

Book 9

Handbooks for Water-Resources Investigations

**National Field Manual  
for the Collection of  
Water-Quality Data**

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**Chapter A6.  
FIELD MEASUREMENTS**

*Edited by*  
**F.D. Wilde and D.B. Radtke**

**U.S. DEPARTMENT OF THE INTERIOR**  
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**U.S. GEOLOGICAL SURVEY**  
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United States Department of the Interior

U.S. Geological Survey

Reston, Virginia 20192

Mail Stop 412

October 1998

Subject: Publication of Chapter A6 of the *National Field Manual for the Collection of Water-Quality Data: Field Measurements*

Dear Environmental Resources Colleague:

Previously, you (or a colleague in your position) received Chapter A7 of the *National Field Manual for the Collection of Water-Quality Data* entitled *Biological Indicators*, and a binder into which Chapter A7 and future chapters of the manual can be inserted. Your name is on our list to receive a copy—or the number of copies requested—of each chapter as it is released. With this letter, please find the following recently published chapter:

Chapter A6. *National Field Manual for the Collection of Water-Quality Data: Field Measurements*, edited by F.D. Wilde and D.B. Radtke.

The *National Field Manual for the Collection of Water-Quality Data* articulates policy, protocols, and recommended procedures for collection of water-quality data by U.S. Geological Survey (USGS) personnel. USGS water-quality specialists are asked to distribute the copies they receive to the appropriate personnel within their purview. The protocols and procedures described in the manual are intended to complement formal training given at the USGS National Training Center.

Please direct any questions, comments, or requests regarding these or other chapters of this manual to the Office of Water Quality:

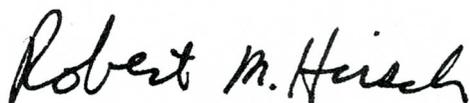
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## FOREWORD

The mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a national field manual is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.



Robert M. Hirsch  
Chief Hydrologist

# Techniques of Water-Resources Investigations

## Book 9

### Handbooks for Water-Resources Investigations

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# National Field Manual for the Collection of Water-Quality Data



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# CHAPTER A6. FIELD MEASUREMENTS

*Edited by F.D. Wilde and D.B. Radtke*

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## ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data* (*National Field Manual*) provides guidelines and standard procedures 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 procedures and guidelines for the collection of data on air and water temperature, and on dissolved-oxygen concentrations, specific electrical conductance, pH, reduction-oxidation potential, alkalinity, and turbidity in water.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Public Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <<http://water.usgs.gov/lookup/get?newpubs>>.

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## INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. A high degree of reliability and standardization of these data are paramount to fulfilling this mission. Documentation of nationally accepted methods used by USGS personnel serves to maintain consistency and technical quality in data-collection activities. The USGS publishes Techniques of Water-Resources Investigations (TWRI) reports that document scientific methods used by USGS personnel. TWRI publications are listed at the end of this report.

TWRIs are grouped under major subject headings called books. The Book 9 series, Handbooks for Water-Resources Investigations, is designed for field use and was developed to summarize, from

other TWRIs and other references, techniques for planning and conducting specialized work in water-resources investigations. The *National Field Manual for the Collection of Water-Quality Data* (*National Field Manual*) is Section A of Book 9. The *National Field Manual* is comprised of individually published chapters. Chapter numbers are preceded by an “A” to indicate that the report is part of the *National Field Manual*.

Chapter A6 on field measurements includes procedures, techniques, and guidelines for planning and conducting specialized work in water-resources investigations. Sections and other chapters in the *National Field Manual* are referred to in this report by the abbreviation “NFM” and the chapter and (or) section number. For example, general information on temperature measurements is covered in section 6.1 of Chapter A6 “Field Measurements” and is cited here as NFM 6.1.

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## PURPOSE AND SCOPE

The *National Field Manual* provides guidelines and standard procedures to be used by USGS personnel for field activities related to water-quality data collection and analysis. This manual is targeted specifically toward data collectors in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (3) provide methods that minimize biasing the data and, when properly applied, that result in data that are reproducible within defined limits of variability.

**Data collectors must have formal training and field apprenticeship in order to correctly implement the procedures described in this report.** The information provided in Chapter A6 is to be used in conjunction with *Water Temperature—Influential Factors, Field Measurement, and Data Presentation* by H.H. Stevens, Jr., J.F. Ficke, and G.F. Smoot (Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 1, Chapter D1, 1975), and *Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents* by W.W. Wood (Techniques of Water-Resources Investigations, Book 1, Chapter D2, 1981).

It is impractical to provide guidance that would encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. The fundamental responsibility of field personnel is to select methods that are compatible with the scientific objective for the field work and to use procedures that are consistent with USGS standard procedures to the extent possible. Under some circumstances, data collectors may have to modify standard procedures. Whenever a standard procedure is modified or an alternative procedure is used, a description of the procedure used and supporting quality-assurance information are to be reported with the data.

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## FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Please send comments or corrections to: NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or send electronic mail to: [nfm-owq@usgs.gov](mailto:nfm-owq@usgs.gov)). Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>.

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## ACKNOWLEDGMENTS

The information included in the *National Field Manual* is based on existing manuals, a variety of reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials included unpublished USGS training and field manuals and technical memorandums. The authors wish to acknowledge those individuals in the USGS who developed the field and training manuals that provided the foundation for this *National Field Manual*: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Iwatsubo, R.T. Kirkland, J.R. Knaption, C.E. Lamb, L.R. Lister, R.F. Middelburg, Jr., J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

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# 6.0 GENERAL INFORMATION AND GUIDELINES

By F.D. Wilde and D.B. Radtke

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# FIELD MEASUREMENTS A6

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## GENERAL INFORMATION 6.0 AND GUIDELINES

*By* F.D. Wilde and D.B. Radtke

This section summarizes information, guidelines, and minimum requirements that generally apply to field measurements for all studies of water quality and the collection of basic data. Another term commonly used for field measurements is field parameters. Guidelines applicable to the individual field measurements are described in detail in the respective sections of this chapter (NFM 6.1 through 6.7). Before proceeding with field work, check each field-measurement section for recommended methods and equipment, detailed descriptions of measurement and quality-control procedures, and guidelines for troubleshooting and data reporting.

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**Field measurements:  
determinations of physical  
or chemical properties that  
are measured onsite, as close  
as possible in time and  
space to the media being  
sampled.**

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## 6.0.1 RECORDS, FIELD INSTRUMENTS, AND QUALITY ASSURANCE

Field-measurement data and other field information must be recorded, either on paper or electronically, while in the field. “Reported” field measurements are defined as those data that are entered into the National Water Information System (NWIS) data base of the USGS (Maddy and others, 1989) as well as data that are to be published but cannot be stored in NWIS. The conventions used for reporting field-measurement data are described at the end of each field-measurement section.

- ▶ Record field-measurement data, methods and equipment selected, and calibration information on field forms and in instrument log books.
  - Field forms include national or study-customized field forms and analytical services request forms; other forms and records (for example, chain-of-custody records) may be required for the study.
  - Instrument log books for each field instrument are required to document calibrations and maintenance.
- ▶ Records are maintained for each uniquely identified sampling location.

Field personnel must be familiar with the instructions provided by equipment manufacturers. This manual provides only generic guidelines for equipment use and maintenance or focuses on a particular instrument or instruments that currently are in common use in the USGS; there is a large variety of available field instruments and field instruments are being continuously updated or replaced using newer technology. Field personnel are encouraged to contact equipment manufacturers for answers to technical questions. Refer questions regarding equipment and supplies obtained from the USGS-WRD Quality of Water Service Unit (QWSU) in Ocala, Fla., the National Water Quality Laboratory (NWQL) in Arvada, Colo., or the Hydrologic Instrumentation Facility (HIF) at Stennis Space Center, Miss., to the respective facility. Information on instrument systems that have been tested and compared for accuracy and precision by HIF is found in the following issues of *Instrument News*, a publication of the HIF: 1991, for Hydrolab H2O™; 1992 and 1993, for pH; 1992, for conductivity; 1993, for dissolved oxygen; and 1994, for temperature, turbidity, and the YSI 3800™.

Field measurements should represent, as closely as possible, the natural condition of the surface-water or ground-water system at the time of sampling. Field teams must determine if the instruments and method to be used will produce data of the type and quality required to fulfill study needs as well as USGS requirements. Experience and knowledge of field conditions often are indispensable for determining the most accurate field-measurement value. To ensure the quality of the data collected:

- ▶ Calibration is required at the field site for most instruments. **Make field measurements only with calibrated instruments.**
- ▶ Each field instrument must have a permanent log book for recording calibrations and repairs. Review the log book before leaving for the field.
- ▶ Test each instrument (meters and sensors) before leaving for the field. Practice your measurement technique if the instrument or measurement is new to you.
- ▶ Have backup instruments readily available and in good working condition.

**Quality-assurance protocols are mandatory for every data-collection effort of the USGS, and include practicing good field procedures and implementing quality-control checks.** Make field measurements in a manner that minimizes artifacts that can bias the result. Check field-measurement precision and accuracy (variability and bias).

- ▶ **Rule of thumb:** For measurements made on subsamples, such as alkalinity, check precision in the field every tenth sample by repeating the measurement three times using separate sample aliquots from the same sample volume.
- ▶ **Requirement:** By using reference samples, document your ability to make an accurate measurement. **Field personnel, including non-USGS employees that collect field-measurement data entered into the NWIS, are required to participate in the National Field Quality Assurance (NFQA) Program (Stanley and others, 1992).** Field teams also are encouraged to verify accuracy of their measurements at least quarterly against reference samples obtained from QWSU.

Before making field measurements, sensors must be allowed to equilibrate to the temperature of the water being monitored. Sensors have equilibrated adequately when instrument readings have “stabilized,” that is, when the variability among measurements does not exceed an established criterion. **The criteria for stabilized field readings are defined operationally in table 6.0–1, for a set of three or more sequential measurements.** The natural variability inherent in surface water or ground water at the time of sampling generally falls within these stability criteria and reflects the accuracy that should be attainable with a calibrated instrument.

**Table 6.0–1.** Stabilization criteria for recording field measurements [±, plus or minus value shown; °C, degrees Celsius; ≤, less than or equal to value shown; μS/cm, microsiemens per centimeter at 25°C; >, greater than value shown; unit, standard pH unit; mg/L, milligram per liter; NTU, nephelometric turbidity unit]

Standard direct field measurement <sup>1</sup>	Stabilization criteria for measurements (variability should be within the value shown)
Temperature: Thermistor thermometer Liquid-in-glass thermometer	± 0.2°C ± 0.5°C
Conductivity: when ≤ 100 μS/cm when > 100 μS/cm	± 5 percent ± 3 percent
pH: Meter displays to 0.01	± 0.1 unit
Dissolved oxygen: Amperometric method	± 0.3 mg/L
Turbidity: Turbidimetric method, in NTU	± 10 percent

<sup>1</sup>Eh is not considered to be a routine or direct field measurement (see NFM 6.5). Alkalinity and acid neutralizing capacity require a titration procedure and, thus, are not direct measurements.

- ▶ **For surface water:** Allow at least 60 seconds (or follow the manufacturer's guidelines) for sensors to equilibrate with sample water. Take instrument readings until the stabilization criteria in table 6.0–1 are met. Record the median of the final three or more readings as the value to be reported for that measurement point (see 6.0.2).
- ▶ **For ground water:** Start recording measurements after sensors have equilibrated with purge water. Take instrument readings until the stabilization criteria in table 6.0–1 are met and the required number of well volumes of ground water have been purged. Record the median of the final five or more readings as the value to be reported for that site (see 6.0.3).
- ▶ **For sites at which variability exceeds the criteria of table 6.0–1:** Allow the instrument a longer equilibration time and record more measurements. To determine the value to be reported for that measurement point or well, either use the median of the final five or more measurements recorded, or apply knowledge of the site and professional judgment to select the most representative of the final readings.

## 6.0.2 SURFACE WATER

Field measurements must accurately represent the body of surface water or that part of the water body being studied. Field teams need to select a method to locate the point(s) of measurement (6.0.2.A) and the method(s) to be used to make the field measurements (6.0.2.B).

Normally, the point(s) at which field measurements are made correspond to the location(s) at which samples are collected. Standard USGS procedures for locating points of sample collection for surface-water sampling are detailed in Chapter A4 (NFM 4) of this *National Field Manual* and in Edwards and Glysson (1998).

**Properties such as temperature, dissolved-oxygen concentration, and Eh must be measured directly in the water body (in situ).** Other properties such as pH, conductivity, and turbidity often are measured in situ, but also may be measured in a subsample of a composited sample collected using discharge-weighted methods. Because determinations of alkalinity or acid-neutralizing capacity (alkalinity/ANC) cannot be made in situ, a discrete sample must be collected or subsampled from a composite.

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## LOCATING POINT(S) OF MEASUREMENT IN STILL AND FLOWING WATER 6.0.2.A

The method selected to locate the point(s) of measurement usually differs for still water and flowing water. If the water system is well-mixed and its chemistry is relatively uniform, a single sample could be sufficient to represent the water body. Often, however, multiple points of measurement are needed to determine a representative set of field-measurement values.

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### Still water

Still-water conditions are found in storage pools, lakes, and reservoirs. Field measurements usually are made in situ at multiple locations and depths. Alternatively, pH, conductivity, and turbidity can be measured in a discrete sample or subsample (see 6.0.2.B). Measurement of alkalinity/ANC must be in a discrete sample. The location, number, and distribution of measurement points are selected according to study objectives.

- ▶ Measurements made at discrete depths through the vertical water column must not be averaged or reported as a median value that represents the entire vertical.
- ▶ Report the value selected to represent each point measured in the vertical as individual stations or distinguish measurements in that vertical by assigning a unique time to each measurement.

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### Flowing water

Flowing water conditions are found in perennial and ephemeral streams. The location and the number of field measurements depend on study objectives (see TECHNICAL NOTE, below). Generally, a single set of field-measurement data is used to represent an entire stream cross section at a sampling site and can be useful when calculating chemical loads.

To obtain data representative of the section, the variability of discharge and field measurements across the stream must be known. This information is used to determine if the equal-discharge-increment (EDI) or equal-width-increment (EWI) method of locating field-measurement points should be used.

1. Check the cross-sectional profile data of the stream site to determine the variability of discharge per unit width of the stream and of field-measurement values across the section.
  - Make individual measurements at a number of equally-spaced verticals along the cross section and at multiple depths within each vertical; or, consult previous records for the site.
  - Make in situ (6.0.2.B) field measurements for the profile.
  - Field-measurement profiles of stream variability are needed for low- and high-flow conditions and should be verified at least every 2 years or as study objectives dictate.
2. Select the EDI or EWI method to locate points of measurement (refer to NFM 4 or Edwards and Glysson (1998) to select and execute the appropriate method).
  - If stream depth and velocities along the cross section are relatively uniform, use the EWI method.
  - If stream depth and velocities along the cross section are highly variable, use the EDI method.
  - In a small and well-mixed stream, a single point at the centroid of flow may be used to represent the cross section. The centroid of flow is defined as the point in the increment at which discharge in that increment is equal on both sides of the point.

TECHNICAL NOTE: Standard USGS procedure is to use either the equal-discharge increment or equal-width increment method for locating measurement points to ensure that chemical loads can be calculated. Different study objectives could dictate different methods for locating the measurement point(s). For example, field measurements designed to correlate water chemistry with benthic invertebrates may require measurements on one or more grab samples that represent populated sections of the stream channel.

## *Equal-Discharge Increments (EDI)*

The stream cross section is divided into increments of equal discharge. Field measurements can be made in situ at the centroid of each increment or by collecting an isokinetic depth-integrated sample at the centroid of each increment and determining the value either of each sample or of a composite of the samples. These methods result in data that are discharge-weighted (Edwards and Glysson, 1998).

- ▶ Knowledge of streamflow distribution in the cross section is required to select verticals at which measurements will be made or subsamples collected. Streamflow distribution can be based on long-term discharge record for the site or on a discharge measurement made just prior to sample collection.
- ▶ **Rule of thumb:** divide the stream into a minimum of four increments. More increments could be needed for a stream site that is poorly mixed.
- ▶ If the stream is well-mixed with relatively uniform discharge, the EDI can consist of a single vertical at the centroid of flow.

### *To divide the cross section into increments of equal discharge:*

1. Visually inspect the stream from bank to bank, observing velocity, width, depth distribution, and the apparent distribution of sediment and aquatic biota in the cross section. Note location of stagnant water, eddies, backwater, reverse flows, areas of faster than normal flow, and piers or other obstructions.
2. If the channel and the control governing the stage are stable, historical streamflow data can be used to determine the measurement locations. If the channel is unstable or if no historical data are available, make a discharge measurement and preliminary field measurements across the selected section of channel.
  - a. From the available discharge data, either
    - construct a graph using cumulative discharge or cumulative percent of total discharge plotted against the cross-sectional width, or
    - determine EDI sections directly from the discharge measurement note sheet.
  - b. If profile values of pH, conductivity, temperature, and DO differ by less than 5 percent and show that the stream is well mixed both across the section and from top to bottom, a single measurement point at the centroid of flow can be used to represent field-measurement values of the cross section.

3. From the graph or measurement notes, determine the number and locations of EDIs and the centroids of those increments.

**EXAMPLE:** If 5 increments will be used, select points of measurement by dividing the total stream discharge by 5 to determine increment discharge: in this case, each EDI equals 20 percent of discharge. The first vertical is located at the centroid of the initial EDI, the point where cumulative discharge equals 10 percent of the total discharge. The remaining 4 centroids are found by adding increment discharge to the discharge at the initial EDI centroid. The EDI centroids will correspond to points along the stream cross section where 10, 30, 50, 70, and 90 percent of the total discharge occur.

*When making field measurements:*

1. Select either the in situ or subsample method and follow the instructions in 6.0.2.B.
  - In-situ method—Go to the centroid of the first equal-discharge increment. Using submersible sensors, measure at mid-depth (or multiple depths) in the vertical. Repeat at each vertical. The value recorded at each vertical represents the median of values observed within approximately 60 seconds after sensor(s) have equilibrated with stream water.
  - Subsample method—Collect an isokinetic depth-integrated sample at the centroid of each equal-discharge increment, emptying the increment sample into a compositing device. Measure field parameters either in the sample collected at each increment or in a subsample taken from the composite of all the increment samples.
2. The final field-measurement value is the mean of the in situ or individual increment-sample value for all the EDI verticals in the section (the composite subsample yields a single value). Note that for pH it is necessary to calculate the mean from the logarithm of each measurement and then convert the answer back to the antilogarithm (refer to NFM 6.4).
3. Enter data on field forms.

**EXAMPLE:** Table 6.0–2 is an example of how mean conductivity measured in situ is calculated using the equal-discharge-increment method.

