Measuring Total Alkalinity and Hardness

(SM 2320B and SM 2340C as adapted from Hach kit instruction manual)

1. SCOPE AND APPLICATION

1.1. These methods are based on Standard Methods 2320B and 2340C as adapted from the HACH Alkalinity and Hardness Kit instruction manual. They are used to measure alkalinity and hardness in aqueous solutions.

1.2. Measuring Limits: Hardness is generally not measured in samples having salinity of > 1‰ (parts per thousand) or conductivity > 5,000 µmhos-cm.

2. SUMMARY OF METHOD

2.1. Sample is measured into titration bottles. Reagents are added and mixed. Samples are then titrated with appropriate titrant until color change is completed. Volume of titrant used is converted to alkalinity or hardness as mg/L Calcium Carbonate ($CaCO_3$).

2.2. Interferences:

2.2.1. **Alkalinity**—include, but not limited to, soaps, oily matter, suspended solids or precipitates

2.2.2. **Hardness**—include, but not limited to, metals (ex. copper, iron, zinc), orthophosphate, highly buffered samples

2.3. Definitions:

2.3.1. **Alkalinity**—an aqueous solution's acid-netralizing capacity

2.3.2. **Hardness**—the soap-consuming capacity of a water sample, or the capacity of precipitation of soap as a characteristic property of water that prevents the lathering of soap.

3. EQUIPMENT AND SUPPLIES

3.1. 10 mL Disposable pipettes

3.2. 2 mL Disposable pipettes, graduated 1/100 mL

3.3. Magnetic stir plate

3.4. 25 mL Titration bottles, 2 per sample

3.5. 6 mm Magnetic stir-bar, 1 per bottle

3.6. Scissors

4. REAGENTS AND STANDARDS

4.1. Alkalinity

4.1.1. Bromo-Cresol Green-Methyl-Red Indicator powder pillows

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4.1.2. Phenolphthalein Indicator Solution

4.1.3. Standard Sulfuric Acid

4.1.4. Alkalinity standard (100 mg/L), Orion® brand, 1000 mg/L

4.1.4.1. To make 100 mg/L standard using 1000 mg/L standard, dilute the 1000 mg/L standard 9 to 1 with DI water (see Section 7)

4.2. Hardness

4.2.1. ManVer II hardness powder pillows

4.2.2. Hardness I buffer

4.2.3. TitraVer titrating solution

4.2.4. Hardness standard, 100 mg/L as $CaCO_3$

5. METHODS

5.1. A Quality Control check should ideally be performed before daily titrations, once a week at the minimum. Refer to Section 7.2 for method.

5.2. For each sample, add a magnetic stir-bar to 2 clean titration bottles per test.

5.3. Pipette 10 mL of sample into each bottle.

5.4. Place titration bottles on the magnetic stir-plate and set stir-plate on low/medium speed.

5.4.1. Up to four bottles can fit on the stir-plate; however, it is not required that all 4 must be used at one time. It is the analyst's choice.

5.5. Add reagents

5.5.1. **Alkalinity:** Add one drop of Phenolphtalein Indicator Solution to each alkalinity titration bottle. If the sample does not turn pink, proceed to Step 5.6. If the sample turns pink:

5.5.1.1. Use the 2 mL pipet to titrate with standard sulfuric acid until the color disappears.

5.5.1.2. Multiply the volume of standard sulfuric acid used by 100. This gives the Phenophthalein Alkalinity in ppm (mg/L) Calcium Carbonate.

5.5.1.3. Record the volumes (mL) of standard sulfuric acid used in the comment section of the *Alkalinity and Hardness Logbook*. Average the two readings and record in parentheses. This result is added to the alkalinity determined in Steps 5.6.-5.9.

5.5.2. **Hardness:** Add 3 drops of Hardness I to each hardness titration bottle.

5.6. Use the scissors to open appropriate indicator powder pillows. Add the contents of one indicator pillow per corresponding bottle.

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5.6.1. **Alkalinity:** Bromo-Cresol Green-Methyl-Red indicator powder; sample should turn green/blue-green

5.6.2. **Hardness:** ManVer II indicator powder; sample should turn pink/red

5.6.2.1. In samples with low hardness and low ionic strength (e.g. water from blackwater swamps), it may require two powder pillows to develop sufficient color to perform the titration.

5.7. Using a 2 mL pipette, accurately titrate the samples.

5.7.1. **Alkalinity:** Titrate with standard sulfuric acid until the color changes from green/blue-green to pink. Titrate slowly toward the endpoint, as it takes a little time for the reaction and resulting color change to take place.

Tip: If it is difficult to determine the exact color break point, titrate until the color shift is complete. Then, subtract 0.1 mL from the volume of sulfuric acid used.

