Water-Quality Principles
QW1022–TEL

Lesson 5, Part 1—Field-Measured Properties and Major Ions: Field Measurements

Source: National Field Manual for the Collection of Water-Quality Data, book 9, *of* USGS Techniques of Water-Resources Investigations (http://water.usgs.gov/owq/FieldManual/)

Chapter A6, FIeld Measurements, Abstract
Chapter A6.1, Temperature (version 2, March 2006), p. T–1 and T–3
Chapter A6.2, Dissolved Oxygen (version 2.1, June 2006), p. DO–1 through DO–3
Chapter A6.3, Specific Electrical Conductance, p. SC–1 and SC–3
Chapter A6.4, pH (version 2, October 2008), p. pH–1, pH–3, and pH–4
Chapter A6.6, Alkalinity and Acid Neutralizing Capacity (version 3, July 2006), p. ALK–1, ALK–3, and ALK–4

U.S. Department of the Interior
U.S. Geological Survey

USGS collects data at the Birds Point-New Madrid Floodway

Search the USGS Water sites:
Google™ Custom Search | Search

Noteworthy

National & Regional Science:

- Press Release: New Science to Help Direct Action on Excessive Nutrients in Rivers and Estuaries
  - Regional SPARROW Model Assessments
  - Interactive Decision Support System
- Water-Quality Sampling after Hurricane Irene
- Press Release: Widely Used Herbicide Commonly Found in Rain and Streams in Mississippi River Basin
- Press Release: Arsenic, Uranium and Other Trace Elements, a Potential Concern in Private Drinking Wells | Report
- Podcast about Emerging Contaminants

Local Science Features:

- Nevada: Endocrine Disruption in Lake Mead
- Arkansas: Determining Potential Effects of Fayetteville Shale Gas Extraction on Water Resources

Past listings...

National Field Manual for the Collection of Water-Quality Data (TWRI Book 9)

Chapter A6. Field Measurements

- Comments/Errata page
- This report is in pdf format. Download a copy of Adobe Reader for free.

Abstract

The *National Field Manual for the Collection of Water-Quality Data* provides protocols, standard procedures, and guidance for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. Chapter A6 presents general information and guidelines for performing field measurements (section 6.0) and specific requirements and guidance for collecting data for water temperature (section 6.1), dissolved oxygen concentrations (section 6.2), specific electrical conductance (section 6.3), pH (section 6.4), reduction-oxidation potential (section 6.5), alkalinity (section 6.6), turbidity (section 6.7), and for the use of multiparameter instruments in making such measurements (section 6.8). Each of these sections is revised periodically and published separately on this Web site.

TEMPERATURE 6.1

Revised by Franceska D. Wilde

Page

Temperature T–3

6.1.1 Equipment and supplies 4

Maintenance, cleaning, and storage 5

6.1.2 Calibration 7

6.1.2.A Calibration thermometers 8

6.1.2.B Field thermometers 9

6.1.3 Measurement 14

6.1.3.A Air 14

6.1.3.B Surface water 15

6.1.3.C Gound water 17

6.1.4 Troubleshooting 18

6.1.5 Reporting 19

Selected references 20

Acknowledgments 22

Tables

6.1–1. Equipment and supplies used for measuring temperature 4

6.1–2. Troubleshooting guide for temperature measurement 18

TEMPERATURE 6.1

Measurements of air and water temperature at a field site are essential for water-quality data collection. Determination of dissolved-oxygen concentrations, conductivity, pH, rate and equilibria of chemical reactions, biological activity, and fluid properties relies on accurate temperature measurements.

Accurate air- and water-temperature data are essential to document thermal alterations to the environment caused by natural phenomena and by human activities. Water temperature can be subject to environmental regulation and monitoring by State and local agencies.

TEMPERATURE: a measure of warmth or coldness of a substance with reference to a standard value.

This section describes methods for measuring temperature in air, surface water, and ground water. The methods are appropriate for fresh to saline waters.

- A thermometer is any device used to measure temperature, consisting of a temperature sensor and some type of calibrated scale or readout device. Liquid-in-glass thermometers and thermistor thermometers are commonly used to measure air and water temperature.[1]
- The U.S. Geological Survey (USGS) uses the Centigrade or Celsius (C) scale for measuring temperature.

[1]Some of the equipment and procedures recommended herein may not reflect the most recent technological advances; in this case, follow the manufacturer's instructions but comply with standard USGS quality-control practices.