**Table 6.0–2.** Example of field notes for a discharge-weighted conductivity measurement

[ft/sec, feet per second; ft, feet; ft<sup>2</sup>, square feet; ft<sup>3</sup>/sec, cubic feet per second;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees Celsius; LEW, left edge of water; —, not available; REW, right edge of water]

Equal discharge increment	Percent of flow in increment	Mean velocity, in ft/sec	Width of increment, in ft	Depth of increment, in ft	Area of increment, in ft <sup>2</sup>	Increment discharge, in ft <sup>3</sup> /sec	Median conductivity, in $\mu\text{S}/\text{cm}$
LEW	0	—	—	—	—	—	—
1	20	2.0	22	5.7	125	250	185
2	20	2.2	11	10.4	114	250	170
3	20	2.3	9	12.0	109	250	155
4	20	3.9	5	12.8	64	250	155
5	20	3.4	10	7.4	74	250	150
REW	0	—	—	—	—	—	—

Calculation of conductivity: mean of median conductivity measurements (815 divided by 5)=163  $\mu\text{S}/\text{cm}$ .

- In the example, the correct value for the discharge-weighted mean conductivity is 163  $\mu\text{S}/\text{cm}$ , calculated from 815 divided by 5 (the sum of the recorded median values divided by the number of median measurements).
- Note that at the midpoint of the center centroid of flow (increment 3) the median conductivity would have been reported as 155  $\mu\text{S}/\text{cm}$ ; if conductivity had been measured near the left edge of the water (increment 1), the conductivity would have been reported as 185  $\mu\text{S}/\text{cm}$ .

### *Equal-width increment (EWI)*

The stream cross section is divided into increments of equal width. Knowledge of the streamflow distribution in the cross section is not required.

- ▶ In situ field measurements are made at the midpoints of each increment. Area-weighted concentrations can be computed from these measurements (table 6.0–3).
- ▶ Subsample field measurements are made in discrete samples that usually are withdrawn from a composite sample collected using an isokinetic sample and isokinetic depth-integrating method. The volume of the isokinetic sample must be proportional to the amount of discharge in each increment and measurements in subsamples taken from the compositing device result in discharge-weighted values.

#### *To divide the cross section into increments of equal width:*

1. Visually inspect the stream from bank to bank, observing velocity, width, depth distribution, and the apparent distribution of sediment and aquatic biota in the cross section. Note location of stagnant water, eddies, backwater, areas of faster than normal flow, and piers or other obstructions.
2. Determine stream width using a tagline or from station markings on bridge railings or cableways.
3. Divide the section into equal-width increments based on flow and stream-channel characteristics along the cross section, field-measurement variability from the cross-section profile, and data objectives for the study. This interval width will govern the number of verticals used, and applies also to streams in which flow is divided (for instance, in a braided channel).

#### **Rule of thumb:**

- In streams 5-ft wide or greater, use a minimum of 10 equal-width increments.
  - In streams less than 5-ft wide, use as many increments as practical, but equally spaced a minimum of 3 inches apart.
4. Locate the midpoint of the first vertical at a distance of one-half of the selected increment width from edge of water. Locate other measurement verticals at the centers of the remaining increments.

**EXAMPLE:** In a stream 60-ft wide that has been divided into 15 increments of 4 ft each, the first measurement vertical would be 2 ft from water's edge and subsequent verticals would be at 6, 10, 14 ft, and so forth, from the starting point at water's edge.

### *When making field measurements:*

1. Select either the in situ or subsample method and follow the instructions in 6.0.2.B.
  - In situ method—Measure at the midpoint of each equal-width increment. Using submersible sensors, measure at mid-depth in the vertical.
  - Subsample method—Collect an isokinetic depth-integrated sample at the midpoint of each equal-width increment, emptying each sample into a compositing device. **Use of the correct sampling equipment is critical to execute this method successfully: standard samplers cannot meet isokinetic requirements when stream velocity is less than 1.5 ft/sec.**
2. Record a value for each field measurement for each vertical. The value recorded represents the stabilized values observed within approximately 60 seconds after the sensor(s) have equilibrated with the stream or subsample water.

**EXAMPLE:** Table 6.0–3 provides an example of an area-weighted median measurement for conductivity measured in situ.

- In the example, the area-weighted median conductivity equals 130  $\mu\text{S/cm}$ .
  - To calculate an area-weighted median, multiply the area of each increment by its corresponding field measurement, sum the products of all the increments, and divide by total cross-sectional area.
  - Note that if the conductivity reported was selected at mid-depth of the vertical of centroid of flow (section 10), it would have been reported as 125  $\mu\text{S/cm}$ ; if the conductivity reported was near the left edge of water, it would have been reported as 150  $\mu\text{S/cm}$ .
- ▶ The final field-measurement value normally is calculated as the mean of the values recorded at all EWI increments, resulting in an area-weighted mean (for pH, calculate the mean from the logarithm of each measurement and then convert the answer back to the antilogarithm).
- ▶ Alternatively for EWI, if the area-weighted median best represents integrated stream chemistry, you can report the median instead of the mean—but, be sure to document this on the field form and in the final data report (a parameter code currently is not available for median values).

**Table 6.0-3.** Example of field notes for an area-weighted conductivity measurement

[ft, feet; LEW, left edge of water; ft<sup>2</sup>, square feet;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees Celsius; —, not available; REW, right edge of water]

Section number	Cumulative percent of flow in section	Vertical location, in ft from LEW	Width of section, in ft	Depth of vertical, in ft	Area of section, in ft <sup>2</sup>	Median conductivity, $\mu\text{S}/\text{cm}$	Product of median conductivity and area
LEW	0	0	—	—	—	—	—
1	2	2	4	1.0	4.0	150	600
2	4	6	4	2.0	8.0	145	1,160
3	6	10	4	2.6	10.4	145	1,508
4	10	14	4	3.2	12.8	140	1,792
5	16	18	4	3.5	14.0	135	1,890
6	22	22	4	4.0	16.0	130	2,080
7	28	26	4	4.5	18.0	130	2,340
8	34	30	4	5.4	21.6	125	2,700
9	42	34	4	6.0	24.0	125	3,000
10	50	38	4	5.7	22.8	125	2,850
11	62	42	4	5.1	20.4	125	2,550
12	76	46	4	4.6	18.4	125	2,300
13	88	50	4	3.5	14.0	125	1,750
14	96	54	4	1.4	5.6	135	756
15	99	58	4	1.0	4.0	140	560
REW	100	60	—	—	—	—	—

Calculation of conductivity: sum of values in last column divided by the total cross-sectional area

$$\left(\frac{22,836}{214} = 130 \mu\text{S}/\text{cm}\right)$$

---

## IN SITU AND SUBSAMPLE MEASUREMENT PROCEDURES 6.0.2.B

In situ and subsample procedures used for making field measurements are summarized in figures 6.0-1 and 6.0-2, respectively. For guidance, specific instructions, and potential interferences to the measurement method, consult the individual field measurement sections of this chapter (NFM 6.1 through 6.7).

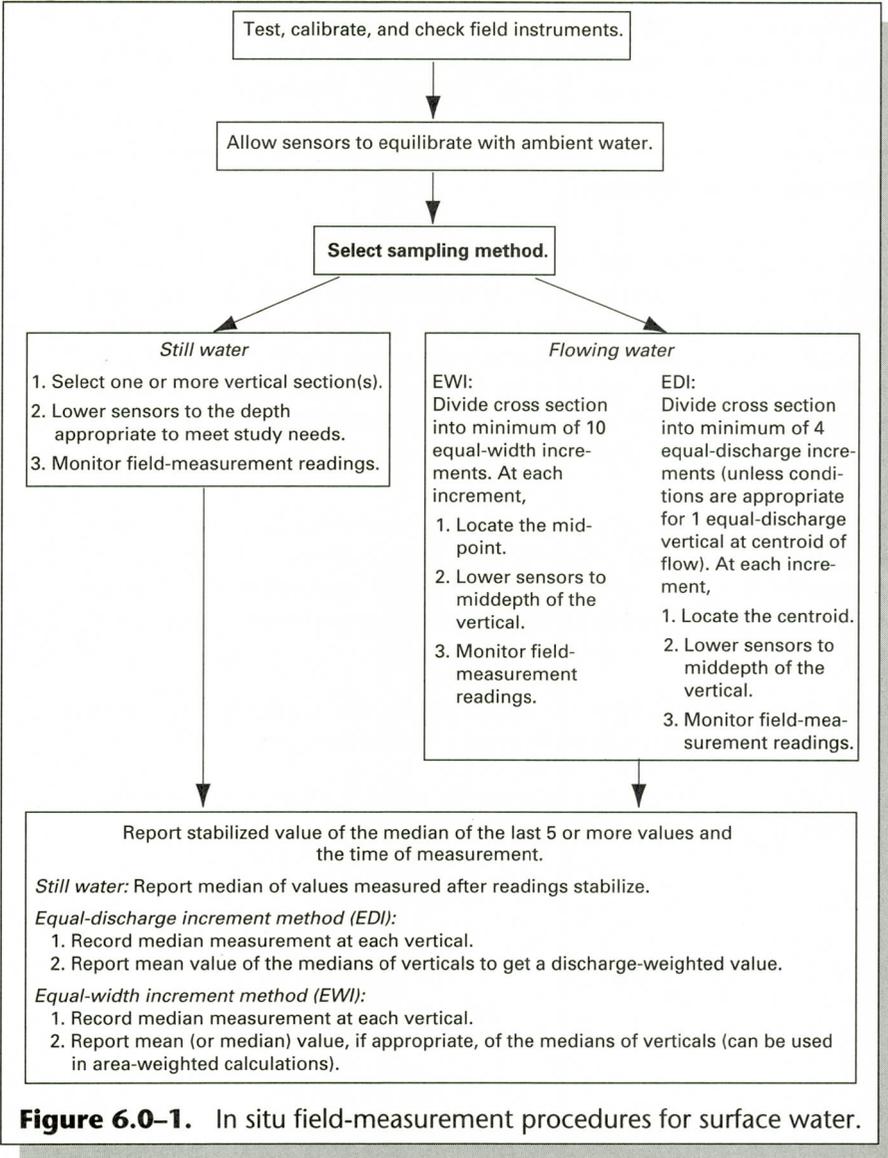
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### In situ measurement

In situ measurement (fig. 6.0-1), made by immersing a field-measurement sensor directly in the water body, is used to determine a profile of variability across a stream section. In situ measurement can be repeated if stream discharge is highly variable and measurement points need to be located at increments of equal discharge. However, in situ measurements are point samples, and, thus, are not depth integrated.

Measurements made directly (in situ) in the surface-water body are preferable in order to avoid changes that result from removing a water sample from its source. **In situ measurement is necessary to avoid changes in chemical properties of anoxic water.**

- ▶ **In situ measurement is mandatory for determination of temperature, dissolved-oxygen concentration, and Eh.**
- ▶ In situ measurement also can be used for pH, conductivity, and turbidity, but not for alkalinity.



**Figure 6.0–1.** In situ field-measurement procedures for surface water.

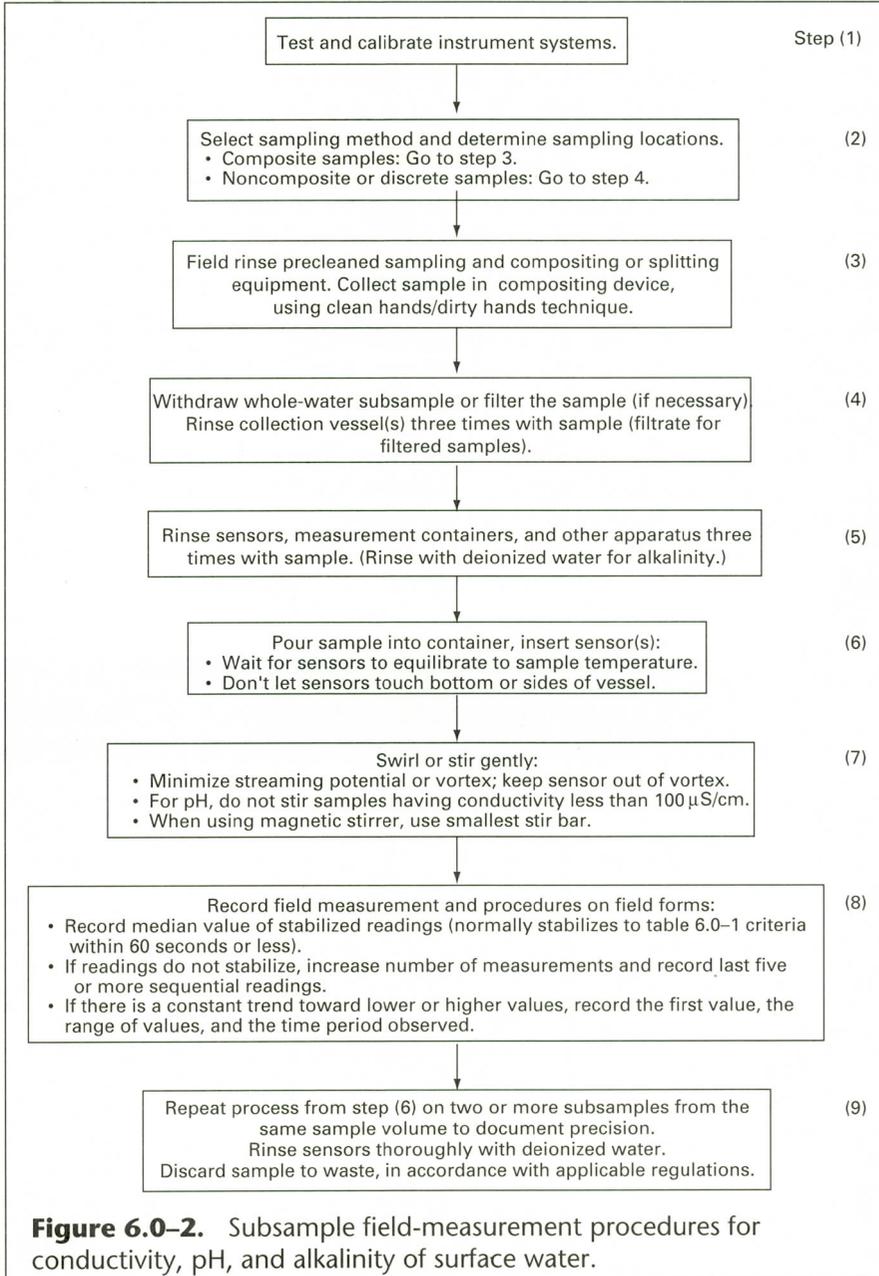
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## Subsample measurement

Depth- and width-integrating sampling methods are used to collect and composite samples that can be subsampled for some field measurements. The same field measurements can be performed on discrete samples collected with thief, bailer, or grab samplers. Subsamples or discrete samples that have been withdrawn from a sample-compositing device or point sampler can yield good data for conductivity, pH, turbidity, and alkalinity as long as correct procedures are followed and the water is not anoxic (fig. 6.0–2).

- ▶ **Subsamples are necessary for alkalinity determinations.**
- ▶ Before using a sample-compositing/splitting device, preclean and field rinse the device in accordance with USGS-approved procedures (Horowitz and others, 1994).
- ▶ When compositing and splitting a sample, follow instructions for the clean hands/dirty hands technique detailed in Horowitz and others (1994), as required.

**Do not measure temperature, dissolved oxygen, or Eh on subsamples.**



## GROUND WATER 6.0.3

Field measurements in ground water must accurately represent the properties of the aquifer. This generally requires purging the well of standing water before making measurements (6.0.3.A), and involves setting up either a flowthrough-chamber or downhole field-measurement system (6.0.3.B). Standard USGS procedures for purging and the use of measurement systems are described below. However, the purging protocol followed and the measurement system to be used also depend on the type of well to be sampled and study objectives (detailed information can be found in Koterba and others, 1995; and Lapham and others, 1997).

Ground water for alkalinity is collected as a discrete sample: use a point-source sampler (for example, a Kemmerer sampler or double-check-valve bailer) or a pump with the intake positioned at the interval corresponding to the depth at which other measurements are made and at which samples will be collected.

### *Measurements at a monitoring well*

- ▶ The standard purging procedure usually is necessary (6.0.3.A).
- ▶ Either a downhole or a flowthrough-chamber system can be used for field measurements (6.0.3.B). If samples will be collected, however, use the flowthrough chamber instead of the downhole system in order to avoid bias of chemical analyses from sample contact with downhole instruments.

### *Measurements at a supply well (a domestic well or a municipal, industrial, commercial, irrigation, or other production well)*

- ▶ The standard purging procedure may not be appropriate (see “Exceptions to the standard USGS three-well-volume purging procedure” in 6.0.3.A).
- ▶ Identify well-construction materials and any equipment permanently installed in the well (such as a pump) that can affect the logistics and quality of the field measurement.
- ▶ Use a flowthrough-chamber type of system (6.0.3.B).
- ▶ Connect the field-measurement system to the wellhead at a point before the sample would pass through holding tanks, backflow pressure tanks, flow meters, or chemical treatment systems.

### 6.0.3.A WELL PURGING: STANDARD PROCEDURE AND EXCEPTIONS

Well purging removes standing water from a well. Purging reduces chemical and biochemical artifacts caused by well installation, inadequate well development, well-construction materials, or infrequent pumping (American Society for Testing and Materials, 1992). Purging also serves to rinse and condition sampling equipment with well water.

When selecting purging equipment for monitoring wells, a portable, submersible nonaerating pump that also will be used for sampling is recommended.

- ▶ When the water table is deeper than 250 ft and (or) a large volume of water must be purged, a dual-pump system often is used: position a submersible pump downhole and a centrifugal pump at the surface. Water from the slow-pumping submersible pump is used for field measurements and to collect the sample, while the centrifugal pump operates at a higher rate to evacuate the required purge volume.
- ▶ When the water table is less than 25 to 30 ft from land surface, a peristaltic pump sometimes is used to purge small-diameter wells; a peristaltic pump or other comparable suction-lift device should not be used if dissolved-oxygen concentrations or Eh are being monitored during purging.
- ▶ To reduce the volume and time required for purging, especially in deep wells or in wells for which purge water must be contained, an inflatable packer sometimes is set above the pump and above the screened or open interval. Packers can fail to form a complete seal between aquifer intervals, and should be used with pressure transducers to indicate water leakage.
- ▶ **A bailer is not recommended for purging.** The plunging action of the bailer can release or stir up particulates that are not ambient in ground-water flow, resulting in biased measurements and analyses. (Refer to “Subsample measurement” in 6.0.3.B for information about using a bailer.)

Steel tapes and electric tapes or acoustic sensors are used to measure water level. An electric tape or other water-level sensor is recommended for continuous monitoring of drawdown during purging—repeated lowering of a weighted steel tape can release or stir up particulate materials and affect turbidity readings.

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## Standard USGS procedure for purging

Purge a minimum of three well volumes while monitoring temperature, pH, conductivity, dissolved-oxygen concentration, and turbidity.

