WATER QUALITY PROGRAMS DIVISION

Standard Operating Procedure for the Measurement of Hardness and Alkalinity in Surface Waters and Groundwater

Revised and Adopted May 2022

Final Copy

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Standard Operating Procedure for the Measurement of Hardness and Alkalinity

Revision Date	Version	Description of Changes	Effective Date
06/2017	1.0		06/2017
02/08/2022	1.1	• Addition of reference tables • Changed wording to clear up confusing language • Updated formatting	02/2022
03/17/2022	1.2	• Addition of methods for measuring hardness and alkalinity using the HACH SL1000 PPA	03/2022
05/05/2022	1.3	• Updated formatting	05/05/2022

STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF HARDNESS AND ALKALINITY IN SURFACE WATERS AND GROUNDWATER

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1.0 General Information

Hardness and Alkalinity data are collected to assist in understanding the mineral content/conductivity of the waterbody. Furthermore, hardness is used in the establishment of hardness-dependent toxicant criteria. Following is a detailed description of sample processing using Hach Field Analysis Kits. Any EPA approved kit may be purchased and used.

2.0 Definitions/Terms

3.0 Safety

Upon reaching the sampling location, site safety determinations should be made by the crew leader before proceeding. Please refer to the OWRB safety manual for information on boat safety, trailering, and working from boats (OWRB, 2017).

4.0 Quality of the Measurement

When sampling for all programs, Quality Assurance/Quality Control (QA/QC) samples will be routinely collected to assure that environmental samples meet the Data Quality Objectives (DQO's) that are outlined in the controlling Quality Assurance Project Plan (QAPP). QA/QC sampling is designed to control each step of the sampling process. Blanks are collected to ensure that field personnel are properly cleaning the plastics and glassware used in field sampling. Duplicate samples are collected to ensure that composite samples are properly processed. Replicate samples may be collected to ensure that the sampling methodology employed is collecting a representative sample. Spike or known samples may be submitted to test the efficacy of the analytical laboratory. The QA/QC protocols and definitions of QA sample type for hardness and alkalinity of surface waters can be found in the documents "Standard Operating Procedure for the Collection of Water Quality Samples in Lakes" and "Standard Operating Procedure for the Collection of Water Quality Samples in Streams."

5.0 Personnel and Equipment

5.1 Personnel

Principal investigators for the Oklahoma Water Resources Board (OWRB) are required to have degrees and/or experience with biological or other applicable sciences. Principal investigators are defined as crew leaders, and this designation may be made upon the leader of a multi- or a one-person crew. Training is required for all standard operating procedures (SOPs) dealing with water quality and quantity collections and measurements as well as habitat assessments and biological collections. In-house training will be conducted for the use of all

meters and digital titrators used for water quality or quantity measurements. Investigators must be familiar with OWRB SOP documents and all training will follow the methods outlined in that document. Extra training will be provided when new SOPs are developed. Training of field crews will be done through dry run exercises in the laboratory to familiarize field crews with sample collection, sample preservation, instrument operation, calibration, and maintenance. In addition, when new personnel are hired or new methods developed, qualified staff will train on sample collection, measurement, and field analysis methods through side-by-side field trips. These trips will familiarize staff with SOP requirements. When training is considered adequate, a qualified staff member will audit field staff for adherence to SOPs.

5.2 Equipment

Equipment used to collect the hardness and alkalinity samples from surface waters is described in the documents "Standard Operating Procedure for the Collection of Water Quality Samples in Lakes" and "Standard Operating Procedure for the Collection of Water Quality Samples in Streams." For natural waters with 3-750 mg/L as $CaCO_3$ hardness and 20 to 700 mg/L $CaCO_3$ alkalinity, the Hach© SL1000 Portable Parallel Analyzer (PPA) can be alternatively used to determine Total Hardness and Total Alkalinity (Hach Company, 2019, 2016).

6.0 Hach Hardness and Alkalinity Kits

6.1 Maintenance

When not in use, the kits should be kept in their blue field case. The glassware, titrators, and chemicals should be kept dry and clean both inside and out. The glassware should be kept free of inner abrasions. After each measurement, all glassware and titrator tubes should be rinsed at least twice with deionized water. Instruments should never be stored in temperatures below freezing or in extremely hot temperatures.

