

24.3050 g/mol = Molar Mass of Magnesium

40.078 g/mol = Molar Mass of Calcium

Hints/Suggestions:

1. Use of a Titrator System enables higher throughput as volume measurement is done by the system, thus freeing up operator time. The system accurately and automatically measures the required volumes of all solutions into the titration cell. Operator intervention is minimal, allowing for a more consistent sample methodology.
2. The use of the TRIS buffer eliminates the potential for pH electrode shocking, commonly seen with the use of ammonium hydroxide/ammonium chloride buffers. This is important for systems measuring additional parameters requiring a pH electrode (i.e. alkalinity, acidity). Following shocking, a pH electrode may be unable to detect or be slow to respond to changes in pH.
3. The EDTA titrant is partially consumed by concentrations of 10ppm and higher of polyphosphates and 20ppm and higher of aluminum, barium, cadmium, cobalt, copper, iron, lead, manganese, nickel, strontium, and zinc. Use the inhibitors discussed in the Standard Method 2340 C when these conditions exist. One may also consider utilizing a blank titration instead of or in addition to the usage of inhibitors.
4. On the following page are a set of titration method settings that were used in the current study. These were found to provide fast and accurate analysis of low and high range samples in the most time efficient manner. Please note that these settings may require customization for particular user requirements.

¹ Acidity, Alkalinity, Ammonia. Hanna Instruments. 8 Oct. 2004. http://www.hannacan.com/fiches_techniques/HI3820.pdf.

² Alkalinity. Water Quality Association. 6 Oct. 2004. <http://www.wqu.org/glossary.cfm?gl=663>.

³ Smith, Roy K. 1999. Handbook of Environmental Analysis: 4th Edition. Genium Publishing, New York, pg 235-236.

⁴ Csuros, Maria. 1997. Environmental Sampling and Analysis: Lab Manual. CRC Press, New York, pg 221-226.

⁵ Harris, Daniel C. 1991. Quantitative Chemical Analysis, Third Edition. W.H. Freeman and Company, New York, pg 285-287

⁶ Water Lab. 2003. http://www.personal.psu.edu/users/l/l/llf136/Water_Lab.htm