

Application Note #119 – Alkalinity and Chloride by Titration

Updated July 2017

Introduction:

The alkalinity of water may be defined as its capacity to neutralize acid. Alkali substances in water include hydroxides or bases¹. Alkalinity analysis is used to monitor water coming from a wide range of sources (i.e. drinking, waste, agriculture, etc). The recommended range for drinking water is 30 to 400 ppm², and alkalinity values of 20-200 ppm are common in freshwater ecosystems³. The properties of water are easily influenced by the presence of alkalinity. High alkalinity (above 500 mg/L [ppm]) has adverse effects on plumbing systems; especially on hot water systems where excessive scale reduces the transfer of heat to the water, thereby resulting in greater power consumption and increased costs². Water with low alkalinity (less than 75 ppm) is subject to changes in pH due to dissolved gasses that may be corrosive to metallic fittings².

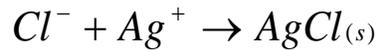
The following chemical equilibrium equations represent the bicarbonate buffering system. They depict the relationships between the three forms of alkalinity: carbonate (CO²⁻), bicarbonate (HCO₃⁻), and hydroxide (OH⁻) alkalinity. Hydroxide alkalinity is present in waters with a pH greater than 9.5⁴. Alkalinity analysis involves the titration of samples with a standard 0.02N sulfuric acid (H₂SO₄) titrant to endpoints of pH 8.3 and 4.5⁵. 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*)⁶.



Chloride, the ionized form of chlorine, is one of the most abundant inorganic ions in natural water and wastewater⁷. Although humans can tolerate chloride in concentrations up to 250 ppm⁷ (solely aesthetics-based), normal surface fresh waters usually contain less than 10 ppm chloride content and quite often contain below 1 ppm⁸. However, a surplus of chloride in the soil/surface water may arise from: natural sources, sewage and industrial effluents, urban runoff containing de-icing salt and saline intrusion⁹. This surplus salinity leads to an overall reduction in plant growth, along with smaller, thicker, and potentially scorched leaves¹⁰.

The potentiometric method of chloride analysis by silver nitrate titration is an effective technique of chloride level determination. This method employs the combination of silver ions from one solution (the titrant) and chloride ions from the other solution (sample to be analyzed) which generate insoluble

silver chloride¹¹. The voltage change as the titration proceeds and ions are being consumed is measured throughout the reaction. The following equation illustrates the net ionic reaction:



This document does not prove the validity of these two methods separately, as Application Notes # 71 and 72 prove separate viability. This document will however prove that these two methods can effectively be run back-to-back on the same sample aliquot. This means that you will be able decrease the necessary sample volume by half. For additional information about running alkalinity or chloride on separate samples please see the application notes for individual methods. Please contact your local MANTECH sales representative to find out how this method can work for you.

Conforms to: EPA, Method No. 310.1 (**Alkalinity**)

Standard Methods, Method No. 2320 (**Alkalinity**)

ASTM, Method No. D 1067-92 (**Alkalinity**)

Standard Methods, Method No. 4500-Cl⁻D (**Chloride**)*

*Nitric Acid (HNO₃) can be used as pre-treatment to eliminate contaminant effects when contaminant concentrations are greater than chloride concentrations, however this procedure was not used in our analysis

Sample: All water samples

Concentration Range: 0.3 – 1000ppm (**Alkalinity**)

1.0 – 1000ppm (**Chloride**)

MDL: 0.3ppm* (**Alkalinity**)

1.0ppm (**Chloride**)

*This measuring range was determined by analyzing laboratory-prepared standards made from sodium chloride and sodium carbonate. The method detection limit (MDL) was determined based on data obtaining a coefficient of variance better than 30%. Results obtained in your laboratory may differ depending on laboratory practices and sample matrix.

