
WATER QUALITY PROGRAMS DIVISION

Standard Operating Procedure for the Measurement of
Hardness and Alkalinity in Streams

Revised and Adopted November 2005

Draft Copy



**OKLAHOMA WATER RESOURCES BOARD
WATER QUALITY PROGRAMS DIVISION
3800 NORTH CLASSEN
OKLAHOMA CITY, OK. 73118**

STANDARD OPERATING PROCEDURE FOR THE MEASUREMENT OF HARDNESS AND ALKALINITY IN STREAMS

REVISED AND ADOPTED NOVEMBER 2005

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 kit may be purchased and used.

2.0 Definitions/Terms

3.0 Safety

Upon reaching the sampling location, site safety determinations should be made before proceeding. These will be different for wadable and bridge sites. Please refer to the OWRB safety manual for instructions on how to sample both kinds of sites. When regulating the flow of traffic is necessary, please refer to the portion of the safety manual outlining "Traffic Safety Protocols".

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 for hardness and alkalinity can be found in the document "Standard Operating Procedure for the Collection of Water Quality Samples".

5.0 Personnel and Equipment

Principle investigators for the OWRB are required to have degrees and/or experience with biological or other applicable sciences. Principle 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 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 document 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 check field staff for adherence to SOPs.

In most instances, the collection of water quality samples requires only one field person. However, depending on the safety requirements of a particular station, additional crew members may be necessary to ensure a safe work zone. Equipment used to collect the hardness and alkalinity samples are described in the document “Standard Operating Procedure for the Collection of Water Quality Samples”.

5.1 Hach© Hardness and Alkalinity Kits.

5.11 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 twice with deionized water. Instruments should never be stored in temperatures below freezing in extremely hot temperatures.

5.12 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.

6.0 Measurement

6.1 Alkalinity Sample Collection and Analysis.

Alkalinity is collected using methods described in the document “Standard Operating Procedure for the Collection of Water Quality Samples”. Alkalinity should be measured at the site. On occasion, this may not be possible, so it must be read within 24 hours of collection. If analysis will be done later, water is collected using a clean plastic bottle. Prime the bottle with native water from the churn splitter and, while churning, completely fill bottle ensuring that the bottle is not aerated. Place on ice until analysis is made. Samples should be brought to ambient temperature before analysis. Do not aerate 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 responding to the expected alkalinity concentration (this chart is in the Hach© “Digital Titrator Manual” on page 33). 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.
- 3) Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
- 4) Use a graduated cylinder to measure the sample volume from table 1 on page 33 in the manual. 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 the contents of one phenolphthalein indicator powder pillow and swirl to mix. "Thump" the powder pillow before opening to ensure that all of the powder is at the bottom.
- 6) If the solution turns pink, 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.
- 7) Calculate: $\text{Digits required} \times \text{digit multiplier} = \text{mg/L CaCO}_3 \text{ P- Alkalinity}$.
- 8) 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 of the powder is at the bottom.
- 9) Continue the titration with sulfuric acid to a light pink (pH 4.5) color. Record the number of digits required.
- 10) Calculate: $\text{total digits required} \times \text{digit multiplier} = \text{mg/L as CaCO}_3 \text{ Total Alkalinity}$
- 11) Report both alkalinity values on the field notes for the station.

6.2 Hardness Sample Collection and Analysis.

Alkalinity is collected using methods described in the document "Standard Operating Procedure for the Collection of Water Quality Samples". Hardness should be measured at the site; however, on occasion this may not be possible, so it must be read within 48 hours of collection. If analysis will be done later, water is collected using a clean plastic bottle. Prime the bottle with native water from the churn splitter and, while churning, completely fill bottle ensuring that the bottle is not aerated. Place on ice until analysis is made. Samples should be brought to ambient temperature before analysis. Do not aerate 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 responding to the expected hardness concentration (this chart is in the Hach© "Digital Titrator Manual" on page 108). 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.
- 3) Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
- 4) Use a graduated cylinder to measure the sample volume from table 1 on page 108 in the manual. 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 Man Ver 2 Hardness Indicator powder pillow to the flask and mix. "Thump" the powder pillow before opening to ensure that all of 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 as CaCO₃ Total Hardness.
- 9) Report total hardness on the field data collection sheet. One duplicate, blank and known sample should be collected for each sampling trip.

7.0 Forms

Hardness and alkalinity data are maintained on the station field form. They are data and should be treated as such. Therefore, they should be written, legible, and complete. To avoid confusion and loss of data, a new sheet should be used at each new project site. Field notes should be initialed and dated by the collecting personnel and data entry personnel. For guidance on proper procedure to complete the field notes, refer to your supervisor and or FTE. Field notes can be found at S:\Monitoring\STREAMS\forms\Field Notes.doc.

8.0 Data Storage

All completed paper copies of forms and data sheets should be maintained with the appropriate station notebook. The data from the field notes and laboratory data sheets should be either entered into or uploaded to the Water Quality Database. Each sample should be maintained electronically in the database under a unique sample number.

9.0 References

Hach Company. Digital Titrator Model 16900-01 Manual. Loveland, CO., 1988.