- ▶ Sequential measurements of these parameters are used as criteria to help determine when water withdrawn from the well is representative of water flowing through the aquifer and when purging should end and sampling begin (table 6.0-1).
- ▶ The criteria normally are met within three well volumes, but well characteristics and study objectives could require removal of additional well volumes.
- ▶ The same pump should be used for purging and sampling, if possible, without stopping or removing the pump (see Koterba and others, 1995), unless the dual-pump system is used.

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## Exceptions to the standard USGS three-well-volume purging procedure

The number of well volumes removed and the parameters used as purge criteria can be subject to data-collection objectives, well characteristics, and equipment.

- ▶ Study objectives could require a different purge volume or require sequential sampling of additional chemical constituents.
- ▶ A lesser purge volume and modified procedures are needed, for example, for wells
  - that are being pumped continuously or regularly every few hours (such as in-service public-supply wells).
  - that are pumped dry or that have a water column of less than 4 ft plus the length of the submersible pump.
  - in which sampling zones are isolated by packers.
  - in which the pump intake is installed permanently within the screened or open interval.

### *Before purging begins:*

1. Check the well-identification number. Check the well's record of water levels, drawdown, and field-measurement variability (if available).

2. Prepare the necessary field forms, such as the well-purge record, national or study field form, and chain-of-custody record. Record the type of equipment being used.
3. Lay plastic sheeting around the well to prevent contaminating the equipment. Unlock the well housing or top of the protective casing and remove the well cap.

### *To purge the well:*

1. Measure and record the depth to static water level (fig. 6.0–3).
2. Calculate and record the well volume as shown on fig. 6.0–3. Note that the depth to the screened or open interval and the inside casing diameter must be known to calculate well volume.
3. In a monitoring well, lower a submersible pump followed by a water-level sensor to the desired location of the pump intake. **The final pump intake position always is located at the point of sample collection.** Note that the pump position is fixed in supply wells and in monitoring wells with a permanently installed sampling system. **Lower the equipment slowly and smoothly to avoid stirring up particulates.**
  - Position the pump intake between 3 ft (~0.9 m) below static water surface and a minimum distance above the top of the open/screened interval of 10 times the well diameter (20 in. for a 2-in. well diameter), if the sample is to be integrated over the entire screened or open area of the aquifer. The location of the intake may be different when the study objective requires collecting the sample from a point within the open/screened interval or from wells in which packers are installed.
  - The water-level sensor should be a maximum of 1 ft (~0.3 m) below water surface.
4. Start the pump. Gradually increase and (or) adjust the pumping rate to limit drawdown to between 0.5 and 1.0 ft (~0.15 to ~0.3 m). Measure the water level as purging progresses.
  - If the final intake position is above the screened or open interval, the final pumping rate should be about 500 to 1,000 milliliters per minute. Do not exceed 1 ft of drawdown.
  - If the final intake position is within the screened or open interval, the final pumping rate should be about 200 to 500 milliliters per minute. Do not exceed 0.5 ft of drawdown.
  - If the pump and intake position are fixed, as in a supply well, control the rate of flow for field measurements through flow-splitting valve(s).

5. **Do not move the pump during purging or sample collection after the intake has been set at the final location.**
6. Purge a minimum of three well volumes or the purge volume dictated by study objectives (note "Exceptions to the standard USGS three-well-volume purging procedure"). Throughout purging, monitor and record field-measurement readings (fig. 6.0–3).
  - Check for special instructions regarding field-measurement or field-analysis requirements dictated by the study objectives.
  - Contain purge water as required by Federal, State, or local regulations.
7. **As the third or last well volume is purged, when the final field measurements are recorded, adjust the purge rate to the pumping rate to be used during sampling.**
  - Record field measurements at regular time intervals—about 3 to 5 minutes apart. For deep wells, the time intervals could be 15 minutes or longer. The time intervals selected will depend on the well characteristics and hydraulic properties of the aquifer, but the intervals must be sufficiently spaced to yield results representative of aquifer properties.
  - Consult criteria for field-measurement stabilization (table 6.0–1). Field experience, understanding of the effects of hydrologic and geochemical conditions, and knowledge of data-collection and data-quality requirements often are necessary to determine the most accurate field value.
 

**If criteria are being met**—record at least five sequential measurements and report the median value.

**If criteria are not being met**—consult the study requirements and objectives. Extend the purge time if readings still do not stabilize; report the median value of the last five or more sequential measurements.

---

## Complete field forms and report the data

Report the median of the recorded field-measurement readings as the final well volume is purged.

- ▶ Record anomalies, difficulties, and adjustments on the field form.
- ▶ Record the purge volume, rate of pumping, initial and final intake locations, and time and respective reading of sequential field measurements (fig. 6.0–3).



## DOWNHOLE, FLOWTHROUGH-CHAMBER, AND SUBSAMPLE MEASUREMENT PROCEDURES 6.0.3.B

A flowthrough-chamber system is recommended for direct field measurements (fig. 6.0-4), if samples also will be collected for chemical analysis. A downhole system is recommended if field measurements will be monitored without sampling. If samples must be bailed from the well, measure only pH and conductivity in subsamples of the bailed volume (fig. 6.0-5).

- ▶ **Downhole or flowthrough-chamber systems are required for reported values of temperature, dissolved oxygen (DO), and Eh**—do not make these measurements in a bailed subsample or other discrete sample.
- ▶ Downhole or flowthrough-chamber systems are preferred for reported values of pH and conductivity.

A positive-displacement submersible pump is recommended for downhole and flowthrough-chamber systems. Lower a length of pipe to check that the well is free from obstructions before lowering a pump or downhole instrument in a well—this practice will prevent loss of costly equipment.

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### Downhole system

A downhole system is used for in situ field measurements. Ground water should flow upward past downhole sensors in order to obtain values representative of the depth interval being sampled; therefore, a submersible pump follows the downhole instrument. Because of this constraint, the downhole method may not be practical at wells with dedicated pumps or when using multiple equipment in small-diameter wells. Figure 6.0-4 shows the steps for downhole measurement of field parameters.

- ▶ The depth at which sensors are located depends on study objectives. If a sample is to represent ground water that is integrated over the screened interval, locate sensors approximately 1 ft above the screened interval in a 2-in. diameter well and just below the pump intake.

- ▶ Remove downhole sensors from the well before collecting samples for chemical analysis in order to prevent these instruments from affecting sample chemistry. Note that the process of removing these instruments and putting the pump back in the well causes disturbances that can affect the quality of samples subsequently collected for chemical analyses (Puls and others, 1991; Kearl and others, 1992; Puls and Powell, 1992).

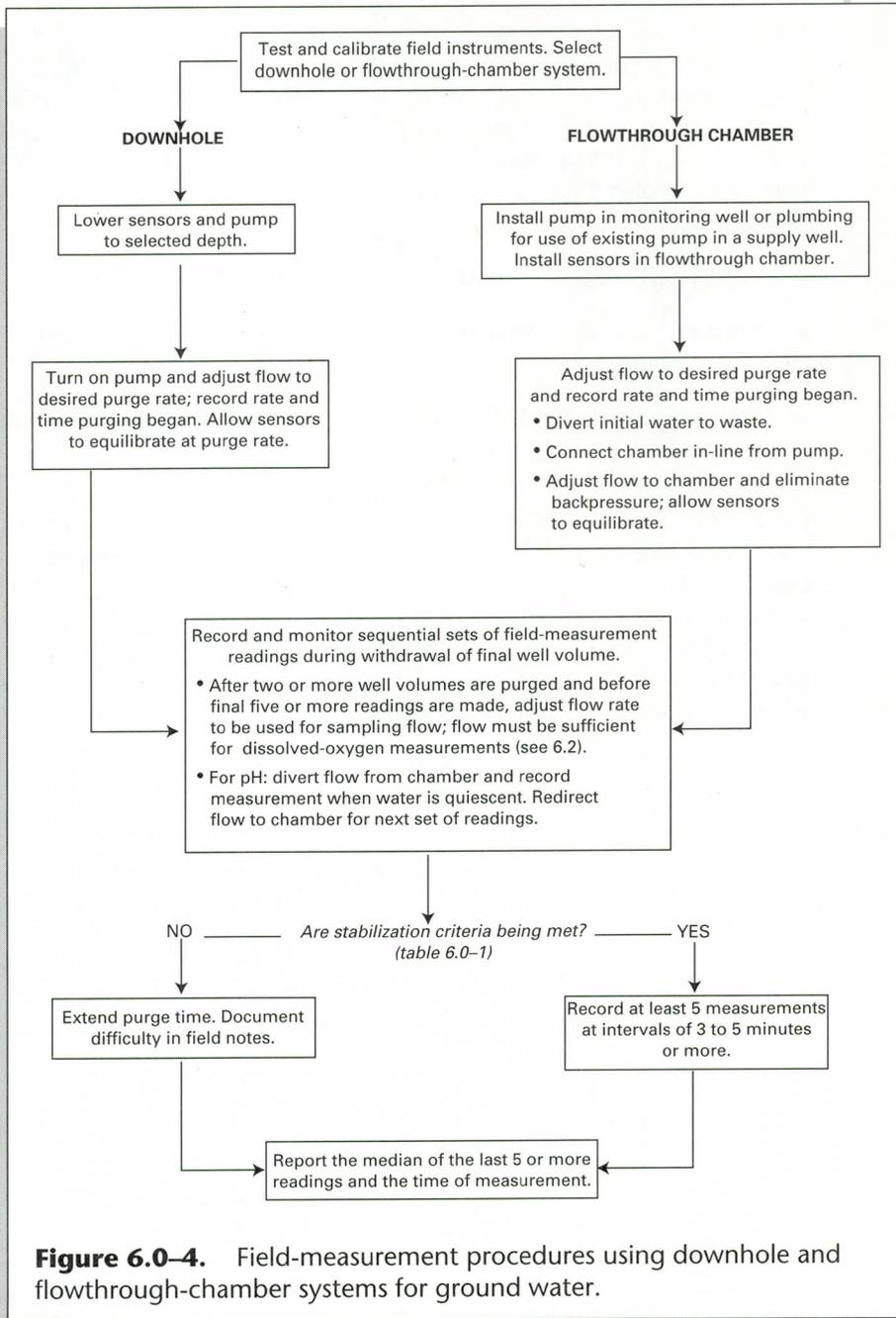
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## Flowthrough-chamber system

A flowthrough chamber is an airtight, transparent vessel with a pressure-relief valve and either (1) grommeted ports to accommodate individual sensors or (2) a multiparameter instrument. Several types of flowthrough-chamber systems are available and can be designed for a specific measurement (for example, see NFM 6.2.2 for the description of a flowthrough cell for the spectrophotometric determination of dissolved-oxygen concentration).

### *When setting up a flowthrough chamber:*

1. Install the chamber in-line from the pump and as close to the wellhead as possible.
  - Keep the chamber, field-measurement instruments, and tubing off the ground, shaded from direct sunlight, and shielded from wind.
  - Keep the tubing as short as possible.
2. Install the dissolved-oxygen sensor immediately downstream from the chamber inflow, and install the pH sensor downstream from the conductivity sensor.
3. Turn on the pump; direct initial flow to waste to avoid introducing sediment into the chamber.
  - Adjust the flow into the chamber so that a constant stream of water is maintained at the rate required for dissolved-oxygen measurements (see NFM 6.2).
  - Correct any backpressure conditions; tilt the chamber to expel trapped air.



**Figure 6.0-4.** Field-measurement procedures using downhole and flowthrough-chamber systems for ground water.

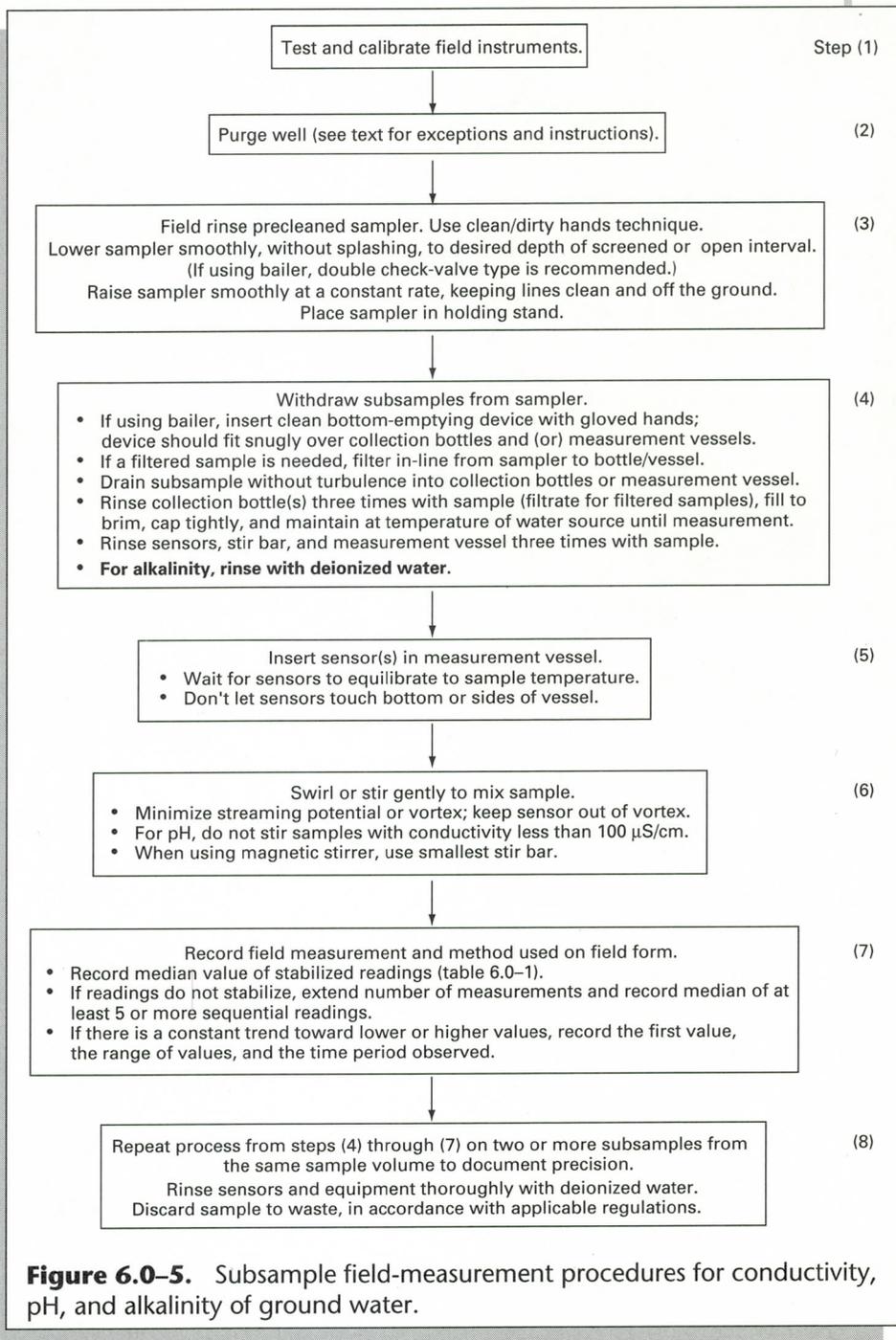
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## Subsample measurement

Subsamples or discrete samples are aliquots of sample collected from a nonpumping sampling device such as a bailer, a thief sampler, or a syringe sampler. Measurements of field parameters made in discrete or nonpumped samples are more vulnerable to bias from changes in temperature, pressure, turbidity, and concentrations of dissolved gases than measurements using a downhole or flowthrough-chamber system.

- ▶ Subsamples can be used for conductivity, pH, and alkalinity.
- ▶ Subsamples must not be used for reported measurements of temperature, dissolved oxygen, Eh, or turbidity.
- ▶ Subsample procedures must not be used in reducing (anoxic) waters.

Figure 6.0–5 shows the steps for measurement of field parameters on a bailed sample. If collecting a sample with a bailer, use one with a double check valve. Field rinse the sampler with sample water before using. To shield the sample from atmospheric contamination, make measurements in a collection chamber or in a glove box filled with inert gas. Indicate on field forms the sampling and measurement procedures used.



**Figure 6.0–5.** Subsample field-measurement procedures for conductivity, pH, and alkalinity of ground water.



# 6.1 TEMPERATURE

By D.B. Radtke, J.K. Kurklin, and F.D. Wilde

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# TEMPERATURE 6.1

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

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

The USGS has adopted the Celsius (C) scale for measuring temperature. This section describes methods for measuring temperature in air, surface water, and ground water. The methods are appropriate for fresh to saline waters.

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

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**Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.**

## 6.1.1 EQUIPMENT AND SUPPLIES

Temperature instruments must be tested before each field trip and cleaned soon after use (table 6.1–1). Each instrument must have a log book in which all calibrations and repairs are recorded, along with the manufacturer make and model description and serial or property number.

**Table 6.1–1.** Equipment and supplies used for measuring temperature<sup>1</sup>

[°C, degrees Celsius; L, liter;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25°C]

- ✓ Calibration thermometer, liquid-in-glass sensor, certified by National Institute of Standards and Technology (NIST)  
Temperature range at least  $-5$  to  $+45^\circ\text{C}$   
 $0.1^\circ\text{C}$  graduated
- ✓ Thermometer, liquid-in-glass sensor  
Temperature range  $-5$  to  $+45^\circ\text{C}$   
Minimum  $0.5^\circ\text{C}$  graduated  
Calibrated accuracy within 1 percent of full scale or  $0.5^\circ\text{C}$ , whichever is less  
Calibrated and District certified against calibration (NIST) thermometer
- ✓ Thermistor thermometer  
Calibrated accuracy within  $0.1^\circ\text{C}$  to  $0.2^\circ\text{C}$   
Digital readout to at least  $0.1^\circ\text{C}$   
Calibrated and District certified against calibration (NIST) thermometer
- ✓ Dewar flask and (or) plastic beakers (assorted sizes)
- ✓ Water bath, refrigerated
- ✓ Soap solution (1 L), nonphosphate laboratory detergent
- ✓ Deionized water (1 L), maximum conductivity of  $1 \mu\text{S}/\text{cm}$
- ✓ Flowthrough chamber (for ground-water applications as an alternative to instruments with downhole capabilities)
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Log book, for recording all calibrations, maintenance, and repairs

<sup>1</sup>Modify this list to meet specific needs of the field effort.

- ▶ 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 most commonly used to measure air and water temperature.
- ▶ Extreme field conditions (for example, frigid climates or thermal waters) may require thermometers capable of measuring a broader temperature range.

**CAUTION: Do not use mercury-filled thermometers in the field.**

The operating instructions for thermometers are provided by the manufacturer.