Apparatus:

1. Interface
2. pH Electrode
3. Silver/Sulfide Electrode
4. 2x Electrode Cable
5. TitraSip
6. 2x MANTECH Buret

7. Reagent Addition Pump (optional, for automated sodium thiosulphate addition)
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. Standard sulphuric acid titrant, 0.02 N: 0.556 mL of concentrated H₂SO₄ in 1L distilled water
2. Sodium carbonate solution: 1000 ppm alkalinity= 1.0589 g Na₂CO₃ in 1L distilled water. Dilute as necessary for other concentrations
3. pH 4, 7, and 10 buffer solutions
4. Standard Silver Nitrate 0.0141 M (from 2.395 g in 1 L deionized water)
5. Sodium Thiosulfate, 0.1 N: 15.812 g in 1L deionized water (optional)

Procedure:

Calibration:

1. Place a minimum of 40mL* 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 an 85mL TitraSip cell, depending on system configuration.
2. The sampler will move to the rinse station where the sample transfer line and 85mL 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 pH 4 buffer solution (if applicable).
4. 25mL of buffer solution will be pumped into the 85mL TitraSip cell, 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 that only 30mL of sample is required for beaker style systems

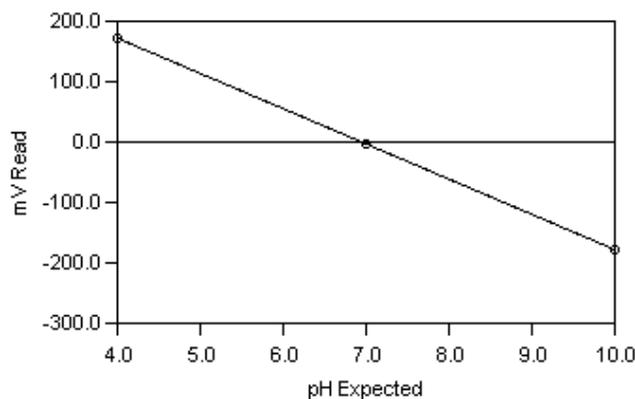


Figure 1: Sample Calibration Curve

Sample Analysis:

1. Place samples in the autosampler rack with a minimum of 40mL* in each sample container.
2. The autosampler will move to the rinse position where the needle and the 85mL TitraSip cell will be rinsed with DI water** (if applicable).
3. The sampler will move to the first sample position where the lines will be primed and the 85mL TitraSip cell rinsed with the sample and DI water (if applicable).
4. 25mL of the sample will be pumped up to the 85mL TitraSip cell (if applicable).
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 sulfuric acid to pH 4.2. This is done to ensure that information for low-level alkalinity calculations is available, when necessary.
7. The total alkalinity of the sample is calculated and reported.
8. The same sample is then titrated with standard silver nitrate until the chloride endpoint is achieved.
9. The stirrer is turned off.
10. The concentration of chloride in the sample is calculated and reported.
11. Steps 2-10 will be repeated for all remaining samples.
12. Following completion of the final sample, the needle will take up the appropriate storage solution to store the electrodes until the next run.

*Note the only 30mL of sample is required for beaker style systems

** If an extra pump is employed, sodium thiosulfate may be added during the rinse routines to remove excess silver chloride precipitate