DISSOLVED OXYGEN 6.2

Revised by Michael E. Lewis

Page

Dissolved oxygen DO–3

6.2.1 Amperometric and luminescent-sensor methods 5

6.2.1.A Equipment and supplies 6

6.2.1.B Calibration 10

One-point and two-point calibrations 10

Correction for atmospheric pressure and salinity..... 11

Calibration procedures..... 13

1. Air-calibration chamber in air 13

2. Calibration with air-saturated water..... 15

3. Air-calibration chamber in water 17

6.2.1.C Measurement.....19

Surface Water 19

Ground Water.....22

6.2.1.D Troubleshooting (amperometric instruments).....24

6.2.2 Spectrophotometric method.....25

6.2.2.A Equipment and supplies 25

6.2.2.B Calibration and interferences 26

6.2.2.C Measurement 27

6.2.3 Iodometric (Winkler) method 29

6.2.3.A Equipment and supplies..... 30

6.2.3.B Measurement 31

6.2.4 Reporting 33

6.2.5 Correction factors for oxygen solubility and salinity 33

Selected references.....46

Acknowledgments 48

Illustrations

6.2–1. Graph showing factors used to correct atmospheric pressures adjusted to sea level 12

Tables

6.2–1 Equipment and supplies for the amperometric and luminescent-sensor methods of dissolved-oxygen determenation 7

6.2–2 Factors used to correct atmospheric pressures adjusted to sea level.....12

6.2–3 Troubleshooting guide for amperometric instruments 24

6.2–4 Equipment and supplies for the spectrophotometric method of dissolved-oxygen determination.....26

6.2–5 Equipment and supplies for the iodometric (Winkler) method of dissolved-oxygen determination.....30

6.2–6 Solubility of oxygen in water at various temperatures and pressures.....35

6.2–7 Salinity correction factors for dissolved oxygen in water (based on conductivity) 41

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

DISSOLVED OXYGEN 6.2

The concentration of dissolved oxygen in water is affected by many factors including ambient temperature, atmospheric pressure, and ion activity. Accurate data on the concentration of dissolved oxygen (DO) in environmental water resources are essential for documenting changes that result from natural phenomena and human activities. Sources of DO in water include atmospheric aeration and photosynthetic activities of aquatic plants. Many chemical and biological reactions in ground water and surface water depend directly or indirectly on the amount of available oxygen. Dissolved oxygen is necessary in aquatic systems for the survival and growth of many aquatic organisms and is used as an indicator of the health of surface-water bodies.

DISSOLVED OXYGEN:
molecular oxygen
(oxygen gas)
dissolved in water.

Standard field methods used by the U.S. Geological Survey (USGS) for determining concentrations of DO in surface and ground waters include the use of amperometric and luminescent-based-sensor instruments and spectrophotometric analysis. Selection of a measurement method should take into consideration environmental conditions, the specific data-quality objectives of the data-collection program, and the inherent benefits of a given technology. Except where noted, these methods are used routinely to determine the concentration of dissolved oxygen in fresh to saline unfiltered surface and ground waters.

SPECIFIC ELECTRICAL CONDUCTANCE 6.3

By D.B. Radtke, J.V. Davis, and F.D. Wilde

Page

Specific electrical conductance SC–3

6.3.1 Equipment and supplies 3

6.3.1.A Conductivity sensors 5

6.3.1.B Equipment maintance 6

6.3.2 Calibration 7

6.3.3 Measurement 11

6.3.3A Surface water 12

In situ measurement 12

Subsample measurement 14

6.3.3.B Ground water 16

Downhole and flowthrough-chamber measurement 16

Subsample measurement 18

6.3.4 Troubleshooting 19

6.3.5 Reporting 21

Selected References 22

SPECIFIC ELECTRICAL CONDUCTANCE 6.3

By **D.B. Radtke, J.V. Davis, and F.D. Wilde**

Electrical conductance is a measure of the capacity of water (or other media) to conduct an electrical current. Electrical conductance of water is a function of the types and quantities of dissolved substances in water, but there is no universal linear relation between total dissolved substances and conductivity.

The USGS reports conductivity in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25°C). The method described in this section for measuring conductivity is applicable to surface water and ground water, from fresh to saline.

SPECIFIC ELECTRICAL CONDUCTANCE (CONDUCTIVITY)—a measure of the electrical conductance of a substance normalized to unit length and unit cross section at a specified temperature.