- ▶ **Liquid-in-glass thermometer**—Recommended liquid-in-glass thermometers are total-immersion thermometers filled with alcohol. Before measuring temperature, check the type of liquid-filled thermometer being used. (Partial-immersion thermometers are not recommended: these have a ring or other mark to indicate the immersion depth required.)
- ▶ **Thermistor thermometer**—A thermistor thermometer is an electrical device made of a solid semiconductor with a large temperature coefficient of resistivity. An electrical signal processor (meter) converts changes in resistance to a readout calibrated in temperature units. Thermistors commonly are incorporated in instruments used for surface-water and ground-water measurements.

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## MAINTENANCE, CLEANING, AND STORAGE 6.1.1.A

Thermometers can easily become damaged or out of calibration. Take care to:

- ▶ Keep thermometers clean (follow manufacturer's recommendations).
- ▶ Carry thermometers in protective cases; thermometers and cases must be free of sand and debris.
- ▶ Store liquid-filled thermometers in a bulb-down position and in a cool place away from direct sunlight.

As an additional precaution on field trips, carry extra calibrated thermometers as spares, and a supply of batteries for instrument systems.

## 6.1.2 CALIBRATION

To calibrate a thermometer, instrument readings are checked across a range of temperatures against those of a thermometer of certified accuracy.

Calibrate liquid-in-glass and thermistor thermometers in the office at regularly scheduled intervals. **Tag acceptable thermometers with date of calibration.**

### *Minimum calibration requirements*

- ▶ **Liquid-in-glass thermometer:**
  - Every 3 to 6 months, using a 2-point calibration, and
  - Annually, using a 3-point calibration.
- ▶ **Thermistor thermometer:**
  - Every 3 to 4 months, check calibration
  - Annually, using a 5-point calibration.
- ▶ The standard thermometer against which all other thermometers are calibrated must be certified by the National Institute of Standards and Technology (NIST). It must be accurate to 0.1°C.

Check the certificate of calibration for the NIST thermometer before calibrating field thermometers. **NIST-certified thermometers are not for field use.**

Thermometers being calibrated must meet NIST specifications to a minimum of three temperatures at approximately 0°, 25°, and 40°C. Thermistors must be calibrated at 5 points within this range. If environmental water or air temperatures will fall below 0°C or rise above 40°C, add additional calibration points to bracket the temperatures to be measured.

**Field checking thermometer calibration by comparing readings with another field thermometer does not substitute for required laboratory calibration procedures. When measuring water temperature in the laboratory:**

- ▶ Submerge the bulb and liquid column of the total-immersion thermometer.
- ▶ Keep the NIST-certified thermometer and the thermistor sensor submerged in the container throughout calibration.

- ▶ Read the NIST-certified thermometer and record the thermistor readings throughout warming and cooling periods.
- ▶ Check the meter batteries periodically for proper voltage.
- ▶ Record the calibration data in the instrument log book for each thermistor thermometer, noting if a sensor has been replaced.

*If using a commercial refrigerated water bath:*

1. Precool the sensor of the thermometer being tested (test thermometer) to 0°C by immersing it in a separate ice/water bath.
2. Immerse the test and NIST-certified thermometer sensors in the refrigerated bath with a water temperature of approximately 0°C.
3. Position the thermometer sensor(s) so that they are properly immersed and so that the scales can be read. Stir the water bath and allow at least 2 minutes for the thermometer readings to stabilize.
4. Without removing the thermometer sensor from the refrigerated water bath, read the test thermometer(s) to the nearest graduation (0.1 to 0.5°C) and the NIST-certified thermometer to the nearest 0.1°C.
  - Take three readings within a 5-minute span for each thermometer.
  - Calculate the mean of the three temperature readings for each thermometer and compare its mean value with the NIST-certified thermometer.
  - If the liquid-filled test thermometer is found to be within  $\pm 1$  percent of full scale or  $\pm 0.5^\circ\text{C}$  of the NIST-certified thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
  - If the test thermistor is found to be within  $\pm 0.2^\circ\text{C}$  of the NIST-certified thermometer, set it aside for calibration checks at higher temperatures.
5. Repeat steps 1–3 in 25°C and 40°C water. Keep the bath temperature constant. Check the thermistors at two or more additional intermediate temperatures (for example, 15°C and 30°C).
6. Tag acceptable thermometers as “District certified” with calibration date and certifier’s initials.

*If a commercial refrigerated water bath is not available:*

1. Freeze several ice cube trays filled with deionized water.
2. Fill a 1,000-mL plastic beaker or Dewar flask three-fourths full of crushed, deionized ice. Add chilled, deionized water to the beaker. Place the beaker of ice/water mixture in a larger, insulated container or Dewar flask. Place the NIST-certified thermometer into the ice/water mixture and make sure that the temperature is uniform at 0°C by stirring and checking at several locations.
3. Precool the test thermometer sensor to 0°C by immersing it in a separate ice/water bath.
4. Add the test thermometer sensor(s) to the ice/water mixture. Position the sensor(s) so that they are properly immersed and so that the scales can be read. Periodically stir the ice/water mixture and allow at least 2 minutes for the thermometer readings to stabilize.
5. When the readings stabilize, compare the temperature of one test thermometer at a time with that of the NIST-certified thermometer. Without removing the temperature sensor(s) from the test bath, read the test thermometer(s) to the nearest graduation (0.1 to 0.5°C) and the NIST-certified thermometer to the nearest 0.1°C.
  - Take three readings for each thermometer within a 5-minute span.
  - Calculate the mean of the three temperature readings for each thermometer and compare its mean value with the NIST thermometer.
  - If the test liquid-filled thermometer is found to be within  $\pm 1$  percent of full scale or  $\pm 0.5^\circ\text{C}$  of the NIST-certified thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
  - If the test thermistor is found to be within  $\pm 0.2^\circ\text{C}$  of the NIST-certified thermometer, set it aside for calibration checks at higher temperatures.
6. For “room temperature” calibration (about 25°C), place a Dewar flask or container filled with about 1 gallon of water in a box filled with packing insulation. (A partially filled insulated ice chest can be used for multiparameter instruments.) Place the calibration container in an area of the room where the temperature is fairly constant (areas away from drafts, vents, windows, and harsh lights).

7. Properly immerse the NIST-certified and test thermometer sensor(s) in the water. Cover the container and allow the water bath and thermometers to equilibrate. Stir the water and check every couple of hours for temperature uniformity using the NIST-certified thermometer—it may be necessary to let the bath equilibrate overnight.
8. Compare one test thermometer at a time with the NIST-certified thermometer. Calibrate as described in step 5 above.
  - For greater than 25°C temperature calibration, place a beaker (1,000 mL or more) of warm water (about 40°C) on a magnetic stirrer plate and repeat procedure as described in step 5 above.
  - Tag acceptable thermometers as “District certified” with calibration date and certifier’s initials.

Corrections can be applied to measurements made with a thermistor instrument system if necessary, using a calibration curve or table plotted in the log book. **Thermometers found to be out of calibration by more than 0.2°C must be recalibrated per manufacturer’s instructions or returned to the manufacturer for proper calibration and (or) repairs.**

Thermistors included in other field-measurement instruments must be calibrated routinely. Accurate determination of other field measurements depends on accurate temperature measurements. This must be underscored for thermistors incorporated in specific electrical conductance, dissolved-oxygen, and pH instruments, because these thermistors are used for automatic temperature compensation of the measurement being made.

**Tag and date acceptable thermometers.**

## 6.1.3 MEASUREMENT

Water-quality sampling should include an air-temperature measurement and a water-temperature measurement. Before measuring temperature:

- ▶ Inspect liquid-in-glass thermometers to be certain liquid columns have not separated.
- ▶ Inspect bulbs to be sure they are clean.
- ▶ Inspect protective cases to be sure they are free of sand or debris.

### 6.1.3.A AIR

Read air temperature with a dry, calibrated thermometer.

- ▶ Place the thermometer about 5 ft above the ground in a shaded area protected from strong winds but open to air circulation. Avoid areas of possible radiant heat effects, such as metal walls, rock exposures, or sides of vehicles.
- ▶ Allow 3 to 5 minutes for the thermometer to equilibrate, then record the temperature and time of day.
- ▶ Measure the air temperature as close as possible to the time when the water temperature is measured.
- ▶ Report routine air temperature measurements to the nearest 0.5°C. If greater accuracy is required, use a thermistor thermometer that has been calibrated to the accuracy needed.

## SURFACE WATER 6.1.3.B

The reported surface-water temperature must be measured in situ—**do not measure temperature on subsamples** from a sample compositing device. Measure temperature in such a manner that the mean or median temperature at the time of observation is represented (consult NFM 6.0 and fig. 6.0–1). Record any deviation from this convention in the data base and report it with the published data.

*To measure the temperature of surface water:*

- ▶ Make a cross-sectional temperature profile to determine temperature variability—A thermistor thermometer works best for this purpose.
  - ▶ Determine from the cross-sectional profile and from study objectives which sampling method to use (see NFM 6.0).
  - ▶ Measure temperature in those sections of the stream that represent most of the water flowing in a reach. Do not make temperature measurements in or directly below stream sections with turbulent flow or from the stream bank (unless this represents the condition to be monitored).
1. Use either a liquid-in-glass thermometer tagged as “District certified” within the past 12 months, or a thermistor thermometer tagged “District certified” within the past 4 months.
  2. Record on field forms the temperature variation from the cross-sectional profile, and the sampling method selected.
    - **Flowing, shallow stream**—wade to the location(s) where temperature is to be measured. To prevent erroneous readings caused by direct solar radiation, stand so that a shadow is cast on the site for temperature measurement.
    - **Stream too deep or swift to wade**—measure temperature by lowering from a bridge, cableway, or boat a thermistor thermometer attached to a weighted cable. Do not attach a weight to the sensor or sensor cable.
    - **Still-water conditions**—measure temperature at multiple depths at several points in the cross section.

3. Immerse the sensor in the water to the correct depth and hold it there for no less than 60 seconds until the sensor equilibrates thermally. The sensor must be immersed properly while reading the temperature; this might require attaching the thermistor to a weighted cable.

TECHNICAL NOTE: For in situ measurement with liquid-filled thermometers—the water depth must be no greater than twice the length of the liquid column of the thermometer in order to make an accurate measurement.

4. Read the temperature to the nearest 0.5°C (0.2°C for thermistor readings)—**do not remove the sensor from the water.**
  - Using a liquid-in-glass thermometer, check the reading three times and record on field forms the median of these values.
  - Using a thermistor thermometer, wait until the readings stabilize to within 0.2°C, then record the median of approximately the last 5 values.
5. Remove the temperature sensor from the water, rinse it thoroughly with deionized water, and store it.
6. Record the stream temperature on field forms:
  - **In still water—median** of three or more sequential values.
  - **EDI—mean** value of subsections measured (use median if measuring one vertical at the centroid of flow).
  - **EWI—mean or median** value of subsections measured.

## GROUND WATER 6.1.3.C

Measurements of ground-water temperature must be made downhole at the end of purging for temperature to represent aquifer conditions (consult NFM 6.0 for guidance).

*To measure the temperature of ground water:*

- ▶ Select either the downhole or flowthrough-chamber sampling system of measurement (see NFM 6.0, fig. 6.0-4) and record on field forms. **Do not report a temperature value measured from a bailed sample.**
  - ▶ Measure temperature with a thermometer that has been District certified and is calibrated within the temperature range to be encountered.
1. Prepare the instruments for either the downhole or the flowthrough-chamber system.
    - **Downhole system**—lower the sensor in the well to just below the pump intake (the intake location depends on the sampling objectives).
    - **Flowthrough-chamber system**—properly immerse the thermistor or liquid-in-glass thermometer in the chamber. Keep the tubing from the well to the chamber as short as possible, out of direct sunlight, and off the ground.
  2. Begin water withdrawal from the well.
  3. Allow the thermometer sensor to equilibrate with the well water for 5 minutes; record the readings and time intervals throughout the period of purging.
  4. Toward the end of purging, record five measurements, spaced at increments of 3 to 5 minutes or more.
    - If the thermistor temperature is stable within the 0.2°C criterion (for a liquid-in-glass thermometer, there should be only slight fluctuation within the 0.5°C interval), report the median of the final five measurements (table 6.0-1).
    - If the stability criterion has not been met, extend the purge time and consult the well-purging objectives of the study. Report the median of the last five (or more) sequential measurements and record any instability on field forms.
  5. Remove and clean the temperature sensors.

## 6.1.4 TROUBLESHOOTING

Contact the instrument manufacturer if the suggestions on table 6.1-2 fail to resolve the problem.

When using thermistor thermometers:

- ▶ Check the voltage of the batteries.
- ▶ Start with good batteries in instruments and carry spares.

**Table 6.1-2.** Troubleshooting guide for temperature measurement

Symptom	Possible cause and corrective action
Liquid-in-glass thermometer doesn't read accurately	<ul style="list-style-type: none"> <li>• Check thermometer to see that the liquid is not separated—if separated, take back to the office to reunite column.</li> </ul>
Thermistor thermometer doesn't read accurately	<ul style="list-style-type: none"> <li>• Dirty sensor—remove dirt and oil film.</li> <li>• Weak batteries—replace with new batteries.</li> </ul>
Erratic thermistor thermometer readings	<ul style="list-style-type: none"> <li>• Bad or dirty connection at meter or sensor—tighten or clean connections.</li> <li>• Break in the cables—replace cables.</li> <li>• Weak batteries—replace with new batteries.</li> </ul>
Thermistor thermometer slow to stabilize	<ul style="list-style-type: none"> <li>• Dirty sensor—clean sensor to remove dirt and oily film.</li> </ul>

## REPORTING 6.1.5

Report temperature measurements in the data base to the nearest 0.5°C.

- ▶ For studies for which greater accuracy is desired, temperatures can be reported to the accuracy requested, provided the thermometer has been calibrated to that accuracy.
- ▶ Enter field measurements of air and water temperature on NWQL Analytical Services Request forms, and in the data base under the correct parameter code.
- ▶ Record the accuracy range of the instrument in the data base, if possible. Report accuracy range with the published values.

**Report only those water temperature values that were measured in situ.**



## 6.2 DISSOLVED OXYGEN

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

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## DISSOLVED OXYGEN 6.2

Accurate data on concentrations of dissolved oxygen (DO) in water are essential for documenting changes to the environment caused by natural phenomena and human activities. Sources of DO in water include atmospheric reaeration 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 oxygen present. Dissolved oxygen is necessary in aquatic systems for the survival and growth of many aquatic organisms.

Two field methods for determining concentrations of dissolved oxygen in surface and ground waters are the amperometric method and the spectrophotometric method.

- ▶ The amperometric method is the standard procedure for determination of DO concentrations.
- ▶ The spectrophotometric method described in this report (the Rhodazine-D<sup>TM,1</sup> technique) is recommended for determining concentrations of DO less than 1.0 mg/L.
- ▶ Except where noted, these methods are applicable to unfiltered surface and ground waters, from fresh to saline.
- ▶ The iodometric (Winkler) method generally is not recommended for field determination of dissolved oxygen because the accuracy and reproducibility achieved depend largely on the experience and technique of the data collector. The iodometric method is described under amperometric calibration procedures (6.2.1.B).

---

**Dissolved oxygen:  
molecular oxygen  
(oxygen gas)  
dissolved in water.**

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**Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.**

<sup>1</sup>Rhodazine-D<sup>TM</sup>, a colorless, reduced phenzone dye, is a proprietary product of CHEMetrics, Incorporated, and constitutes approximately 0.01 volume percent of solution in the ampoule. Remaining constituents in the ampoule are water, diethylene glycol, hydroxymethyl aminomethane, and potassium hydroxide.

## 6.2.1 AMPEROMETRIC METHOD

The most commonly used field method for measuring DO in water is the amperometric method, in which DO concentration is determined with a temperature-compensating instrument or meter that works with a polarographic membrane-type sensor.

### 6.2.1.A EQUIPMENT AND SUPPLIES

The instrument system used to measure DO must be tested before each field trip and cleaned soon after each use. Battery-powered instruments are recommended. A variety of DO meters and sensors are available—**read thoroughly the instructions provided by the manufacturer.** Every DO instrument and the barometer must have a log book in which repairs and calibrations are recorded, along with the manufacturer make and model description, and the serial or property number.

- ▶ The term “dissolved-oxygen sensor” refers to the entire sensor assembly, including the electrodes, electrolyte solutions, membranes, and thermistor thermometers.
- ▶ Dissolved-oxygen sensors must be temperature compensating: the permeability of the membrane and solubility of oxygen in water change as a function of temperature.
- ▶ The type of membrane selected for the sensor depends on the anticipated rate of flow. **For ground water, “low-flow” membranes should be used.**
- ▶ All built-in thermistor thermometers must be calibrated and field checked before use (see section 6.1, “Temperature”).

Yellow Springs Instrument Company (YSI) DO instruments are used as an example in this chapter because they are in common use by USGS field personnel. The YSI 5700 series sensors have two separate thermistors. The temperature of the solution is measured by the temperature-display thermistor, mounted in a stainless steel tube on the side of the sensor. Next to the temperature-display thermistor is the temperature-compensation thermistor that compensates for temperature-caused changes in membrane-oxygen permeability. **The permeability of the Teflon™ membrane changes about 3 percent for each 1°C change in temperature.**

**Table 6.2-1.** Equipment and supplies used for amperometric method of dissolved-oxygen determination<sup>1</sup>

[DO, dissolved oxygen; YSI, Yellow Springs Instrument Company; mm, millimeter; g, gram; mL, milliliter; L, liter; DIW, deionized water]

- ✓ DO instrument and DO sensor or multiparameter instrument with DO capability
  - Temperature readout display, analog or digital
  - Temperature and pressure compensated
  - Operating range at least  $-5^{\circ}\text{C}$  to  $+45^{\circ}\text{C}$
  - Measure concentrations  $\geq 1$  to 20 mg/L
  - Minimum scale readability, preferably 0.05 mg/L DO
  - Calibrated accuracy within 5 percent or  $\pm 0.3$  mg/L DO, whichever is less
- ✓ DO sensor membrane replacement kit: membranes, O-rings, filling solution
- ✓ Stirrer attachment for DO sensor
- ✓ Calibration chamber: YSI model 5075A sensor, or equivalent
- ✓ Pocket altimeter-barometer, calibrated; measures to nearest 2 mm, Thommen model 2000
- ✓ Thermometer, calibrated (see section 6.1 for selection and calibration criteria)
- ✓ Zero DO calibration solution<sup>2</sup>: dissolve 1 g sodium sulfite and a few crystals of cobalt chloride in 1 L DIW
- ✓ Flowthrough chamber for determining DO in ground water
- ✓ Oxygen solubility table (table 6.2-6)
- ✓ Waste disposal container or equivalent
- ✓ Spare batteries, filling solution, and membranes
- ✓ Log books for DO instrument and barometer for recording all calibrations, maintenance, and repairs

<sup>1</sup>Modify this list to meet specific needs of the field effort. See table 6.2-3 for equipment list for iodometric DO determination and Table 6.2-5 for equipment list for Rhodazine-D™ DO determination.