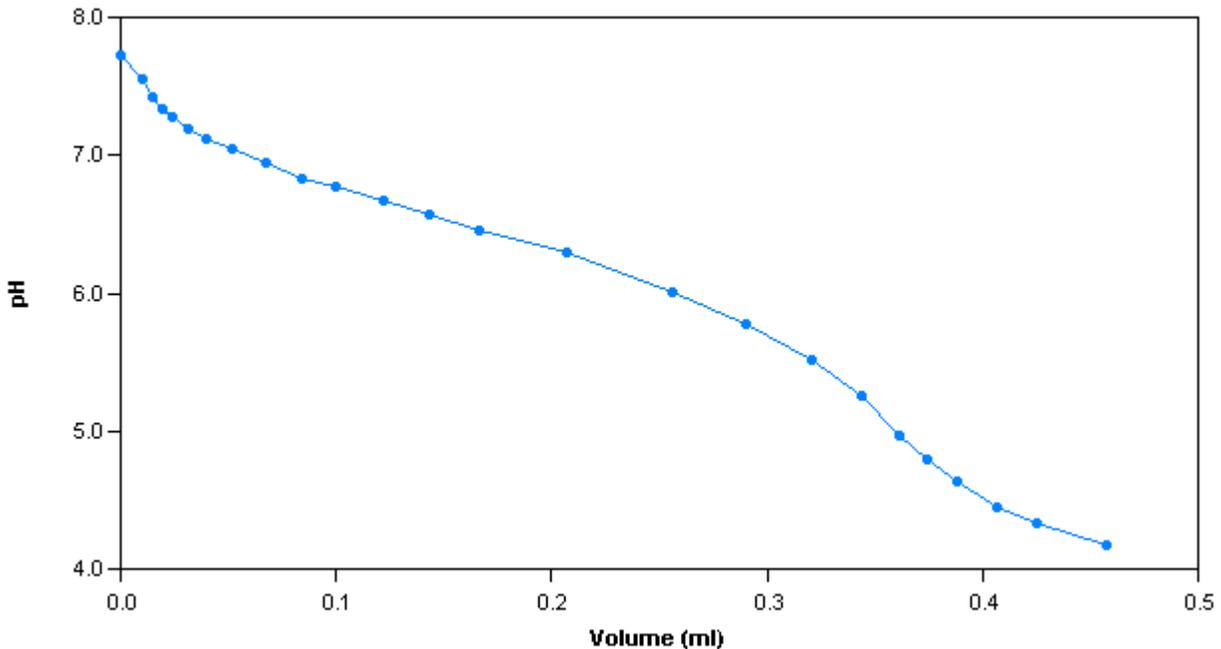


Figure 2: Sample Titration Curve for a 10ppm Alkalinity Sample

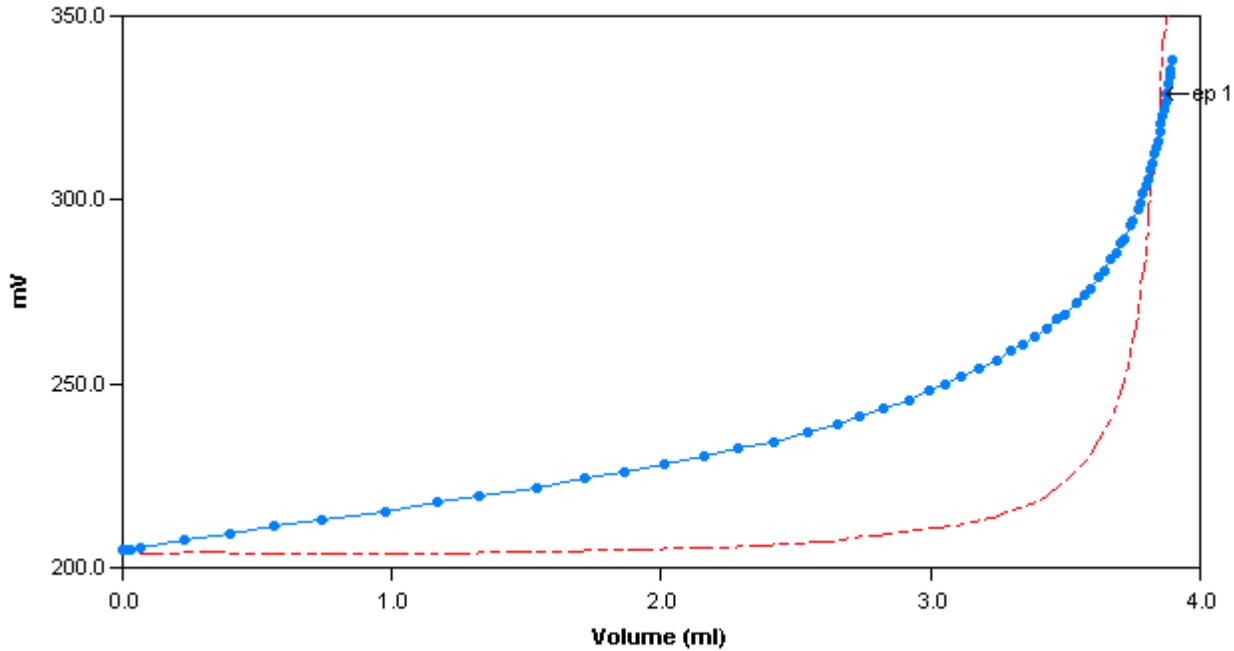


Figure 3: Sample Titration Curve for a Nestle Bottled Water Chloride sample

Calculations:

Alkalinity Equation Set

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 methods⁷
- 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 methods⁷
- 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 methods⁷
- svol= volume of sample titrated (mL)

*Low-level alkalinity method is only used for samples with alkalinity values calculated at less than 20ppm⁷.

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

Chloride Equation Set

$$Cl^- = \frac{ve1 * tcon * 35.453 * 1000}{svol}$$

- Cl⁻ = Chloride concentration (ppm)
- ve1 = total volume of silver nitrate added at the endpoint (mL)
- tcon = silver nitrate titrant concentration (M)