6.2 Calibration of Titrators

Titrators do not require specific calibration and should maintain calibration throughout their life. However, a known sample should be run periodically to ensure that titrators have maintained calibration.

7.0 Hach SL1000 PPA (Portable Parallel Analyzer)

7.1 Maintenance

Unless charging or in use, all components of the SL1000 PPA (including handheld instrument, Chemkeys, charging cables (2) and sample cup) should be stored in the designated areas of their blue field case. The sample cup should be rinsed at least twice with deionized water in between uses. Instruments should never be stored in temperatures below freezing or in extremely hot temperatures, nor in high humidity conditions. Expired Chemkeys need to be periodically replaced with non-expired ones and the SL1000 needs to be periodically charged. Four sets of non-expired Chemkeys should always be available for use: Low Range Hardness, Low Range Alkalinity, High Range Hardness, and High Range Alkalinity. Other basic maintenance (such as replacing the battery, hand strap installation, etc.) is available in "Basic User Manual: SL1000 DOC022.97.80457" (Hach Company, 2017).

7.2 Instrument Calibration

Each of the four Chemkeys have specific known solutions which should be used to test their accuracy periodically. Along with the general measurement procedure, methods for preparing these known solutions are described by Hach in: "Alkalinity, Total, HR, Colorimetric Method 10283, Chemkey Reagents DOC316.53.01513" for High Range Alkalinity, "Alkalinity, Total, LR, Colorimetric Method 10280, Chemkeys Reagents DOC316.53.01510" for Low Range Alkalinity, "Hardness, Total, HR, Colorimetric Method 10285, Chemkey Reagents DOC316.53.01522" for High Range Hardness, and "Hardness, Total, LR, Colorimetric Method 10284, Chemkey Reagents DOC316.53.01514" for Low Range Hardness (Hach Company, 2019,

2016). Once the known solutions are prepared, follow the procedure in section 5.4 to obtain readings for each solution. If the readings fall outside of the 95% confidence intervals shown in the reference materials above, the instrument should not be used for field measurements and Hach technical support should be contacted to calibrate the instrument (Hach, 2017).

Additionally, the System Verification Chemkey can be used to verify instrument performance; simply insert the Chemkey as described in section 5.4 step 4 and follow the on-screen prompts (Hach, 2017). Again, Hach technical support should be contacted if this process does not run successfully, and the instrument should not be used in the field. Before each project sampling period, all four Chemkeys should be verified with their known solutions and the system verification Chemkey should be used.

8.0 Alkalinity Sample Collection and Analysis

Alkalinity of surface waters is collected using methods described in the documents "Standard Operating Procedure for the Collection of Water Quality Samples in Lakes" and "Standard Operating Procedure for the Measurement of Hardness and Alkalinity in Streams." **Alkalinity should be measured in the field, upon return from the field, or within 24 hours of collection.** Samples should be brought to ambient temperature before analysis. Take caution to minimize aeration of the sample before testing. Both "phenolphthalein alkalinity" and "total alkalinity" will be measured and recorded.

To perform the test, follow these steps:

1) Select the sample volume and **sulfuric acid titration cartridge** corresponding to the expected alkalinity concentration (reference Table 1 below). The expected concentration can be ascertained from trip field sheet.
2) Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See page 13 of Hach© "Digital Titrator Manual" for assembly instructions, if necessary (Hach, 2013).
3) Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and rinse the tip with deionized water.
4) Ensure all glassware has been rinsed with deionized water and primed with native water before analysis begins.
5) Use a graduated cylinder to measure the sample volume from Table 1. Dilute with deionized water to the 100-ml mark if necessary. Transfer the sample to a clean 250-ml Erlenmeyer flask.
6) Add the contents of one **phenolphthalein indicator** powder pillow and swirl to mix. "Thump" the powder pillow before opening to ensure that all the powder is at the bottom.
7) If the solution turns pink, staff will need to titrate to a colorless end point. Place the delivery tube tip into the solution and swirl the flask while titrating with **sulfuric acid**. Record the number or digits required to reach end point. If the solution stays clear, continue to step 8.
8) Calculate: Digits required X digit multiplier = mg/L $CaCO_3$ P- Alkalinity.
9) Add the contents of one **bromocresol green-methyl red indicator** powder pillow to the flask and mix. "Thump" the powder pillow before opening to ensure that all the powder is at the bottom.
10) Continue the titration with **sulfuric acid** to a light greenish blue-gray (pH 5.1), a light violet-gray (pH 4.8), or a light pink (pH 4.5) color, as required by the sample composition (reference Table 2 below). Record the number of digits required.
11) Calculate: total digits required X digit multiplier = mg/L as $CaCO_3$ Total Alkalinity
12) Report both alkalinity values on the field notes for the station.

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (H_2SO_4)	Catalog Number	Digit Multiplier
10-40	100	0.1600	14388-01	0.1
40-160	25	0.1600	14388-01	0.4
100-400	100	1.600	14389-01	1.0
200-800	50	1.600	14389-01	2.0
500-2000	20	1.600	14389-01	5.0
1000-4000	10	1.600	14389-01	10.0

Table 2

Sample Composition	End Point
Alkalinity about 30 mg/L	pH 4.9
Alkalinity about 150 mg/L	pH 4.6
Alkalinity about 500 mg/L	pH 4.3
Silicates or Phosphates present	pH 4.5
Industrial waste or complex system	pH 4.5

9.0 Hardness Sample Collection and Analysis

Hardness of surface waters is collected using methods described in the documents "Standard Operating Procedure for the Collection of Water Quality Samples in Lakes" and "Standard Operating Procedure for the Collection of Water Quality Samples in Streams." **Hardness should be measured in the field, upon return from the field, or within 24 hours of collection.** Samples should be brought to ambient temperature before analysis. Take caution to minimize aeration of the sample before testing. "Total hardness" will be measured and recorded.

To perform the test, follow these steps:

1) Select the sample volume and **EDTA titration cartridge** corresponding to the expected hardness concentration (reference Table 3 below). The expected concentration can be ascertained from trip notebook.
2) Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See page 13 of Hach© "Digital Titrator Manual" for assembly instructions, if necessary (Hach, 2013).
3) Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and rinse the tip with deionized water.
4) Use a graduated cylinder to measure the sample volume from Table 3. Dilute with deionized water to the 100-ml mark if necessary. Transfer the sample to a clean 250-ml Erlenmeyer flask. Make sure that all glassware has been rinsed with deionized water and primed with native water before analysis begins.
5) Add 2 ml's of **Hardness 1 Buffer Solution** and swirl to mix well.
6) Add the contents of one **ManVer 2 Hardness Indicator** powder pillow to the flask and mix. "Thump" the powder pillow before opening to ensure that all the powder is at the bottom.
7) Titrate with appropriate **EDTA titrant** from red to a pure blue color. Record the number of digits required.
8) Calculate: total digits required X digit multiplier = mg/L Total Hardness as $CaCO_3$.
9) Report total hardness on the field data collection sheet.

Table 3

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit multiplier
10-40	100	0.0800	14364-01	0.1
40-160	25	0.0800	14364-01	0.4
100-400	100	0.800	14399-01	1.0
200-800	50	0.800	14399-01	2.0
500-2000	20	0.800	14399-01	5.0
1000-4000	10	0.800	14399-01	10.0

10.0 Hardness and Alkalinity Sample Collection using the Hach© SL1000 PPA

The general procedure for obtaining a measurement from the SL1000 PPA is outlined in the documents listed in section 5.2. **Hardness and Alkalinity should be measured in the field, upon return from the field, or within 24 hours of collection FROM A FILTERED SAMPLE.** Samples should be brought to ambient temperature before analysis. Other than the necessary disturbance required to fill the sample cup and move it to a suitable location, the sample should stay relatively undisturbed to reduce aeration. "Total hardness" and "Total Alkalinity" will be measured and recorded.