<sup>2</sup>Prepare fresh zero DO solution before each field trip.

Analog YSI instruments have two thermistors that compensate for the effects of temperature. Digital YSI instruments do not contain instrument-compensating thermistors, but rely on the temperature-display thermistor in the sensor to calculate membrane permeability.

**CAUTION: Before handling any chemicals, refer to the Material Safety Data Sheet (MSDS) for safety precautions.**

---

## Maintenance and storage

Dissolved-oxygen instruments and sensors are sophisticated electronic equipment that require care in handling and operation.

- ▶ Follow the manufacturer's recommendations for short-term (field) and long-term (office) storage of sensors and for performance checks.
- ▶ Protect instruments and sensors from being jostled during transportation, from sudden impacts, sudden temperature changes, and extremes of heat and cold.

### *Before each field trip:*

1. Check the temperature-display thermistor in the DO sensor against a certified thermometer over the normal operating range of the instrument. If a thermistor reading is incorrect, apply a correction or return the instrument to the manufacturer for adjustment.
2. Recondition the DO sensor if it fails a performance check.
3. Check the instrument batteries and all electrical connections.
4. Test the instrument to ensure that it will read zero in a DO-free solution.
  - If the instrument reading exceeds 0.2 mg/L, then the sensor membrane and electrolyte (if present) need to be replaced or the sensor needs to be repaired.
  - Before repairing or replacing the sensor, check zero DO again with a freshly prepared zero DO solution.
5. On analog instruments:
  - Check mechanical zero (if applicable) before turning the instrument on; adjust it if necessary.
  - Check redline and zero readings (if applicable) and adjust as needed.
  - If the instrument cannot be adjusted, recharge or replace the batteries.
6. Calibrate the pocket altimeter-barometer.

---

**CALIBRATION 6.2.1.B**

Calibration and operation procedures for the amperometric method differ among instrument types and makes—refer to manufacturer's instructions. Record all calibration information in instrument log books and copy calibration data onto field forms at the time of calibration.

Atmospheric pressure, temperature of the water or water vapor, and conductivity (or salinity) of the water must be known to determine the theoretical amount of oxygen that can be dissolved in water. Although the salinity correction can be made either during calibration or after measurement, **the preferred USGS method is to apply salinity correction factors after calibration and measurement** (recalibration is necessary for each field variation in salinity and temperature if the correction is made during calibration). For salinity-correction procedures, see section 6.2.4.

---

### Atmospheric pressure correction

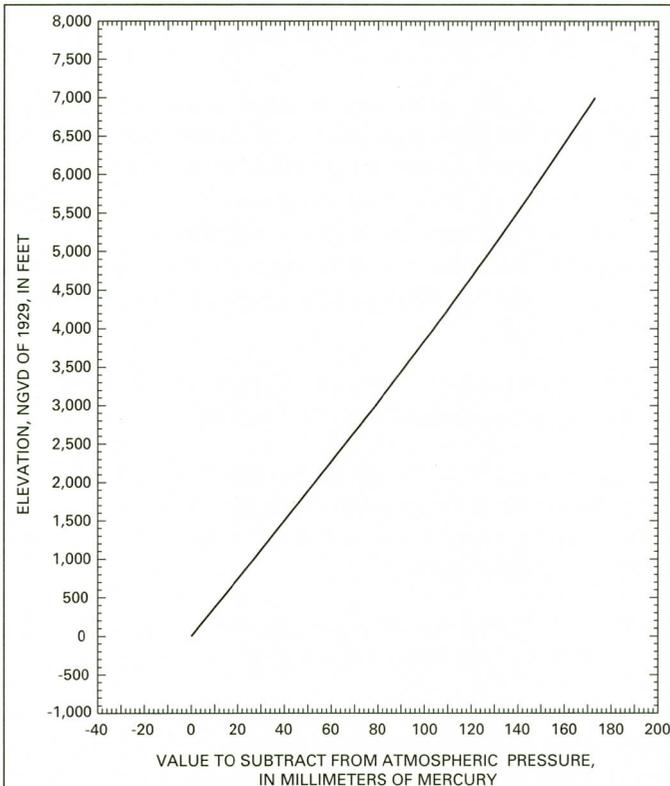
**Ambient atmospheric pressure is true atmospheric pressure at the measurement site, not that which has been adjusted to sea level.** Atmospheric pressure reported by the National Weather Service generally is not the true (ambient) value. Weather Service atmospheric readings usually are adjusted to sea level and must be adjusted back to the elevation of the weather station. Upon request, a weather station sometimes provides unadjusted atmospheric pressure.

- ▶ Use a calibrated pocket altimeter-barometer to determine ambient atmospheric pressure to the nearest 1 mm of mercury.
- ▶ Check the accuracy of all field barometers before each field trip, and record readings and adjustments in the log book. If possible, check barometer accuracy with information from an official weather station.
- ▶ Use table 6.2-2 and figure 6.2-1 if the value used for atmospheric pressure has been adjusted to sea level.
- ▶ To correct weather station readings adjusted to sea level to ambient atmospheric pressure: subtract appropriate values shown (table 6.2-2, fig. 6.2-1) from atmospheric readings adjusted to sea level (shown in millimeters of mercury).

Although atmospheric pressure does not decrease linearly with increases in elevation, linear interpolation is acceptable within the elevation ranges given in table 6.2–2. Alternatively, plot the values from table 6.2–2 and extrapolate subtraction factors directly from the graph. Section 6.2.4 contains the table of oxygen solubilities at various temperatures and pressures.

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

Elevation of weather station (feet above sea level)	Value to subtract (millimeters of mercury)
0	0
1,000	27
2,000	53
3,000	79
4,000	104
5,000	128
6,000	151



**Figure 6.2–1.** Factors used to correct atmospheric pressures adjusted to sea level.

## Calibration procedures

Four procedures are described below for calibrating a DO system: (1) air-calibration chamber in water, (2) calibration with air-saturated water, (3) air-calibration chamber in air, and (4) iodometric (Winkler) titration.

When using an analog instrument:

- ▶ Do not change scales without either recalibrating or verifying that identical readings are obtained on both scales.
- ▶ Place an analog instrument in its operating position—either vertical, tilted, or on its back—before calibration. More readjustments may be necessary if the operating position is changed, so do not change the position of the meter until DO measurement is complete.

### *Procedure 1—Air-calibration chamber in water*

An air-calibration chamber permits calibration of the DO sensor at the temperature of the water in which DO concentration is to be measured. This calibration procedure minimizes errors caused by temperature differences. Keep the interior of the chamber just moist during the calibration procedure, not filled with water.

1. Dip the calibration chamber into the surface or ground water to be measured; pour out the excess water (leave a few drops).
  - Insert the DO sensor into the wet chamber (this ensures 100-percent humidity).
  - If a YSI model 5739 sensor is used, the pressure-compensating diaphragm on the side of the sensor must be enclosed within the calibration chamber during calibration.
2. Immerse the calibration chamber into the water to be measured. Allow 10 to 15 minutes for the air temperature inside the chamber to equilibrate with the water (see TECHNICAL NOTE at end of Procedure 1).
  - For streams, choose an area of the stream that closely approximates mean stream temperature. In shallow streams, try to place the chamber in an area that represents the stream but that is shaded from direct sunlight.

**Use of an air calibration chamber in water is the preferred field procedure.**

- For ground water, use temperature-stabilized purge water.
  - Check that no water can leak into the calibration chamber and that the membrane does not have droplets of water adhering to it. The water droplets reduce the rate of oxygen diffusion through a membrane, producing erroneous results. If water has entered the chamber, repeat the procedure from step 1.
3. Determine the ambient atmospheric pressure with a calibrated pocket altimeter-barometer to the nearest 1 mm of mercury.
  4. Read the temperature within the chamber to the nearest 0.5°C.
    - The temperature inside the chamber should approximate the water temperature, measured with a calibrated thermometer.
    - If the two temperatures do not match, allow additional time for equilibration of the chamber with the water temperature.
    - If the temperature in the chamber still does not approximate the water temperature, the thermistor in the DO sensor might be malfunctioning. Measure the water temperature with a calibrated field thermometer.
  5. Use the tables in section 6.2.4 to determine the DO saturation value at the measured water temperature and atmospheric pressure (table 6.2–6). If a salinity correction will be applied during calibration, consult the instructions in section 6.2.4.
  6. Select a proper scale:
    - Analog YSI instruments—0 to 10 or 0 to 20 mg/L.
    - Digital YSI instruments—0.1 or 0.01 mg/L.
  7. Adjust the calibration control until the instrument reads a DO saturation value determined from oxygen solubility (table 6.2–6).
    - The instrument is now calibrated and ready for use. Remove the sensor from the calibration chamber.
    - As long as no excess water is in the chamber, the sensor is ready to be placed in the environment to be measured.

TECHNICAL NOTE: The YSI 5075A calibration chamber is designed to allow the membrane surface of a DO electrode (model 5739) to be at ambient atmospheric pressure while in the chamber. Because the pressure-compensating diaphragm must remain at atmospheric pressure, check the calibration chamber vent tube (from chamber through end of handle) to ensure that it is not plugged with debris or filled with water.

**Do not let water leak from or droplets adhere to the dissolved-oxygen membrane.**

### *Procedure 2—Air-saturated water*

In this procedure, the DO sensor or instrument system is calibrated against water that is saturated with oxygen at a known temperature and ambient atmospheric pressure.

1. The temperature and conductivity of water used for calibration should be about the same as the temperature and conductivity of the water to be measured.
  - **At the field site**—obtain about 1 L of water from the water body to be measured.
  - **In the laboratory**—obtain about 1 L of deionized or tap water.
2. Place the DO sensor and calibration water in a large beaker or open-mouth container.
  - Allow the sensor to come to thermal equilibrium with the water temperature.
  - Shield the beaker or container from direct sunlight and wind to minimize temperature variations.
3. Aerate the water for 5 to 10 minutes. Using a battery-operated aquarium pump or minnow-bucket aerator and a short piece of tubing, attach a gas diffusion stone to the end of the tubing and place it at the bottom of the beaker of calibration water.
4. Determine if the water is 100 percent saturated with oxygen.
  - Switch the DO instrument to the 0- to 10-mg/L scale on an analog instrument or to the 0.1-mg/L scale on a digital instrument.
  - Adjust the instrument reading to approximately 8 mg/L with the calibration control.
  - Observe the instrument while aerating the calibration water. When no change in the DO reading is observed on the instrument for 4 to 5 minutes, assume that the water is saturated.
5. Read the ambient atmospheric pressure from the pocket altimeter-barometer to the nearest 1 mm of mercury.
6. Check mechanical zero. Adjust if necessary.

7. Read the temperature of the calibration water to the nearest 0.5°C.

**Calibration must be completed with the temperature of calibration water at the value measured, to ensure that the actual DO saturation of calibration water is not less than 100 percent (undersaturated) or greater than 100 percent (oversaturated).**

8. Using the oxygen solubility table 6.2–6, determine the DO saturation value at the measured temperature and atmospheric pressure of the calibration water. (Refer to section 6.2.4 and table 6.2–7 for salinity corrections.)
9. Select a proper scale:
  - Analog YSI instruments—0 to 10 or 0 to 20 mg/L.
  - Digital YSI instruments—0.1 or 0.01 mg/L.
10. Turn off the aerator and adjust the calibration control until the instrument reads a saturation value of DO as determined above. The instrument is now calibrated and ready for use.

**For accurate calibration, be sure that the water is 100 percent saturated with oxygen (step 4 above).**

### *Procedure 3—Air-calibration chamber in air*

This procedure is similar to the procedure for air-calibration chamber in water, except that the calibration chamber is in air rather than in water.

- ▶ The air-calibration-chamber-in-air procedure requires sensors in which the temperature-sensing thermometer is adjacent to the membrane.
  - ▶ The DO instrument used must be able to automatically compensate for temperature changes. The YSI analog and digital DO instruments are automatically temperature compensating for changes in the solubility of oxygen in water and in the permeability of the sensor membrane.
1. Wet the inside of the calibration chamber with water—pour out the excess water (leave a few drops) and insert the sensor into the chamber (this ensures 100-percent humidity).
  2. Allow 10 to 15 minutes for the DO sensor and the air inside the calibration chamber to equilibrate.

3. Read the ambient atmospheric pressure (from the pocket altimeter-barometer) to the nearest 1 mm of mercury.
4. Check mechanical zero. Adjust if necessary.
5. Measure the temperature in the calibration chamber and observe the readings until the instrument stabilizes. Read the temperature to the nearest 0.5°C.
  - The temperature inside the chamber should approximate the water temperature, measured with a calibrated thermometer.
  - If the two temperatures do not match, allow additional time for the chamber and the water temperature to equilibrate.
  - If the temperature in the chamber still does not approximate the water temperature, the thermistor in the DO sensor might be malfunctioning. Measure the water temperature with a calibrated field thermometer.
6. Use the oxygen-solubility table 6.2–6 to determine the DO saturation at the measured temperature and atmospheric pressure. (Refer to section 6.2.4 and table 6.2–7 for salinity corrections.)
7. Select a proper scale:
  - Analog YSI instruments—0 to 10 or 0 to 20 mg/L.
  - Digital YSI instruments—0.1 or 0.01 mg/L.
8. Adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table. The instrument is now calibrated and ready for use.

**Do not use the air-calibration-in-air procedure if the calibration chamber temperature differs from the temperature of the water to be measured.**

#### *Procedure 4—Iodometric (Winkler) titration*

The iodometric (Winkler) procedure is excellent for calibrating DO instrument systems in a laboratory environment (see TECHNICAL NOTE).

The USGS currently uses the Alsterberg-Azide modification to the Winkler titration procedure for iodometric determination of DO. **The accuracy of measurements using this method should be within at least  $\pm 0.05$  mg/L.**

Equipment and supplies needed for the iodometric titration are listed in table 6.2–3. The procedure involves the use of reagent packets that are available in premeasured pillow packets from QWSU and from commercial suppliers, or they can be prepared as described in Skougstad and others (1979) and American Public Health Association and others (1992). Clean all equipment before use.

**Table 6.2–3.** Equipment and supplies used for the iodometric dissolved-oxygen determination

[mL, milliliter; *N*, normal;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees Celsius]

- ✓ Beaker, 2,000 mL, glass or Teflon™
- ✓ Bottles for biological oxygen demand (BOD) analysis, glass stoppered, 300 mL
- ✓ Stirrer, magnetic
- ✓ Stirring bars, Teflon™ coated
- ✓ Cylinder, graduated, 250 mL
- ✓ Flask, Erlenmeyer, 250 mL
- ✓ Buret, 25-mL capacity with 0.05-mL graduations and Teflon™ stopcock
- ✓ Buret, support stand
- ✓ Buret, clamp, double
- ✓ Alkaline iodide-azide reagent
- ✓ Manganous sulfate reagent
- ✓ Sulfamic acid granules
- ✓ Phenylarsine oxide (PAO), 0.025 *N* titrant
- ✓ Starch indicator solution
- ✓ Clippers, for opening reagent pillows
- ✓ Appropriate safety gloves, glasses, and apron
- ✓ Waste disposal container
- ✓ White background sheet
- ✓ Deionized water (maximum conductivity of 1  $\mu\text{S}/\text{cm}$ )
- ✓ Bottle, squeeze dispenser, for deionized water
- ✓ Thermometer, calibrated (see NFM 6.1 for selection and calibration criteria)
- ✓ Pocket altimeter-barometer, calibrated, Thommen model 2000™ or equivalent

TECHNICAL NOTE: The iodometric procedure might be appropriate under some circumstances for making field measurements of DO. It is not recommended for routine determination of DO in surface and ground water because (1) the accuracy achievable can be variable and is dependent on the experience and technique of the data collector, and (2) field conditions can make preventing exposure of the sample to atmospheric oxygen difficult.

- ▶ When calibrating instruments in the laboratory using the Winkler procedure, the DO instrument is calibrated against deionized water (or the pure saline solution equivalent to that of the ambient water to be measured) in which the DO concentration has been determined iodometrically.
- ▶ If a saline solution is used to approximate the environmental water, do not apply a salinity correction factor.

**Measure DO on at least two subsamples, for quality control.** Results of two iodometric titrations should agree within 1 mg/L. If they do not agree, repeat the titration on a third subsample.

1. Fill a 2,000-mL beaker with deionized water that is near DO saturation. The water temperature should be close to the ambient laboratory temperature.
2. Prepare the DO instrument system for operation per the manufacturer's instructions.
3. Place the DO sensor in a beaker of distilled water. With a magnetic stirrer, maintain a velocity of at least 1 ft/s past the DO sensor.
4. Monitor the DO concentrations of the deionized water with the DO instrument system. After the DO instrument reading has stabilized, fill two BOD bottles with deionized water from the beaker.
5. Determine the DO concentration of the water in each BOD bottle, as follows:
  - a. Add one each of the following dry reagent pillow packets:
    - alkaline iodide-azide (white powder).
    - manganous sulfate (pinkish-colored powder).
  - b. Recap the bottle. **Do not allow air bubbles to be trapped in the bottle.**

- c. Invert the bottle 25 times or more to completely dissolve the reagents.
  - A brown flocculent indicates the presence of DO.
  - Allow the brown flocculent to settle halfway down the bottle (approximately 5 minutes).
  - Invert the bottle 25 times again; let the flocculent settle again.
- d. Invert the bottle another 25 times; add one reagent pillow of sulfamic acid (grayish granules, the longest of the three pillows).
- e. Recap the bottle without introducing air or air bubbles. Invert the bottle 25 times, until all of the flocculent and granules are dissolved.
- f. Fill a clean 25-mL buret with 0.025 N phenylarsine oxide (PAO) titrant. Remove any air bubbles beneath the stopcock and zero the meniscus.
- g. Use a clean graduated cylinder to measure 200 mL of the sample and pour the sample into a clean, wide-mouth Erlenmeyer flask.
- h. Place the flask on a magnetic stirrer. Add a clean Teflon™ stirring bar and stir the sample at a moderate rate **without aerating the sample**.
- i. Add increments of PAO titrant until the color turns pale straw-yellow.
- j. Add 1 to 2 mL of starch solution (this causes the sample to turn blue).
- k. Very slowly add more PAO titrant until the sample just turns clear (a white background behind the bottle will help you see the color change).
- l. Record the volume of PAO titrant used, in milliliters.
  - For a 200-mL sample, the volume of titrant added is directly proportional to the amount of DO in milligrams per liter.
  - To calculate DO for a sample volume greater or less than 200 mL,
 
$$DO(\text{mg/L}) = \left( \frac{200}{\text{sample volume}} \right) \times \text{titrant added (in mL)}$$
- m. Record the DO value. Rinse the equipment with deionized water.
- n. **Quality control**—Repeat steps 1 through 5 on a second subsample. Both titration values should agree within 0.1 mg/L. If they do not, repeat titration on a third bottle.
- o. Recheck the field instrument for proper functioning per the manufacturer's instructions: adjust the calibration control until the DO instrument system reads the DO concentration determined.