- svol = sample volume (mL)

Quality Control:

Ten replicates were run for a concentration of 10ppm alkalinity/chloride standard, Nestle bottled water, and tap water. Please make note that the alkalinity and chloride readings for each respective sample were taken from 1 aliquot per replicate [i.e. sample #1 of "10ppm Standard (Alkalinity)" is the same sample aliquot as sample #1 of "10ppm Standard (Chloride)"]. Statistical data is displayed below.

10ppm Standard (Alkalinity):

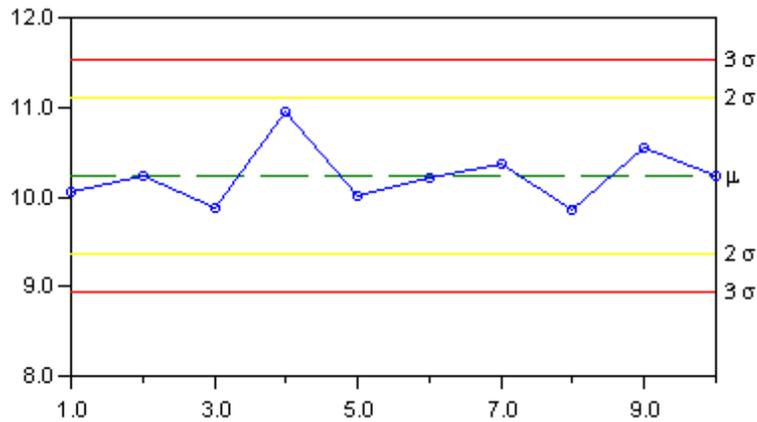


Figure 4: Control Limits Plot for **ALKALINITY PORTION** of a 10ppm Alkalinity/Chloride Standard

Control Limits – Individuals

$\mu = 10.234$
 $\sigma = 0.435$
 CV = 4.25%

95% Confidence Limits

$\mu - 2\sigma = 9.364$
 $\mu + 2\sigma = 11.104$

99.7% Confidence Limits

$\mu - 3\sigma = 8.929$
 $\mu + 3\sigma = 11.539$

10ppm Standard (Chloride):