EQUIPMENT AND SUPPLIES 6.3.1

The instrument system used to measure conductivity must be tested before each field trip and cleaned soon after use. Many conductivity instruments are available, including multiparameter instruments that include conductivity sensors. This section provides detailed information on the use of conductivity-specific instruments only, although instructions regarding conductivity standards and measurement methods are applicable in general. Users must be familiar with the instructions provided by the manufacturer. Every conductivity (or multiparameter) instrument must have a log book in which repairs and calibrations are recorded, along with manufacturer make and model description and serial or property number.

pH 6.4

Revised by George F. Ritz and Jim A. Collins

Page

6.4 pH pH-3
6.4.1 Equipment and supplies 4
6.4.1.A pH meters 6
6.4.1.B pH electrodes 6
6.4.1.C pH buffer solutions 9
6.4.2 Maintenance of pH instruments 10
6.4.2.A Electrode care and cleaning 10
6.4.2.B Reconditioning of liquid-filled electrodes 12
6.4.2.C Electrode storage 13
6.4.3 Calibration of the pH instrument system 14
6.4.3.A Calibration procedure under standard aqueous conditions 16
6.4.3.B Calibration for low ionic-strength water 19
6.4.3.C Calibration for high ionic-strength water 20
6.4.3.D Calibration for the pH sensor in multiparameter instruments 21
6.4.4 Measurement 21
6.4.4.A pH measurement in surface water 22
6.4.4.B pH measurement in ground water 24
6.4.5 Troubleshooting 27
6.4.6 Reporting 28
6.4.7 Selected references 28
6.4.8 Acknowledgments 30

pH 6.4

Revised by **George F. Ritz and Jim A. Collins**

pH is a primary factor governing the chemistry of natural water systems and is measured routinely in U.S. Geological Survey (USGS) studies of water quality. The pH of water directly affects physiological functions of plants and animals and is, therefore, an important indicator of the health of a water system.

pH: A mathematical notation defined as the negative base-ten logarithm of the hydrogen-ion activity, measured in moles per liter of a solution.

The pH of an aqueous system can be understood as an estimation of the activity, or effective concentration,[1] of hydrogen ions (H^+) affecting that system. The theoretical basis of H^+ activity and measurement are described in greater detail in Hem (1989) and in Pankow (1991).

By definition,

$$pH = -log_{10}[H^+], \text{ and}$$

$$[H^+] = 10^{-pH}.$$

- Logarithmic units are used to express H^+ activity because the concentration of H^+ in most environmental waters is usually too low to be expressed as milligrams per liter, micrograms per liter, or moles per liter, in contrast to most other chemical species (Hem, 1989).
- pH is reported on a scale that most commonly is shown to range from 0 to 14 (see TECHNICAL NOTE below). The pH scale is related directly to H^+ and hydroxide (OH^-) concentrations at a given temperature.
  - A solution is defined as having a neutral pH (pH = 7.00 at 25°C) when the H^+ concentration is equal to the OH^- concentration.
  - A solution is defined as acidic if the H^+ activity (concentration) is greater than that of the OH^- ion (pH is less than 7 at 25°C).
  - A solution is defined as basic, or alkaline, when the OH^- concentration is greater than the H^+ concentration (pH is greater than 7 at 25°C).

[1]The majority of natural freshwater systems for which water-quality data are routinely collected by the USGS are considered to be dilute; that is, the volume of dissolved solids is less than 50 milligrams per liter and the ionic strength of the solution (the strength of the electrostatic field caused by the ions) is less than 10^{-4}. For dilute solutions, activity values can be assumed to be equal to measured ion concentrations (Hem, 1989). Therefore, throughout the text of this section, the terms "activity" and "concentration," as they relate to the hydrogen ion, are used interchangeably.

- Temperature affects the chemical equilibria of ionic activities in aqueous solutions, including that of H^+ (Hem, 1989). For example, neutral pH for pure water at 30°C is calculated to be 6.92, whereas at 0°C, neutral pH is 7.48. The pH of pure water at 25°C is defined as 7.00. Therefore, the temperature of the solution must be taken into account when measuring and recording pH.

TECHNICAL NOTE: Although pH commonly is reported on a scale ranging from 0 to 14, pH values of less than 0 can be measured in highly acidic solutions, and pH values greater than 14 can be measured in concentrated base solutions (Nordstrom and Alpers, 1999; Hem, 1989).

6.4.1 EQUIPMENT AND SUPPLIES

The instrument system that is used to measure pH consists of a pH meter, sensor(s) (a pH electrode and often a temperature sensor), and buffer solutions (table 6.4–1). Since a variety of instrument systems are available from manufacturers (multiparameter instruments, for example, are described in NFM 6.8), the procedures described in this section may not be applicable or may need to be modified, depending on the specific instrument system being used. Field personnel should:

- Be thoroughly familiar with the information provided in the manufacturer's user manual.
- Adhere to USGS protocols for quality control and assurance of pH measurements.
- Test the meter and electrode before each field trip.