## MEASUREMENT 6.2.1.C

The solubility of oxygen in water depends on the partial pressure of oxygen in air, the temperature of the water, and the dissolved-solids content of the water.

- ▶ The higher the atmospheric pressure and the lower the temperature and conductivity, the more oxygen can be dissolved in the water.
- ▶ Degassing, mineral precipitation, and other chemical, physical, and biological reactions can cause the DO concentration of a water sample to change significantly within minutes after sample collection.
- ▶ The solubility of oxygen in water decreases as salinity increases. Correction factors for salinity normally are applied after measuring DO. Information about oxygen solubility and salinity and a salinity correction factors table are in 6.2.4.

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### Surface water

Standard DO determination for surface water represents the cross-sectional median or mean concentration of dissolved oxygen at the time of observation.

- ▶ Measuring DO concentration at one distinct spot in a cross section is valid only for flowing water with a cross-sectional DO variation of less than 0.5 mg/L.
- ▶ Determining DO in a single vertical at the centroid of flow at the midpoint of the vertical is only representative of the cross section under ideal mixing conditions.
- ▶ Do not measure DO in or directly below sections with turbulent flow, in still water, or from the bank, unless these conditions represent most of the reach or are required by the study objectives.
- ▶ Apply salinity correction, if needed, after measurement.

**Dissolved oxygen must be measured in situ.  
Never measure DO in subsamples from a sample splitter.**

*Follow the 7 steps below to measure DO in surface water:*

1. Calibrate the DO instrument system at the field site and check that the temperature thermistor has been District-certified within the past 4 months (within 12 months if a liquid-in-glass thermometer is used).
2. Record the DO variation from the cross-sectional profile and select the sampling method (NFM 6.0):
  - **Flowing, shallow stream**—Wade to the location(s) where DO is to be measured.
  - **Stream too deep or swift to wade**—Lower a weighted DO sensor with calibrated temperature sensor from a bridge, cableway, or boat. (Do not attach the weight to the sensors or sensor cables.)
  - **Still-water conditions**—Measure DO at multiple depths at several points in the cross section.
3. Immerse the DO and temperature sensors directly into the water body and allow the sensors to equilibrate to the water temperature (no less than 60 seconds).
  - If the water velocity at the point of measurement is less than about 1 ft/s, use a stirring device or stir by hand to increase the velocity (to hand stir, raise and lower the sensor at a rate of about 1 ft/s, but do not break the surface of the water).
  - Very high velocities can cause erroneous DO measurements.
4. Record the temperature without removing the sensors from the water. Turn the operation switch to the range that was used during instrument calibration.
5. After the instrument reading has stabilized (allow 1 to 2 minutes and  $\pm 0.3$  mg/L), record the median DO concentration (see NFM 6.0).
6. For EWI or EDI measurements, proceed to the next station in the cross section and repeat steps 3 through 5. When measurements for the stream have been completed, remove the sensor from the water, rinse it with deionized water, and store it according to the manufacturer's instructions.
7. Record DO concentrations on the field forms:
  - **In still water—median** of three or more sequential values.
  - **EDI—mean** value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
  - **EWI—mean (or median)** of all subsections measured.

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## Ground water

To determine the concentration of DO in an aquifer, the water being measured must not contact air. Study objectives and site characteristics will dictate the specific procedures selected. **If the DO concentration is less than 1 mg/L, refer to the spectrophotometric method (section 6.2.2).**

- ▶ Throughout measurement, use equipment that avoids aeration, and operate equipment to mitigate losses or gains of dissolved gases (consult NFM 6.0 for proper downhole and flowthrough-chamber sampling procedures).
- ▶ Use a positive-displacement submersible pump and high-density plastic sample tubing that is relatively gas impermeable, if possible.
- ▶ Use optically clear materials for the tubing and chamber (to check that entrained bubbles are not present). Air bubbles that adhere to the sides of the tubing and flowthrough chamber will add significant error to low-level DO measurements (A.F. White, U.S. Geological Survey, written commun., 1993).

**Never use a bailed or other discrete sample for DO determination.**

*Follow the 7 steps below to measure DO in ground water:*

1. Calibrate the DO system on site. Check that the thermistor thermometer has been District certified within the past 4 months.
2. Install the DO equipment (see section 6.0.3, "Ground Water"):
  - **Downhole system**—Lower the DO and temperature sensors to the sampling point, followed by the pump, to monitor DO variation during purging. If a downhole system will be used only for final DO determination after the samples are collected and the pump is removed, attach a stirrer to the DO instrument before lowering it to the sampling point.
  - **Flowthrough-chamber system**—Refer to section 6.0.3 for installation guidelines. Be sure to:

- a. Install the DO sensor through an air-tight grommet, checking that the seal is intact. Check that the sensors are properly immersed.
  - b. Flush air bubbles from the tubing walls and flowthrough chamber—Tap the tubing with the blunt end of a tool to dislodge entrained air bubbles (see TECHNICAL NOTE).
  - c. Check for and eliminate backpressure in the chamber.
3. Keep flow passing the DO sensor laminar and constant.
  4. Measure and record DO at regular intervals throughout purging. Allow the sensors to equilibrate with ground water for 5 minutes or more at the flow rate to be used for sampling.
  5. Check the stability (variability) of DO toward the end of purging.
    - The stability criterion is met when five consecutive readings made at regularly spaced intervals of 3 to 5 minutes or more are within 0.3 mg/L. (For each reading, monitor fluctuations for 30 to 60 seconds and record the median value, if necessary.)
    - If the  $\pm 0.3$  mg/L criterion is not met, lengthen the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals.
  6. Report sample DO as the median of the final five DO readings recorded. Record any difficulty with stabilization on field forms.
  7. Remove the sensor from water and rinse it with deionized water.

TECHNICAL NOTE: Anomalously high DO measurements commonly are caused by aeration of ground water during pumping. This can result from air leakage through loose fittings on production-well pumps (for example, turbine pumps) and also if drawdown in the aquifer introduces air into the cone of depression or through well-screen perforations. To avoid these problems, review information about the pump, well-construction and drawdown data, and previous data records (A.F. White, U.S. Geological Survey, written commun., 1993).

**Air bubbles in the lines and flowthrough chamber can add significant error to low DO readings.**

## TROUBLESHOOTING (AMPEROMETRIC METHOD) 6.2.1.D

The troubleshooting suggestions given in table 6.2-4 are not exhaustive; consult the instrument manufacturer for additional guidance. Faulty batteries can cause erratic readings.

- ▶ Check the voltage of the batteries.
- ▶ Start with good batteries in the instrument and carry spares.

**Table 6.2-4.** Troubleshooting guide for amperometric determination of dissolved-oxygen concentration

Symptom	Possible cause and corrective action
Instrument does not adjust to red line	<ul style="list-style-type: none"> <li>• Weak batteries—replace.</li> <li>• Faulty meter compensation thermistor (analog instruments only)—repair.</li> </ul>
Instrument drifts or takes excessive time to stabilize	<ul style="list-style-type: none"> <li>• Thermal equilibrium of DO sensor with water has not been reached—wait longer.</li> <li>• Weak batteries—replace.</li> <li>• DO sensor needs maintenance—recondition.</li> </ul>
Erratic instrument readings	<ul style="list-style-type: none"> <li>• Break in cable—replace cable.</li> <li>• Faulty connection at instrument or sensor—clean contact and tighten connection.</li> <li>• Hole in membrane—replace membrane, recondition.</li> <li>• Air bubble in sensor—recondition sensor.</li> <li>• Weak batteries—replace with new batteries.</li> </ul>
Instrument is slow to react	<ul style="list-style-type: none"> <li>• Gold cathode tarnished—buff with pencil eraser and recondition sensor.</li> <li>• Fouled membrane—recondition sensor and replace membrane.</li> </ul>
Instrument will not read zero in sodium sulfite solution.	<ul style="list-style-type: none"> <li>• Solution contains oxygen—add additional sodium sulfite.</li> <li>• Instrument still does not read zero—recondition sensor.</li> <li>• Faulty oxygen or polarizing thermistors (analog instruments only)—replace or repair.</li> </ul>
Instrument cannot be calibrated to read standards	<ul style="list-style-type: none"> <li>• Unable to adjust upward—check if more than one membrane is on the sensor.</li> <li>• Unable to adjust downward (membrane is probably too tight or too thin)—replace membrane.</li> <li>• Faulty polarizing voltage thermistor (analog instruments only)—repair.</li> <li>• Faulty meter compensation thermistor (analog instruments only)—repair.</li> <li>• Faulty oxygen thermistor (analog instruments only)—repair.</li> </ul>
Instrument shows inaccurate temperature	<ul style="list-style-type: none"> <li>• Faulty or uncalibrated temperature thermistor—calibrate, repair, or replace.</li> </ul>

## 6.2.2 SPECTROPHOTOMETRIC METHOD

The spectrophotometric method described here is recommended for accurate determination of DO concentrations in suboxic waters (less than 1.0 mg/L DO concentration). The method is based on a Rhodazine-D™ colorimetric technique adapted by White and others (1990), which minimizes atmospheric interaction with the water sampled.

- ▶ This technique has a sensitivity to 0.2 μmoles/L (0.006 mg/L)—an order of magnitude lower than the amperometric method.
- ▶ The technique was developed for ground water but it can be adapted for work in anoxic zones of lakes and reservoirs.

### 6.2.2.A EQUIPMENT AND SUPPLIES

Two sampling systems can be used: an in situ (downhole) sampler (see White and others, 1990) or a closed-system flowthrough cell through which sample water is pumped. Either sampling system uses partially evacuated oxygen-free glass ampoules containing Rhodazine-D™, that are broken along a prescored capillary tip while they are submerged in the water to be analyzed. Equipment and supplies needed for this method are listed on table 6.2–5.

**Table 6.2–5.** Equipment and supplies (Rhodazine-D™ technique)  
[mL, milliliters; μS/cm, microsiemens per centimeter at 25 degrees Celsius]

- ✓ Portable spectrophotometer, Bausch and Lomb Minispect-10™ or equivalent
- ✓ Ampoules with reagents, 10-mL glass, CHEMetrics Inc., Model K7553™
- ✓ Downhole sampler, to meet criteria described in White and others (1990)
- ✓ Flowthrough cell, modified to a closed-system device (alternative to sampling tool)
- ✓ Safety gloves, glasses, and apron
- ✓ Waste disposal container
- ✓ White background sheet
- ✓ Deionized water (maximum conductivity of 1 μS/cm)
- ✓ Bottle, squeeze dispenser, for deionized water

Kits available from CHEMetrics Incorporated contain prepackaged glass ampoules filled with a Rhodazine-D™ dye solution for two concentration ranges of dissolved oxygen: 0 to 1 mg/L (0 to 310  $\mu$ moles/L) or 0 to 40 mg/L (0 to 13  $\mu$ moles/L).

White and others (1990) used a portable Milton Roy Minispect-10™ battery-powered spectrophotometer. Any spectrophotometer of equal or better quality can be used.

TECHNICAL NOTE: The closed-system cell is not the same as the flowthrough-chamber system used in routine ground-water field measurements. The cell consists of a three-way tee to which inflow, outflow, and discharge tubing sections are fitted tightly; outflow is fitted with a short length of 3/8-in. tubing.

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## CALIBRATION AND INTERFERENCES 6.2.2.B

Dissolved oxygen is measured as percent absorbance by the spectrophotometer.

- ▶ A calibration chart is provided in the CHEMetrics kit, along with a regression formula to convert absorbance to micrograms per liter of DO for use with the Minispect-10™ spectrophotometer. No other standards are provided.
- ▶ The CHEMetrics kit contains a blank ampoule used to zero the spectrophotometer.
- ▶ Interferences from total salinity and major dissolved inorganic species are negligible.
- ▶ The method is affected significantly by the presence of reducible inorganic species such as ferric and cupric ions and hexavalent chromium, resulting in high-biased DO readings. The effect from reducible inorganic species can be corrected if the concentrations of the interfering species are known.
- ▶ Additional calibration is needed if the method will be used for heavily contaminated or acidic waters, by equilibrating a water sample with known partial pressures of atmospheric oxygen (White and others, 1990). Atmospheric oxygen standards are available from suppliers of gas chromatography equipment.

### 6.2.2.C MEASUREMENT

Rhodazine-D<sup>TM</sup> reagent reacts with DO to produce an oxidized complex characterized by a red-blue color. The color intensity is proportional to the concentration of the initial DO present.

*Follow the 7 steps below to measure DO using the Rhodazine-D<sup>TM</sup> method:*

1. Zero the spectrophotometer, using the blank provided in the kit (follow the manufacturer's instructions).
2. Set the spectrophotometer to the correct wavelength.
  - The Minispect-10<sup>TM</sup> spectrophotometer is set at a wavelength of 615 nm for calibrating and measuring.
  - Refer to the manufacturer's instructions for the correct wavelength when using a different spectrophotometer.
3. Collect the sample. Install either the downhole sampling tool (White and others, 1990) or use a closed-system flowthrough cell with a suitable pump.
  - **Downhole system—**
    - a. Carefully lower a sampling tool attached to a wire line.
    - b. At the collection point (in the well or surface water), break the scored tip of the ampoule using a sharp upward tug on the sampling tool. (This permits sample water to be drawn into the ampoule. During transit to the surface, progressively decreasing pressure in the ampoule prevents cross contamination from overlying water through the capillary tip.)
  - **Closed-system flowthrough cell—**
    - a. Fit inflow, outflow, and discharge tubing tightly into the three-way tee. Fit the outflow with a short length of 3/8-in. tubing. All fittings must be airtight to prevent aerating the sample.
    - b. Insert the glass ampoule, tip first, into the outflow tubing. The seal must be airtight.
    - c. Pinch the tubing so that the scored tip of the ampoule will break in the flow of water.

4. Insert the ampoule directly into the 1.27-cm spectrophotometer cell holder immediately after retrieval.
5. Read absorbance to the nearest 0.2  $\mu\text{moles/L}$  on the analog meter.
  - Allow the readings to stabilize first (usually within 2 minutes).
  - Read each DO value three times and record the median value.
6. Calculate the DO concentrations using regression equations (White and others, 1990).
  - To correct for appreciable concentrations of oxidized species of transition metals, use the stoichiometric relationships as described by White and others (1990).
7. **Quality control**—
  - Repeat steps 4 through 6 twice to document precision.
  - To document the variability of DO concentrations within the water system, repeat steps 3 through 6 on three sequentially collected samples.

**Analyze samples in the field immediately.**

## 6.2.3 REPORTING

Dissolved-oxygen concentrations are determined to the nearest 0.1 mg/L for amperometric measurements.

- ▶ Values less than 0.1 mg/L can be stored in the current NWIS data base, but will print out as "0.0" unless the data are retrieved as a flat file.
- ▶ If the concentration exceeds 20 mg/L, report ">20 mg/L."
- ▶ Note that the percentage of saturation can be greater than 100.
- ▶ Record the accuracy range of the instrument system or the method used in the data base (if possible). Report the accuracy range with the published values.
- ▶ Enter the DO value on the NWQL Analytical Services Request form and on the field form under the correct parameter code for the method used.

## CORRECTION FACTORS FOR OXYGEN SOLUBILITY AND SALINITY 6.2.4

Correction factors for the solubility of oxygen at various temperatures and pressures and for salinity based on conductivity are given in tables 6.2–6 and 6.2–7, respectively. Tables 6.2–6 and 6.2–7 were generated from the equations of Weiss (1970) and can be customized to cover the range and decimal places needed (see OWQ Technical Memorandum 81.11).

You can convert oxygen-saturation values for salinity using correction factors based on chloride concentration or conductivity. Refer to the manufacturer's instructions for the DO instrument before applying a salinity correction.

- ▶ Correcting DO solubility for saline waters (salinities greater than 2,000  $\mu\text{S}/\text{cm}$  or 1,000 mg/L chloride) varies with instrument type, calibration method, and the salts in solution.
- ▶ The correction based on conductivity (table 6.2–7) is more useful because accurate conductivity can be easily determined from a field measurement. Salinity correction factors based on chloride can be calculated using information provided in OWQ Technical Memorandum 79.10.
- ▶ Dissolved-oxygen instruments use either an automatic internal salinity correction, a manual salinity control knob for internal correction, or the calibration control knob for manual salinity correction.
- ▶ Check that instruments with automatic internal salinity correction use approved salinity correction factors.

### *Example of salinity correction:*

$$8.2 \text{ mg/L} \times 0.951 = 7.8 \text{ mg/L}$$

where,

8.2 mg/L is 100 percent DO saturation from table 6.2–6,

0.951 is the correction factor from table 6.2–7, and

7.8 mg/L is the corrected value.

For this example, you would adjust the DO instrument to 7.8 mg/L from 8.2 mg/L.