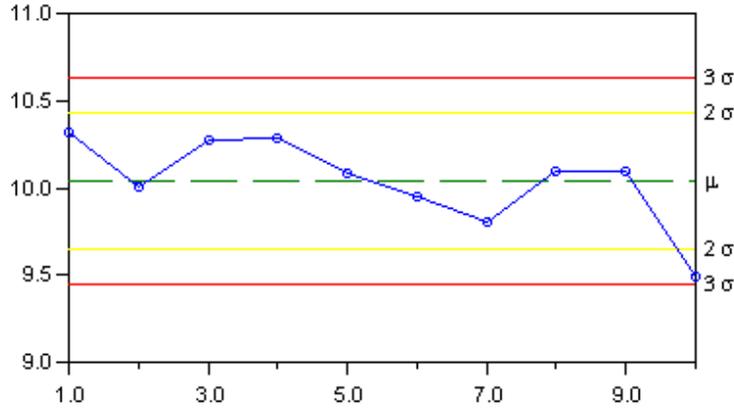


Figure 5: Control Limits Plot for CHLORIDE PORTION of a 10ppm Alkalinity/Chloride Standard

Control Limits – Individuals

$\mu = 10.039$
 $\sigma = 0.196$
 CV = 1.95%

95% Confidence Limits

$\mu - 2\sigma = 9.647$
 $\mu + 2\sigma = 10.432$

99.7% Confidence Limits

$\mu - 3\sigma = 9.451$
 $\mu + 3\sigma = 10.628$

Nestle Bottle Water (Alkalinity):

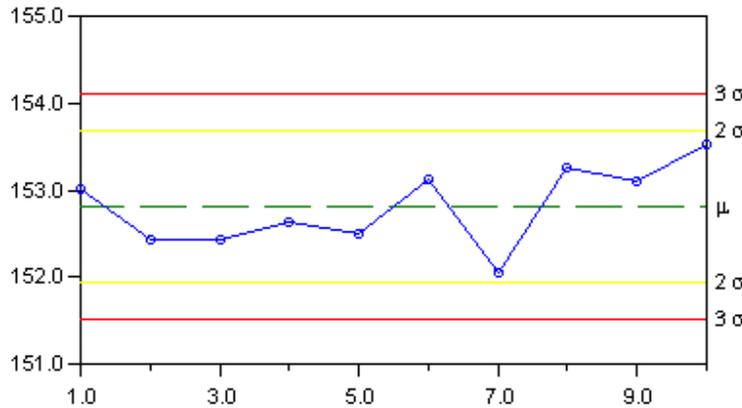


Figure 6: Control Limits Plot for ALKALINITY PORTION of a Nestle Bottled Water Sample

Control Limits – Individuals

$\mu = 152.809$
 $\sigma = 0.435$
 CV = 0.28%

95% Confidence Limits

$\mu - 2\sigma = 151.939$
 $\mu + 2\sigma = 153.678$

99.7% Confidence Limits

$\mu - 3\sigma = 151.504$
 $\mu + 3\sigma = 154.113$

Nestle Bottle Water (Chloride):

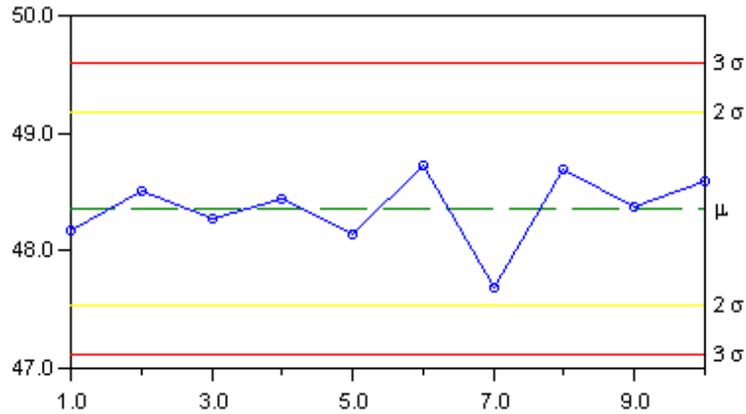


Figure 7: Control Limits Plot for CHLORIDE PORTION of a Nestle Bottled Water Sample

Control Limits – Individuals

$\mu = 48.361$
 $\sigma = 0.412$
 CV = 0.85%

95% Confidence Limits

$\mu - 2\sigma = 47.537$
 $\mu + 2\sigma = 49.186$

99.7% Confidence Limits

$\mu - 3\sigma = 47.125$
 $\mu + 3\sigma = 49.598$

Tap Water (Alkalinity):