Temperature affects the operation of pH meters, electrodes, and buffer solutions.

ALKALINITY AND ACID NEUTRALIZING CAPACITY 6.6

Revised by S.A. Rounds

Page

Alkalinity and acid neutralizing capacity ALK–3

6.6.1 Equipment and supplies 5

6.6.1.A Maintenance, cleaning, and storage 8

6.6.2 Calibration and standardization 9

6.6.3 Collection and processing 11

Surface water 12

Ground water 12

6.6.4 Measurement 13

6.6.4.A Titration systems and procedures 14

Digital titrator 20

Buret titrator 23

6.6.4.B Inflection point titration method 26

6.6.4.C Gran function plot method 34

6.6.5 Calculations 44

6.6.5.A Alkalinity or ANC 44

6.6.5.B Carbonate-speciation equations for samples with pH ≤ 9.2 45

6.6.5.C Computer-program analysis of titration data 47

6.6.6 Troubleshooting 48

6.6.7 Reporting 48

Selected references 51

Acknowledgments 53

ALKALINITY AND ACID NEUTRALIZING CAPACITY 6.6

Alkalinity and acid neutralizing capacity (ANC) are measures of the ability of a sample to neutralize strong acid. They are determined using identical electrometric procedures involving the acidimetric titration of a sample; the only difference is that the alkalinity sample is filtered, whereas the ANC sample is not filtered (raw, or unfiltered). The terms alkalinity, ANC, and carbonate alkalinity are used in this manual as follows:

- **Alkalinity** is the acid neutralizing capacity of solutes in a water sample, reported in milliequivalents or microequivalents per liter. Alkalinity consists of the sum of titratable carbonate and noncarbonate chemical species in a **filtered water sample** (filter membrane of 0.45-micrometer (µm) pore size or smaller). [1]

ALKALINITY: the capacity of solutes in an aqueous system to neutralize acid.

ANC: the capacity of solutes plus particulates in an aqueous system to neutralize acid.

- **ANC** is the acid-neutralizing capacity of solutes plus particulates in an **unfiltered water sample**, reported in milliequivalents or microequivalents per liter. ANC is equivalent to alkalinity for samples without titratable particulate matter.
- **Carbonate alkalinity** is the acid-neutralizing capacity attributable to carbonate solutes (bicarbonate and carbonate), reported either in milliequivalents or microequivalents per liter, or in milligrams per liter as a carbonate species, and titrated on a **filtered water sample**. In many aqueous systems, alkalinity is controlled by carbonate chemistry and most commonly is attributable to bicarbonate (HCO_3^-) and less frequently to carbonate (CO_3^{2-}).

[1] Currently, a filtered sample is operationally defined as having passed through a 0.45-µm pore filter membrane without clogging the filter.

Alkalinity is used routinely to check the charge balance of a solution and to gain insights regarding the evolution of aqueous systems. Alkalinity and ANC provide information on the suitability of water for uses such as irrigation, for determining the efficiency of wastewater processes and the presence of contamination by anthropogenic wastes, and for maintaining ecosystem health.

Any substance in the water sample that reacts with strong acid titrant can contribute to the acid neutralizing capacity of the water body being sampled.

- Important noncarbonate contributors may include organic ligands (especially acetate and propionate) as well as hydroxide, silicate, borate, and less commonly ammonia and sulfide (Hem, 1985). When found in unusually high concentrations, phosphate and arsenate also may contribute to the acid neutralizing capacity of the sample (Stumm and Morgan, 1981).
- Except for unusual natural waters and waters substantially affected by human activity, noncarbonate ionized contributors generally are not present in large enough quantities to affect alkalinity or ANC determinations.
- Particulate matter can be an important contributor, and must be removed by filtration before titrating the sample for the alkalinity determination.

Alkalinity is determined on a filtered sample. ANC is determined on an unfiltered sample.

TECHNICAL NOTE: Alkalinity and ANC are measured relative to a solution of carbon dioxide in water; therefore, they are independent of any exchange of carbon dioxide or other common gases between the sample and the atmosphere. However, atmospheric gas exchange can alter the concentrations of individual species, such as bicarbonate. Also, aeration of a sample during filtration can cause mineral precipitation on the filter—this may alter the alkalinity, especially in water systems closed to the atmosphere under ambient conditions.