To express results as percent saturation, use the following equation:

$$\text{DO (percent saturation)} = \frac{\text{measured DO (mg/L)}}{\text{DO (mg/L at 100 percent saturation)}} \times 100$$

**Table 6.2–6.** Solubility of oxygen in water at various temperatures and pressures  
 [From R.F. Weiss (1970). Temp °C, temperature in degrees Celsius; atmospheric pressures from 695 to 600 millimeters mercury begin after 40°C]

Temp °C	Atmospheric pressure, in millimeters of mercury																			
	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	700
0.0	15.3	15.2	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4
0.5	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2
1.0	14.8	14.7	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2	13.2	13.1
1.5	14.6	14.5	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2	13.2	13.1	13.0	12.9
2.0	14.4	14.3	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7
2.5	14.2	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.5
3.0	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.5	12.5	12.4
3.5	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4	12.3	12.2
4.0	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4	12.3	12.2	12.1	12.0
4.5	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.1	12.0	11.9
5.0	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7
5.5	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7	11.7	11.6
6.0	13.0	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4
6.5	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.9	11.8	11.7	11.6	11.5	11.5	11.4	11.3
7.0	12.7	12.6	12.5	12.4	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2	11.1	11.1
7.5	12.5	12.4	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0
8.0	12.4	12.3	12.2	12.1	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0	10.9
8.5	12.2	12.1	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7
9.0	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.8	10.7	10.6
9.5	11.9	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.6	10.5
10.0	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4
10.5	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2
11.0	11.5	11.4	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.3	10.2	10.1	10.1
11.5	11.4	11.3	11.2	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0
12.0	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.0	10.0	9.9
12.5	11.1	11.1	11.0	10.9	10.8	10.8	10.7	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8
13.0	11.0	10.9	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.7
13.5	10.9	10.8	10.7	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.6
14.0	10.8	10.7	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5
14.5	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4

**Table 6.2-6.** Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																			
	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	700
15.0	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3
15.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.2
16.0	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.1	9.1
16.5	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.2	9.1	9.0	9.0	9.0
17.0	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9
17.5	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.8
18.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.7
18.5	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6
19.0	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5
19.5	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4
20.0	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.3
20.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3
21.0	9.3	9.2	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2
21.5	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1
22.0	9.1	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8.0
22.5	9.0	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9
23.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9
23.5	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8
24.0	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7
24.5	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6
25.0	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6
25.5	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5
26.0	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4
26.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4
27.0	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3
27.5	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2
28.0	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2
28.5	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1
29.0	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0
29.5	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0

**Table 6.2-6.** Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																				
	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	700	
30.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9
30.5	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.9
31.0	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.8
31.5	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.8	6.7
32.0	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.7
32.5	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.7	6.6
33.0	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.6
33.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.6	6.5
34.0	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.5
34.5	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4
35.0	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.4	6.3
35.5	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.4	6.3	6.3
36.0	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.3	6.2
36.5	7.1	7.0	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.2
37.0	7.0	7.0	6.9	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.2	6.1
37.5	7.0	6.9	6.9	6.8	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.1
38.0	6.9	6.9	6.8	6.8	6.7	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.1	6.0
38.5	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	6.0
39.0	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	6.0	6.0
39.5	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	6.0	6.0	5.9
40.0	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.9	5.9

**Table 6.2-6.** Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																			
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605	600
0.0	13.3	13.2	13.1	13.0	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5
0.5	13.1	13.1	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3
1.0	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2
1.5	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.0
2.0	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9
2.5	12.4	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.0	10.9	10.8	10.7
3.0	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6
3.5	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7	10.6	10.5	10.4
4.0	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3
4.5	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.5	10.4	10.3	10.3	10.2
5.0	11.6	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2	10.1	10.0
5.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9
6.0	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.0	9.9	9.9	9.8
6.5	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.7	9.7
7.0	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.3	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.6	9.5
7.5	10.9	10.9	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4
8.0	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.6	9.5	9.5	9.4	9.3
8.5	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.3	9.3	9.2
9.0	10.5	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1
9.5	10.4	10.3	10.3	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.0	9.0
10.0	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	8.9	8.9
10.5	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8	8.8
11.0	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.7	8.7
11.5	9.9	9.9	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8	8.8	8.7	8.6	8.6
12.0	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.7	8.7	8.6	8.5	8.5
12.5	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.6	8.6	8.5	8.4	8.4
13.0	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.5	8.5	8.4	8.3	8.3
13.5	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.2	8.2
14.0	9.4	9.3	9.3	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1
14.5	9.3	9.2	9.2	9.1	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0

**Table 6.2-6.** Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																			
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605	600
15.0	9.2	9.1	9.1	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9
15.5	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8
16.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.7
16.5	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7
17.0	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.6	7.6
17.5	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5
18.0	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.5	7.5	7.4
18.5	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.3
19.0	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3
19.5	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.2	7.2
20.0	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1
20.5	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.0
21.0	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0
21.5	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9
22.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.8
22.5	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8
23.0	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7
23.5	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6
24.0	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6	6.6
24.5	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5
25.0	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.4
25.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.4	6.4
26.0	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.5	6.5	6.4	6.4	6.3
26.5	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
27.0	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2
27.5	7.2	7.1	7.1	7.0	7.0	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2
28.0	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.1	6.1
28.5	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.2	6.2	6.1	6.1	6.0
29.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.2	6.2	6.1	6.1	6.0	6.0
29.5	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9

**Table 6.2-6.** Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																			
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605	600
30.0	6.9	6.8	6.8	6.7	6.7	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9
30.5	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8
31.0	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8
31.5	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7
32.0	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7
32.5	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6
33.0	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6
33.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5
34.0	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5
34.5	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4
35.0	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4
35.5	6.2	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3
36.0	6.2	6.1	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3
36.5	6.1	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.2
37.0	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2
37.5	6.0	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2	5.2
38.0	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2	5.2	5.1
38.5	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1
39.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0
39.5	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0	5.0
40.0	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0	5.0	5.0

**Table 6.2-7.** Salinity correction factors for dissolved oxygen in water (based on conductivity)

[From R.F. Weiss (1970). Temp °C, temperature in degrees Celsius; salinity correction factors at 30 to 35 degrees Celsius are shown at the end of this table]

Temp °C	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
	0	1000	2000	3000	4000	5000	6000	7000	8000	9000	10000	11000	12000	13000	14000	15000	16000
0.0	1.000	0.996	0.992	0.989	0.985	0.981	0.977	0.973	0.969	0.965	0.961	0.957	0.953	0.950	0.946	0.942	0.938
1.0	1.000	0.996	0.992	0.989	0.985	0.981	0.977	0.973	0.969	0.965	0.962	0.958	0.954	0.950	0.946	0.942	0.938
2.0	1.000	0.996	0.992	0.989	0.985	0.981	0.977	0.973	0.970	0.966	0.962	0.958	0.954	0.950	0.946	0.942	0.938
3.0	1.000	0.996	0.993	0.989	0.985	0.981	0.977	0.974	0.970	0.966	0.962	0.958	0.954	0.951	0.947	0.943	0.939
4.0	1.000	0.996	0.993	0.989	0.985	0.981	0.978	0.974	0.970	0.966	0.962	0.959	0.955	0.951	0.947	0.943	0.939
5.0	1.000	0.996	0.993	0.989	0.985	0.981	0.978	0.974	0.970	0.966	0.963	0.959	0.955	0.951	0.947	0.944	0.940
6.0	1.000	0.996	0.993	0.989	0.985	0.982	0.978	0.974	0.970	0.967	0.963	0.959	0.955	0.952	0.948	0.944	0.940
7.0	1.000	0.996	0.993	0.989	0.985	0.982	0.978	0.974	0.971	0.967	0.963	0.959	0.956	0.952	0.948	0.944	0.941
8.0	1.000	0.996	0.993	0.989	0.986	0.982	0.978	0.975	0.971	0.967	0.963	0.960	0.956	0.952	0.949	0.945	0.941
9.0	1.000	0.996	0.993	0.989	0.986	0.982	0.978	0.975	0.971	0.967	0.964	0.960	0.956	0.953	0.949	0.945	0.941
10.0	1.000	0.996	0.993	0.989	0.986	0.982	0.979	0.975	0.971	0.968	0.964	0.960	0.957	0.953	0.949	0.946	0.942
11.0	1.000	0.996	0.993	0.989	0.986	0.982	0.979	0.975	0.971	0.968	0.964	0.961	0.957	0.953	0.950	0.946	0.942
12.0	1.000	0.997	0.993	0.989	0.986	0.982	0.979	0.975	0.972	0.968	0.965	0.961	0.957	0.954	0.950	0.946	0.943
13.0	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.975	0.972	0.968	0.965	0.961	0.958	0.954	0.950	0.947	0.943
14.0	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.976	0.972	0.969	0.965	0.961	0.958	0.954	0.951	0.947	0.943
15.0	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.976	0.972	0.969	0.965	0.962	0.958	0.955	0.951	0.947	0.944
16.0	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.976	0.972	0.969	0.966	0.962	0.958	0.955	0.951	0.948	0.944
17.0	1.000	0.997	0.993	0.990	0.986	0.983	0.980	0.976	0.973	0.969	0.966	0.962	0.959	0.955	0.952	0.948	0.945
18.0	1.000	0.997	0.993	0.990	0.987	0.983	0.980	0.976	0.973	0.969	0.966	0.963	0.959	0.956	0.952	0.949	0.945
19.0	1.000	0.997	0.993	0.990	0.987	0.983	0.980	0.976	0.973	0.970	0.966	0.963	0.959	0.956	0.952	0.949	0.945
20.0	1.000	0.997	0.993	0.990	0.987	0.983	0.980	0.977	0.973	0.970	0.966	0.963	0.960	0.956	0.953	0.949	0.946
21.0	1.000	0.997	0.993	0.990	0.987	0.984	0.980	0.977	0.973	0.970	0.967	0.963	0.960	0.957	0.953	0.950	0.946
22.0	1.000	0.997	0.993	0.990	0.987	0.984	0.980	0.977	0.974	0.970	0.967	0.964	0.960	0.957	0.953	0.950	0.947
23.0	1.000	0.997	0.994	0.990	0.987	0.984	0.980	0.977	0.974	0.971	0.967	0.964	0.960	0.957	0.954	0.950	0.947
24.0	1.000	0.997	0.994	0.990	0.987	0.984	0.981	0.977	0.974	0.971	0.967	0.964	0.961	0.957	0.954	0.951	0.947
25.0	1.000	0.997	0.994	0.990	0.987	0.984	0.981	0.977	0.974	0.971	0.968	0.964	0.961	0.958	0.954	0.951	0.948
26.0	1.000	0.997	0.994	0.990	0.987	0.984	0.981	0.978	0.974	0.971	0.968	0.965	0.961	0.958	0.955	0.951	0.948
27.0	1.000	0.997	0.994	0.991	0.987	0.984	0.981	0.978	0.975	0.971	0.968	0.965	0.962	0.958	0.955	0.952	0.948
28.0	1.000	0.997	0.994	0.991	0.987	0.984	0.981	0.978	0.975	0.972	0.968	0.965	0.962	0.959	0.955	0.952	0.949
29.0	1.000	0.997	0.994	0.991	0.988	0.984	0.981	0.978	0.975	0.972	0.969	0.965	0.962	0.959	0.956	0.952	0.949

**Table 6.2-7.** Salinity correction factors for dissolved oxygen in water (based on conductivity)—Continued

Temp °C	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
	17000	18000	19000	20000	21000	22000	23000	24000	25000	26000	27000	28000	29000	30000	31000	32000	33000
0.0	0.934	0.930	0.926	0.922	0.918	0.914	0.910	0.905	0.901	0.897	0.893	0.889	0.885	0.881	0.877	0.873	0.869
1.0	0.934	0.930	0.926	0.922	0.918	0.914	0.910	0.906	0.902	0.898	0.894	0.890	0.886	0.882	0.878	0.874	0.870
2.0	0.935	0.931	0.927	0.923	0.919	0.915	0.911	0.907	0.903	0.899	0.895	0.891	0.887	0.883	0.879	0.875	0.871
3.0	0.935	0.931	0.927	0.923	0.919	0.915	0.911	0.907	0.903	0.899	0.895	0.891	0.887	0.883	0.879	0.875	0.871
4.0	0.935	0.932	0.928	0.924	0.920	0.916	0.912	0.908	0.904	0.900	0.896	0.892	0.888	0.884	0.880	0.876	0.872
5.0	0.936	0.932	0.928	0.924	0.920	0.917	0.913	0.909	0.905	0.901	0.897	0.893	0.889	0.885	0.881	0.877	0.873
6.0	0.936	0.933	0.929	0.925	0.921	0.917	0.913	0.909	0.905	0.902	0.898	0.894	0.890	0.886	0.882	0.878	0.874
7.0	0.937	0.933	0.929	0.925	0.922	0.918	0.914	0.910	0.906	0.902	0.898	0.894	0.891	0.887	0.883	0.879	0.875
8.0	0.937	0.933	0.930	0.926	0.922	0.918	0.914	0.911	0.907	0.903	0.899	0.895	0.891	0.887	0.884	0.880	0.876
9.0	0.938	0.934	0.930	0.926	0.923	0.919	0.915	0.911	0.907	0.904	0.900	0.896	0.892	0.888	0.884	0.880	0.877
10.0	0.938	0.934	0.931	0.927	0.923	0.919	0.916	0.912	0.908	0.904	0.900	0.897	0.893	0.889	0.885	0.881	0.877
11.0	0.939	0.935	0.931	0.927	0.924	0.920	0.916	0.912	0.909	0.905	0.901	0.897	0.894	0.890	0.886	0.882	0.878
12.0	0.939	0.935	0.932	0.928	0.924	0.920	0.917	0.913	0.909	0.906	0.902	0.898	0.894	0.890	0.887	0.883	0.879
13.0	0.939	0.936	0.932	0.928	0.925	0.921	0.917	0.914	0.910	0.906	0.902	0.899	0.895	0.891	0.887	0.884	0.880
14.0	0.940	0.936	0.933	0.929	0.925	0.922	0.918	0.914	0.911	0.907	0.903	0.899	0.896	0.892	0.888	0.884	0.881
15.0	0.940	0.937	0.933	0.929	0.926	0.922	0.918	0.915	0.911	0.907	0.904	0.900	0.896	0.893	0.889	0.885	0.882
16.0	0.941	0.937	0.934	0.930	0.926	0.923	0.919	0.915	0.912	0.908	0.904	0.901	0.897	0.893	0.890	0.886	0.882
17.0	0.941	0.938	0.934	0.930	0.927	0.923	0.920	0.916	0.912	0.909	0.905	0.901	0.898	0.894	0.891	0.887	0.883
18.0	0.942	0.938	0.934	0.931	0.927	0.924	0.920	0.917	0.913	0.909	0.906	0.902	0.899	0.895	0.891	0.888	0.884
19.0	0.942	0.938	0.935	0.931	0.928	0.924	0.921	0.917	0.914	0.910	0.906	0.903	0.899	0.896	0.892	0.888	0.885
20.0	0.942	0.939	0.935	0.932	0.928	0.925	0.921	0.918	0.914	0.911	0.907	0.903	0.900	0.896	0.893	0.889	0.886
21.0	0.943	0.939	0.936	0.932	0.929	0.925	0.922	0.918	0.915	0.911	0.908	0.904	0.901	0.897	0.893	0.890	0.886
22.0	0.943	0.940	0.936	0.933	0.929	0.926	0.922	0.919	0.915	0.912	0.908	0.905	0.901	0.898	0.894	0.891	0.887
23.0	0.944	0.940	0.937	0.933	0.930	0.926	0.923	0.919	0.916	0.912	0.909	0.905	0.902	0.898	0.895	0.891	0.888
24.0	0.944	0.941	0.937	0.934	0.930	0.927	0.923	0.920	0.917	0.913	0.910	0.906	0.903	0.899	0.896	0.892	0.889
25.0	0.944	0.941	0.938	0.934	0.931	0.927	0.924	0.921	0.917	0.914	0.910	0.907	0.903	0.900	0.896	0.893	0.889
26.0	0.945	0.941	0.938	0.935	0.931	0.928	0.925	0.921	0.918	0.914	0.911	0.907	0.904	0.901	0.897	0.894	0.890
27.0	0.945	0.942	0.938	0.935	0.932	0.928	0.925	0.922	0.918	0.915	0.911	0.908	0.905	0.901	0.898	0.894	0.891
28.0	0.946	0.942	0.939	0.936	0.932	0.929	0.926	0.922	0.919	0.915	0.912	0.909	0.905	0.902	0.898	0.895	0.892
29.0	0.946	0.943	0.939	0.936	0.933	0.929	0.926	0.923	0.919	0.916	0.913	0.909	0.906	0.903	0.899	0.896	0.892

**Table 6.2-7.** Salinity correction factors for dissolved oxygen in water (based on conductivity)—Continued

Temp °C	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
	34000	35000	36000	37000	38000	39000	40000	41000	42000	43000	44000	45000	46000	47000	48000	49000	50000
0.0	0.865	0.861	0.856	0.852	0.848	0.844	0.840	0.836	0.832	0.828	0.823	0.819	0.815	0.811	0.807	0.803	0.799
1.0	0.866	0.862	0.857	0.853	0.849	0.845	0.841	0.837	0.833	0.829	0.825	0.821	0.816	0.812	0.808	0.804	0.800
2.0	0.867	0.862	0.858	0.854	0.850	0.846	0.842	0.838	0.834	0.830	0.826	0.822	0.818	0.814	0.809	0.805	0.801
3.0	0.867	0.863	0.859	0.855	0.851	0.847	0.843	0.839	0.835	0.831	0.827	0.823	0.819	0.815	0.811	0.807	0.803
4.0	0.868	0.864	0.860	0.856	0.852	0.848	0.844	0.840	0.836	0.832	0.828	0.824	0.820	0.816	0.812	0.808	0.804
5.0	0.869	0.865	0.861	0.857	0.853	0.849	0.845	0.841	0.837	0.833	0.829	0.825	0.821	0.817	0.813	0.809	0.805
6.0	0.870	0.866	0.862	0.858	0.854	0.850	0.846	0.842	0.838	0.834	0.830	0.826	0.822	0.818	0.814	0.810	0.806
7.0	0.871	0.867	0.863	0.859	0.855	0.851	0.847	0.843	0.839	0.835	0.831	0.828	0.824	0.820	0.816	0.812	0.808
8.0	0.872	0.868	0.864	0.860	0.856	0.852	0.848	0.844	0.840	0.837	0.833	0.829	0.825	0.821	0.817	0.813	0.809
9.0	0.873	0.869	0.865	0.861	0.857	0.853	0.849	0.845	0.842	0.838	0.834	0.830	0.826	0.822	0.818	0.814	0.810
10.0	0.874	0.870	0.866	0.862	0.858	0.854	0.850	0.846	0.843	0.839	0.835	0.831	0.827	0.823	0.819	0.815	0.811
11.0	0.874	0.871	0.867	0.863	0.859	0.855	0.851	0.848	0.844	0.840	0.836	0.832	0.828	0.824	0.820	0.817	0.813
12.0	0.875	0.871	0.868	0.864	0.860	0.856	0.852	0.849	0.845	0.841	0.837	0.833	0.829	0.825	0.822	0.818	0.814
13.0	0.876	0.872	0.869	0.865	0.861	0.857	0.853	0.850	0.846	0.842	0.838	0.834	0.830	0.827	0.823	0.819	0.815
14.0	0.877	0.873	0.869	0.866	0.862	0.858	0.854	0.851	0.847	0.843	0.839	0.835	0.832	0.828	0.824	0.820	0.816
15.0	0.878	0.874	0.870	0.867	0.863	0.859	0.855	0.852	0.848	0.844	0.840	0.836	0.833	0.829	0.825	0.821	0.817
16.0	0.879	0.875	0.871	0.867	0.864	0.860	0.856	0.853	0.849	0.845	0.841	0.838	0.834	0.830	0.826	0.822	0.819
17.0	0.879	0.876	0.872	0.868	0.865	0.861	0.857	0.854	0.850	0.846	0.842	0.839	0.835	0.831	0.827	0.824	0.820
18.0	0.880	0.877	0.873	0.869	0.866	0.862	0.858	0.855	0.851	0.847	0.843	0.840	0.836	0.832	0.829	0.825	0.821
19.0	0.881	0.877	0.874	0.870	0.867	0.863	0.859	0.855	0.852	0.848	0.844	0.841	0.837	0.833	0.830	0.826	0.822
20.0	0.882	0.878	0.875	0.871	0.867	0.864	0.860	0.856	0.853	0.849	0.845	0.842	0.838	0.834	0.831	0.827	0.823
21.0	0.883	0.879	0.876	0.872	0.868	0.865	0.861	0.857	0.854	0.850	0.846	0.843	0.839	0.836	0.832	0.828	0.825
22.0	0.884	0.880	0.876	0.873	0.869	0.866	0.862	0.858	0.855	0.851	0.848	0.844	0.840	0.837	0.833	0.829	0.826
23.0	0.884	0.881	0.877	0.874	0.870	0.866	0.863	0.859	0.856	0.852	0.849	0.845	0.841	0.838	0.834	0.830	0.827
24.0	0.885	0.882	0.878	0.874	0.871	0.867	0.864	0.860	0.857	0.853	0.850	0.846	0.842	0.839	0.835	0.832	0.828
25.0	0.886	0.882	0.879	0.875	0.872	0.868	0.865	0.861	0.858	0.854	0.851	0.847	0.843	0.840	0.836	0.833	0.829
26.0	0.887	0.883	0.880	0.876	0.873	0.869	0.866	0.862	0.859	0.855	0.852	0.848	0.844	0.841	0.837	0.834	0.830
27.0	0.887	0.884	0.880	0.877	0.874	0.870	0.867	0.863	0.860	0.856	0.853	0.849	0.845	0.842	0.838	0.835	0.831
28.0	0.888	0.885	0.881	0.878	0.874	0.871	0.867	0.864	0.860	0.857	0.853	0.850	0.846	0.843	0.839	0.836	0.832
29.0	0.889	0.886	0.882	0.879	0.875	0.872	0.868	0.865	0.861	0.858	0.854	0.851	0.848	0.844	0.841	0.837	0.834