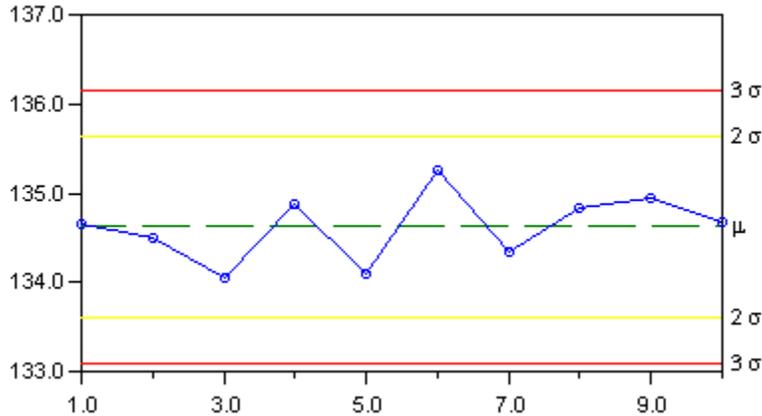


Figure 8: Control Limits Plot for ALKALINITY PORTION of Tap Water Samples

Control Limits – Individuals

$\mu = 134.621$
 $\sigma = 0.507$
 CV = 0.38%

95% Confidence Limits

$\mu - 2\sigma = 133.606$
 $\mu + 2\sigma = 135.636$

99.7% Confidence Limits

$\mu - 3\sigma = 133.099$
 $\mu + 3\sigma = 136.143$

Tap Water (Chloride):

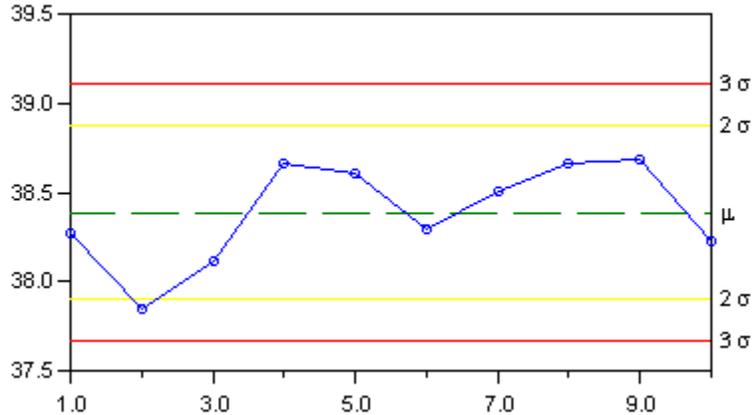


Figure 9: Control Limits Plot for **CHLORIDE PORTION** of Tap Water Samples

Control Limits – Individuals

$\mu = 38.387$
 $\sigma = 0.242$
 CV = 0.63%

95% Confidence Limits

$\mu - 2\sigma = 37.904$
 $\mu + 2\sigma = 38.870$

99.7% Confidence Limits

$\mu - 3\sigma = 37.662$
 $\mu + 3\sigma = 39.112$

Hints/Suggestions:

General

1. Rinse all sample containers with deionized water prior to sample addition to prevent contamination of samples due to tap water impurities.
2. Avoid the use of soaps or cleaners for washing plastic or glassware. Detergents can contain sodium carbonate which will interfere with alkalinity readings. The use of disposable tubes or cups is recommended.
3. Ensure that the electrodes are completely filled with solution before each run. In this case, one must use KNO_3 in lieu of KCl as the latter would interfere with the chloride titration.
4. Purge burets daily to ensure the most accurate sample analysis.
5. When not in use, both electrodes can be stored in a combination of pH 4.0 buffer solution and a weak chloride solution for convenience. Storing electrodes is of the utmost importance in ensuring their longevity.