To perform the tests, follow these steps:

1) Turn on the SL1000
2) If the range of alkalinity and hardness are known from previous site visits, select one alkalinity Chemkey and one hardness Chemkey in the appropriate range from the proper boxes. If the range of hardness and alkalinity for the site are unknown, select both low and high range Chemkeys for both alkalinity and hardness (4 total keys)
3) Without touching it, peel the wrapper partially away from each Chemkey such that the end with three prongs is exposed and the other end is still protected by the wrapper
4) Slowly insert the Chemkey into an open slot in the SL1000 in a single fluid motion, removing the wrapper once it is fully inserted. The instrument should chime and show the name of the inserted Chemkey when it is properly installed.
5) Repeat steps 3 and 4 with the other selected Chemkeys (either 1 or 3)
6) Rinse the sample cup at least 3 times with FILTERED sample water
7) Fill the sample cup up to the fill line with FILTERED sample water and place it in the designated location in the blue case
8) Gently lower the SL1000 all the way into the sample cup, Chemkeys facing down
9) Wait for the instrument to beep and/or for the meter removal animation to appear
10) Once the instrument beeps, immediately remove it from the sample cup and place it on a flat surface in an area protected from dust and wind
11) When all measurements are shown as complete on the SL1000 display, they can be recorded on the electronic field form. If two Chemkeys were used, the displayed measurements should be recorded as "Total Alkalinity" and "Total Hardness" in mg/L $CaCO_3$. If all four Chemkeys were used, determine which ranges (either high or low) the measurements fall in and record the measurements from the Chemkeys with the proper ranges as "Total Alkalinity" and "Total Hardness" in mg/L $CaCO_3$
12) Rinse the sample cup with deionized water at least twice; dispose of the used Chemkeys

11.0 Forms

Hardness and alkalinity data are maintained on the electronic field form. They are considered field data and should be treated with diligence and care. If a paper field sheet is necessary, they should be written, legible, and complete. For guidance on proper procedure to complete the field sheets, refer to your supervisor and/or FTE.

12.0 Data Storage

When weather permits, the electronic lakes field sheet should be completed on a laptop or tablet and saved in the format "Trip ID Site Name Season Year." If the paper copy is used it should be transcribed into an electronic field data sheet as soon as possible and stored in the appropriate binder and on the Water Quality network drive. These data associated notes and comments will be uploaded to the AQWMS Water Quality Database for permanent cloud storage.

13.0 References

Hach Company. Alkalinity, Total, HR, Colorimetric Method 10283, Chemkey Reagents DOC316.53.01513, 4 Ed. Loveland, CO., 2016. https://www.hach.com/sl1000-ppa-portable-parallel-analyzer-portable-colorimeter-with-usb/product-downloads?id=22361943508

Hach Company. Hardness, Total, HR, Colorimetric Method 10285, Chemkey Reagents DOC316.53.01522, 3 Ed. Loveland, CO., 2019. https://www.hach.com/sl1000-ppa-portable-parallel-analyzer-portable-colorimeter-with-usb/product-downloads?id=22361943508

Hach Company. Alkalinity, Total, LR, Colorimetric Method 10280, Chemkeys Reagents DOC316.53.01510, 4 Ed. Loveland, CO., 2016. https://www.hach.com/sl1000-ppa-portable-parallel-analyzer-portable-colorimeter-with-usb/product-downloads?id=22361943508

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Hach Company. Basic User Manual: SL1000 DOC022.97.80457, 5 Ed. Loveland, CO., 2017 https://www.hach.com/sl1000-ppa-portable-parallel-analyzer-portable-colorimeter-with-usb/product-downloads?id=22361943508

Hach Company. Digital Titrator Model 16900-08 Manual. Loveland, CO., 2013 https://www.hach.com/asset-get.download-en.jsa?id=7639982643

OWRB. (January 2013). Standard Operating Procedure for the Collection of Water Quality Samples in Streams. Oklahoma City: OWRB.

OWRB. (July 2018). Standard Operating Procedure for the Collection of Water Quality Samples in Lakes. Oklahoma City: OWRB.