5.7.2. **Hardness:** Titrate with TitraVer Solution until the color changes from pink/red to blue. Titrate slowly toward the endpoint, as it takes a little time for the reaction and resulting color change to take place. If more than 4 mL of TitraVer is needed to reach the endpoint, the sample can be diluted; or the analyses can be stopped and the result reported as > 400 mg/L hardness.

Tip: Just before the hardness titration endpoint, the solution will turn purple. It usually takes only one to two more drops of titrant to turn the solution blue (i.e., reach the endpoint).

5.8. Record the volume of titrant used in the *Alkalinity and Hardness Logbook.*

5.9. Calculate the final alkalinity and hardness values. Be sure to correct for any dilutions by multiplying the result by the dilution factor.

5.9.1. **Alkalinity:** Multiply the volume of acid used by 100. Average the two results obtained for one sample. Add any phenolphthalein alkalinity determined in Step 5.5. This is the total alkalinity of the water in mg/L as $CaCO_3$.

5.9.2. **Hardness:** Multiply the volume of TitraVer used by 100. Average the two results obtained for one sample. This is the total hardness of the water in mg/L as $CaCO_3$.

5.10. Repeat Steps 5.2.-5.9. for each sample.

5.11. At the sink, use the deionized (DI) water to rinse the titration bottles at least three times. Shake/drain residual water from titration bottles, making sure that no residual DI water is in the bottle that would dilute the sample.

6. DATA ARCHIVAL

6.1. Use a black, waterproof pen for all bench sheets and logbooks. Record total alkalinity and hardness results in the *Alkalinity and Hardness Logbook.*

6.2. Make sure that the lot numbers of the standards are recorded in the logbook.

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6.3. To correct raw data entries, place a single line through the incorrect or illegible entry. Write the corrected entry near the error, date and initial the correction. Do not overwrite entries.

6.3.1. The corrected entry is written as near its appropriate space as possible or else in the comment box on the appropriate bench sheet.

6.3.2. If the correction requires an explanation, write a comment and reference the error. Initial and date the explanation.

6.3.2.1. Use sequential alphabetical annotation to identify errors and corresponding comments (use A for first error and use A for corresponding explanatory comment; use B for second error, etc.).

7. QUALITY CONTROL

7.1. Ideally, a quality control check is performed before daily titrations. If not done daily, then at least once per week that samples are analyzed.

7.1.1. **Alkalinity:** Perform Steps 5.2.-5.9. substituting the 100 mg/L alkalinity standard for the sample. The standard result should be 100 mg/L (after subtraction of the alkalinity of the preparation water – see Note). If the result differs from 100 by more than ±10%, prepare a second standard and test. Review the Hach manual for trouble-shooting instructions. Record in the *Alkalinity and Hardness Logbook*.

NOTE: When the alkalinity standard is prepared, the alkalinity of the deionized water (~10-15 mg/L as $CaCO_3$) used to prepare the 100 mg/L standard is measured and recorded in the *Alkalinity and Hardness Logbook*.

7.1.2. **Hardness:** Perform Steps 5.2.-5.9. substituting the 100 mg/L hardness standard for the sample. The standard result should be 100 mg/L. If the result differs from 100 by more than ±10%, prepare a second standard and test. Review the Hach manual for trouble-shooting instructions. Record in the *Alkalinity and Hardness Logbook*.

7.2. Two alkalinity measurements are made per sample. This procedure covers the 0-250 ppm alkalinity range. If the results are >250 ppm, dilute the sample with deionized water and perform the procedure again. Multiply the result by the dilution factor.

7.3. Two hardness measurements are made per sample (see 1.2 for exclusions). When the hardness titration exceeds 4 ml of (400 mg/L as CaCO3) stop the titration and report the values as > 400 mg/L as CaCO3.

7.4. Titration bottles are thoroughly rinsed and dried before use.

7.5. A new, sterile pipette is used for each sample. Proper pipetting techniques are used to ensure the accuracy of the volumes being measured.

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8. SAFETY/HAZARDOUS WASTE MANAGEMENT

8.1. Proper laboratory protection, including lab hood or ventilation system, lab coat, gloves and safety glasses, is required when working with chemicals and unprocessed samples.

8.2. Refer to Laboratory Quality Manual for sample disposal

8.3. Refer to the Laboratory Health and Safety Manual and Hazardous Waste Management

8.4. Read MSDS information for reagent handling and disposal.

9. REFERENCES

9.1. Instruction Manual for HACH alkalinity and hardness kit

9.2. Laboratory Quality Manual http://www.dep.state.fl.us/labs/library/lab_sops.htm

9.3. Laboratory Health and Safety Manual https://www.fldepnet.org/content/dear/bureau-laboratories-safety-documents

9.4. MSDS safety sheets

APPENDIX OF CHANGES

07/29/2013 Combined and reformatted SOPs TA-06.08-3.16 and TA-06.09-4.16.

07/01/2014 Added comments for hardness in 7.4.

01/30/2015 Formatted for 508 compliance.

07/09/2015 Update links.

07/09/2016 Update links

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