Alkalinity

6. Samples with high alkalinity values should not be left exposed to air for an extended period of time. These samples will slowly decompose, resulting in low alkalinity readings.
7. It is important to note that the alkalinity standards were made from sodium carbonate (Na_2CO_3), while the total alkalinity is reported as mg/L of calcium carbonate ($CaCO_3$). Calcium carbonate is nearly insoluble in water.

Chloride

8. It is suggested that the standard silver nitrate titrant be stored in an amber bottle to minimize decomposition as it is light-sensitive.
9. If deposits of silver chloride precipitate are seen in the TitraSip cell, it can be cleared by adding a few milliliters of 0.1 N sodium thiosulphate solution. Testing shows that this solution will clean the TitraSip analysis cell by dissolving precipitate after titrating samples of up to 1000 ppm chloride. It is also suggested that sodium thiosulphate be stored in an amber bottle to minimize decomposition. More concentrated chloride precipitates can be cleaned using an NH_4OH wash followed by an acid rinse.
10. If desired, a chloride ion selective electrode (ISE), or a silver billet electrode may be used as an alternative to the silver sulfide electrode.
11. It may be possible to expand the detectable chloride range. For very low chloride concentrations (less than 1 ppm), higher sample volumes should be used. For very high chloride concentrations (greater than 1000 ppm), lower sample volumes should be used and diluted, though harsh cleaning agents may be necessary to dissolve any precipitate, as mentioned above.
12. A simple way to determine the approximate chloride concentration of an unknown sample is to measure the conductivity. The majority of water samples will have high chloride concentrations when the conductivity is high. An automated system can be set up to auto-dilute samples based on conductivity measurements.
13. Interferences to the silver/sulfide electrode include: strongly reducing solutions (as they will form a surface layer of silver metal), high levels of ions able to form insoluble salts (polishing electrode will restore performance), mercury, biological samples, and protein in food (remedied by acidifying to pH 2-3 with HNO_3).

¹ "Alkalinity of Drinking Water Explained," 16 March 2009.

<http://www.freedrinkingwater.com/water-education2/74-alkalinity-water.htm>

² "Commonly Found Substances in Drinking Water and Available Treatment", Illinois Department of Public Health, 16 March 2009.

<http://www.idph.state.il.us/envhealth/pdf/DrinkingWater.pdf>

³ "Acid Mine Drainage: Alkalinity." Exploring the Environment: Water Quality. Wheeling Jesuit University. 16 March 2009.

<http://www.cotf.edu/ete/modules/waterq/wqalkalinity.html>.

⁴ Alkalinity. Water Quality Association. 16 March 2009. <http://www.wqa.org/glossary.cfm?gl=663>.

⁵ Smith, Roy K. 1999. "Handbook of Environmental Analysis": 4th Edition. Genium Publishing, New York, pp 235-236.

⁶ Csuros, Maria. 1997. "Environmental Sampling and Analysis: Lab Manual." CRC Press, New York, pp 221-226.

⁷ Clesceri, Lenore S., Greenberg, Arnold E., & Eaton, Andrew D. 2005. "Standard Methods for the Examination of Water and Wastewater": 21st Edition, pp 4-73 to 4-74, 4500-CL-: Potentiometric Method

⁸ "Chloride," Environmental and Workplace Health, Health Canada. 17 March 2009.

<http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/chloride-chlorure/index-eng.php>

⁹ "Chemical Fact Sheets, #12.22: Chloride," World Health Organization: Water Sanitation Health. 17 March 2009.

http://www.who.int/water_sanitation_health/dwg/gdwq0506_12.pdf

¹⁰ "Chloride- An Essential Element," Tetra Chemicals- Agriculture Nutrients. 17 March 2009.

http://www.tetrachemicals.com/Products/Agriculture/Chloride_-_An_Essential_Element.aqf

¹¹ "Precipitation Reactions," Rockwood School District, Lafayette High School. 17 March 2009.

<http://www.rockwood.k12.mo.us/lafayette/kupfer/precipitation.htm>