**Table 6.2-7.** Salinity correction factors for dissolved oxygen in water (based on conductivity)—Continued

Temp °C	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
	51000	52000	53000	54000	55000	56000	57000	58000	59000	60000	61000	62000	63000	64000	65000	66000	67000
0.0	0.795	0.790	0.786	0.782	0.778	0.774	0.770	0.766	0.761	0.757	0.753	0.749	0.745	0.741	0.737	0.732	0.728
1.0	0.796	0.792	0.788	0.783	0.779	0.775	0.771	0.767	0.763	0.759	0.755	0.751	0.746	0.742	0.738	0.734	0.730
2.0	0.797	0.793	0.789	0.785	0.781	0.777	0.773	0.768	0.764	0.760	0.756	0.752	0.748	0.744	0.740	0.736	0.732
3.0	0.798	0.794	0.790	0.786	0.782	0.778	0.774	0.770	0.766	0.762	0.758	0.754	0.750	0.746	0.741	0.737	0.733
4.0	0.800	0.796	0.792	0.788	0.784	0.780	0.775	0.771	0.767	0.763	0.759	0.755	0.751	0.747	0.743	0.739	0.735
5.0	0.801	0.797	0.793	0.789	0.785	0.781	0.777	0.773	0.769	0.765	0.761	0.757	0.753	0.749	0.745	0.741	0.737
6.0	0.802	0.798	0.794	0.790	0.786	0.782	0.778	0.774	0.770	0.766	0.762	0.758	0.754	0.750	0.746	0.742	0.738
7.0	0.804	0.800	0.796	0.792	0.788	0.784	0.780	0.776	0.772	0.768	0.764	0.760	0.756	0.752	0.748	0.744	0.740
8.0	0.805	0.801	0.797	0.793	0.789	0.785	0.781	0.777	0.773	0.769	0.765	0.761	0.757	0.753	0.749	0.745	0.742
9.0	0.806	0.802	0.798	0.794	0.790	0.787	0.783	0.779	0.775	0.771	0.767	0.763	0.759	0.755	0.751	0.747	0.743
10.0	0.807	0.804	0.800	0.796	0.792	0.788	0.784	0.780	0.776	0.772	0.768	0.764	0.760	0.757	0.753	0.749	0.745
11.0	0.809	0.805	0.801	0.797	0.793	0.789	0.785	0.781	0.778	0.774	0.770	0.766	0.762	0.758	0.754	0.750	0.746
12.0	0.810	0.806	0.802	0.798	0.794	0.791	0.787	0.783	0.779	0.775	0.771	0.767	0.763	0.760	0.756	0.752	0.748
13.0	0.811	0.807	0.804	0.800	0.796	0.792	0.788	0.784	0.780	0.777	0.773	0.769	0.765	0.761	0.757	0.753	0.750
14.0	0.812	0.809	0.805	0.801	0.797	0.793	0.789	0.786	0.782	0.778	0.774	0.770	0.766	0.763	0.759	0.755	0.751
15.0	0.814	0.810	0.806	0.802	0.798	0.795	0.791	0.787	0.783	0.779	0.776	0.772	0.768	0.764	0.760	0.756	0.753
16.0	0.815	0.811	0.807	0.804	0.800	0.796	0.792	0.788	0.785	0.781	0.777	0.773	0.769	0.766	0.762	0.758	0.754
17.0	0.816	0.812	0.809	0.805	0.801	0.797	0.794	0.790	0.786	0.782	0.778	0.775	0.771	0.767	0.763	0.760	0.756
18.0	0.817	0.814	0.810	0.806	0.802	0.799	0.795	0.791	0.787	0.784	0.780	0.776	0.772	0.769	0.765	0.761	0.757
19.0	0.819	0.815	0.811	0.807	0.804	0.800	0.796	0.792	0.789	0.785	0.781	0.777	0.774	0.770	0.766	0.763	0.759
20.0	0.820	0.816	0.812	0.809	0.805	0.801	0.797	0.794	0.790	0.786	0.783	0.779	0.775	0.771	0.768	0.764	0.760
21.0	0.821	0.817	0.814	0.810	0.806	0.802	0.799	0.795	0.791	0.788	0.784	0.780	0.777	0.773	0.769	0.766	0.762
22.0	0.822	0.818	0.815	0.811	0.807	0.804	0.800	0.796	0.793	0.789	0.785	0.782	0.778	0.774	0.771	0.767	0.763
23.0	0.823	0.820	0.816	0.812	0.809	0.805	0.801	0.798	0.794	0.790	0.787	0.783	0.779	0.776	0.772	0.768	0.765
24.0	0.824	0.821	0.817	0.814	0.810	0.806	0.803	0.799	0.795	0.792	0.788	0.785	0.781	0.777	0.774	0.770	0.766
25.0	0.826	0.822	0.818	0.815	0.811	0.808	0.804	0.800	0.797	0.793	0.789	0.786	0.782	0.779	0.775	0.771	0.768
26.0	0.827	0.823	0.820	0.816	0.812	0.809	0.805	0.802	0.798	0.794	0.791	0.787	0.784	0.780	0.776	0.773	0.769
27.0	0.828	0.824	0.821	0.817	0.814	0.810	0.806	0.803	0.799	0.796	0.792	0.789	0.785	0.781	0.778	0.774	0.771
28.0	0.829	0.825	0.822	0.818	0.815	0.811	0.808	0.804	0.801	0.797	0.794	0.790	0.786	0.783	0.779	0.776	0.772
29.0	0.830	0.827	0.823	0.820	0.816	0.812	0.809	0.805	0.802	0.798	0.795	0.791	0.788	0.784	0.781	0.777	0.774

**Table 6.2-7.** Salinity correction factors for dissolved oxygen in water (based on conductivity)—Continued

Temp °C	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
	0	1000	2000	3000	4000	5000	6000	7000	8000	9000	10000	11000	12000	13000	14000	15000	16000
30.0	1.000	0.997	0.994	0.991	0.988	0.985	0.981	0.978	0.975	0.972	0.969	0.966	0.962	0.959	0.956	0.953	0.950
31.0	1.000	0.997	0.994	0.991	0.988	0.985	0.982	0.978	0.975	0.972	0.969	0.966	0.963	0.959	0.956	0.953	0.950
32.0	1.000	0.997	0.994	0.991	0.988	0.985	0.982	0.979	0.975	0.972	0.969	0.966	0.963	0.960	0.957	0.953	0.950
33.0	1.000	0.997	0.994	0.991	0.988	0.985	0.982	0.979	0.976	0.973	0.969	0.966	0.963	0.960	0.957	0.954	0.951
34.0	1.000	0.997	0.994	0.991	0.988	0.985	0.982	0.979	0.976	0.973	0.970	0.967	0.963	0.960	0.957	0.954	0.951
35.0	1.000	0.997	0.994	0.991	0.988	0.985	0.982	0.979	0.976	0.973	0.970	0.967	0.964	0.961	0.957	0.954	0.951

Temp °C	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
	17000	18000	19000	20000	21000	22000	23000	24000	25000	26000	27000	28000	29000	30000	31000	32000	33000
30.0	0.946	0.943	0.940	0.936	0.933	0.930	0.927	0.923	0.920	0.917	0.913	0.910	0.907	0.903	0.900	0.896	0.893
31.0	0.947	0.943	0.940	0.937	0.934	0.930	0.927	0.924	0.920	0.917	0.914	0.911	0.907	0.904	0.901	0.897	0.894
32.0	0.947	0.944	0.941	0.937	0.934	0.931	0.928	0.924	0.921	0.918	0.914	0.911	0.908	0.905	0.901	0.898	0.895
33.0	0.947	0.944	0.941	0.938	0.935	0.931	0.928	0.925	0.922	0.918	0.915	0.912	0.908	0.905	0.902	0.899	0.895
34.0	0.948	0.945	0.941	0.938	0.935	0.932	0.929	0.925	0.922	0.919	0.916	0.912	0.909	0.906	0.903	0.899	0.896
35.0	0.948	0.945	0.942	0.939	0.935	0.932	0.929	0.926	0.923	0.919	0.916	0.913	0.910	0.906	0.903	0.900	0.897

Temp °C	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
	34000	35000	36000	37000	38000	39000	40000	41000	42000	43000	44000	45000	46000	47000	48000	49000	50000
30.0	0.890	0.886	0.883	0.879	0.876	0.873	0.869	0.866	0.862	0.859	0.855	0.852	0.849	0.845	0.842	0.838	0.835
31.0	0.890	0.887	0.884	0.880	0.877	0.873	0.870	0.867	0.863	0.860	0.856	0.853	0.850	0.846	0.843	0.839	0.836
32.0	0.891	0.888	0.884	0.881	0.878	0.874	0.871	0.868	0.864	0.861	0.857	0.854	0.851	0.847	0.844	0.840	0.837
33.0	0.892	0.889	0.885	0.882	0.879	0.875	0.872	0.868	0.865	0.862	0.858	0.855	0.851	0.848	0.845	0.841	0.838
34.0	0.893	0.889	0.886	0.883	0.879	0.876	0.873	0.869	0.866	0.863	0.859	0.856	0.852	0.849	0.846	0.842	0.839
35.0	0.893	0.890	0.887	0.883	0.880	0.877	0.874	0.870	0.867	0.863	0.860	0.857	0.853	0.850	0.847	0.843	0.840

Temp °C	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
	51000	52000	53000	54000	55000	56000	57000	58000	59000	60000	61000	62000	63000	64000	65000	66000	67000
30.0	0.831	0.828	0.824	0.821	0.817	0.814	0.810	0.807	0.803	0.800	0.796	0.793	0.789	0.786	0.782	0.779	0.775
31.0	0.832	0.829	0.825	0.822	0.818	0.815	0.811	0.808	0.804	0.801	0.797	0.794	0.790	0.787	0.783	0.780	0.776
32.0	0.833	0.830	0.826	0.823	0.820	0.816	0.813	0.809	0.806	0.802	0.799	0.795	0.792	0.788	0.785	0.781	0.778
33.0	0.834	0.831	0.828	0.824	0.821	0.817	0.814	0.810	0.807	0.803	0.800	0.797	0.793	0.790	0.786	0.783	0.779
34.0	0.836	0.832	0.829	0.825	0.822	0.818	0.815	0.812	0.808	0.805	0.801	0.798	0.794	0.791	0.788	0.784	0.781
35.0	0.837	0.833	0.830	0.826	0.823	0.820	0.816	0.813	0.809	0.806	0.803	0.799	0.796	0.792	0.789	0.785	0.782



## 6.3 SPECIFIC ELECTRICAL CONDUCTANCE

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

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# SPECIFIC ELECTRICAL CONDUCTANCE 6.3

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 ( $\mu\text{S}/\text{cm}$  at  $25^\circ\text{C}$ ). The method described in this section for measuring conductivity is applicable to surface water and ground water, from fresh to saline.

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**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.**

---

## 6.3.1 EQUIPMENT AND SUPPLIES

The instrument system used to measure conductivity must be tested before each field trip and cleaned soon after use. Every conductivity 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.

**Table 6.3–1.** Equipment and supplies used for measuring conductivity<sup>1</sup>  
[°C, degrees Celsius; L, liter;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees Celsius]

- ✓ Conductivity instrument and conductivity sensor
  - Battery powered Wheatstone bridge
  - Direct readout
  - Temperature range at least  $-5$  to  $+45^\circ\text{C}$
  - Temperature compensating ( $25^\circ\text{C}$ )
  - Accuracy: Conductivity  $\leq 100 \mu\text{S}/\text{cm}$ , within 5 percent of full scale
  - Conductivity  $> 100 \mu\text{S}/\text{cm}$ , within 3 percent of full scale
- ✓ Thermistor thermometer sensor (for automatic temperature-compensating models)
- ✓ Thermometer, liquid-in-glass or thermistor
- ✓ Extra sensors (if possible) and batteries, or backup instrument
- ✓ Conductivity standards at conductivities that approximate and bracket field values
- ✓ Compositing and splitting device for surface-water samples
- ✓ Flowthrough chamber or downhole instrument for ground-water measurements
- ✓ Plastic beakers (assorted sizes)
- ✓ Soap solution, nonphosphate (1 L)
- ✓ Hydrochloric acid solution, 5 percent volume-to-volume (1 L)
- ✓ Deionized water, 1 L, maximum conductivity of  $1 \mu\text{S}/\text{cm}$
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Brush (small, soft)
- ✓ Waste disposal container
- ✓ Minnow bucket with tether (or equivalent) for equilibrating buffer solutions to sample temperature
- ✓ Instrument log book for recording calibrations, maintenance, and repairs

<sup>1</sup>Modify this list to meet the specific needs of the field effort.

- ▶ Many conductivity instruments are available; the specifications and instructions provided here are general. Users must be familiar with the instructions provided by the manufacturer.
- ▶ Conductivity sensors are either contacting-type sensors with electrodes or electrodeless-type sensors.
  - **Contacting-type sensors with electrodes.** Three types of cells are available: (1) a dip cell that can be suspended in the sample, (2) a cup cell that contains the sample, or (3) a flow cell that is connected to a fluid line. Choose a cell constant on the basis of expected conductivity (table 6.3–2). The greater the cell constant, the greater the conductivity that can be measured. The cell constant is the distance between electrodes (in centimeters) divided by the effective cross-sectional area of the conducting path (in square centimeters).
  - **Electrodeless-type sensors.** These operate by inducing an alternating current in a closed loop of solution, and they measure the magnitude of the current. Electrodeless sensors avoid errors caused by electrode polarization or electrode fouling.

Quality-controlled conductivity standards ranging from 50 to 50,000  $\mu\text{S}/\text{cm}$  at 25°C can be obtained from QWSU. Prepare standards outside this range or order them from suppliers of chemical reagents. Conductivity standards usually consist of potassium chloride dissolved in reagent-grade water.

**Table 6.3–2.** Example of cell constants for contacting-type sensors with electrodes and corresponding conductivity ranges

Conductivity range, in microsiemens per centimeter	Cell constant, in 1/centimeter
0.005–20	0.01
1–200	.1
10–2,000	1.0
100–20,000	10.0
1,000–200,000	50.0

### 6.3.1.A MAINTENANCE, CLEANING, AND STORAGE

As soon as possible after delivery to the office, label conductivity standards with the date of expiration. Discard standards that have expired, been frozen, have begun to evaporate, or that were decanted from the storage container.

#### *Maintenance*

Maintenance of conductivity equipment includes periodic office checks of instrument operation. To help keep equipment in good operating condition:

- ▶ Protect the conductivity system from dust and excessive heat and cold.
- ▶ Keep all cable connectors dry and free of dirt and extraneous matter.
- ▶ Protect connector ends in a clean plastic bag when not in use.

#### *Sensor cleaning*

Conductivity sensors must be clean to produce accurate results; residues from previous samples can coat surfaces of sensors and cause erroneous readings.

- ▶ Clean sensors thoroughly with deionized water (DIW) before and after making a measurement (this is sufficient cleaning in most cases).
- ▶ Remove oily residue or other chemical residues (salts) with a detergent solution. Sensors can soak in detergent solution for many hours without damage.
- ▶ If oil or other residues persist, dip the sensor in a dilute hydrochloric acid solution. **Never leave the sensor in contact with acid solution for more than a few minutes.** Check the manufacturer's recommendations before using acid solution on sensors.
- ▶ Clean carbon and stainless steel sensors with a soft brush. Never use a brush on platinum-coated sensors.

### *Sensor storage*

Refer to the manufacturer's recommendations.

- ▶ Sensors may be temporarily stored in deionized water between measurements and when the system is in daily use.
- ▶ For long-term storage, store sensors clean and dry.

**CAUTION: Before handling conductivity standards or acids, refer to Material Safety Data Sheets (MSDS) for safety precautions.**

**Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.**

## 6.3.2 CALIBRATION

Conductivity systems must be calibrated before every water-quality field trip and again at each site before samples are measured. Calibration readings are recorded in the instrument log book and on field forms at the time the instrument is calibrated. Remember, the temperature sensor on the conductivity sensor must be calibrated and District certified within the past 4 months.

**Calibration and operating procedures differ, depending on instrument and sensor type.**

- ▶ Some conductivity sensors may need to be soaked overnight in deionized water before use—Check the manufacturer's instructions.
- ▶ Some analog instruments require an initial mechanical zero adjustment of the indicator needle.
- ▶ For a cup-type cell, calibration and measurement procedures described for the dip-type cell apply; the only difference is that standards are poured directly into the cup-type cell.
- ▶ When using a dip-type cell, do not let the cell rest on the bottom or sides of the measuring container.

**Calibrate at your field site—bring standards to sample temperature.**

Conductivity systems normally are calibrated with at least two standards. Calibrate sensors against a standard that approximates sample conductivity and use the second standard as a calibration check. The general procedures described in steps 1–15 below apply to most instruments used for field measurements—check the instrument manual for specific instructions.

1. Inspect the instrument and the conductivity sensor for damage. Check the battery voltage. Make sure that all cables are clean and connected properly.
2. Turn the instrument on and allow sufficient time for electronic stabilization.

3. Select the correct instrument calibration scale for expected conductivity.
4. Select the sensor type and the cell constant that will most accurately measure expected conductivity.
5. Select two conductivity standards that will bracket the expected sample conductivity. Verify that the date on the standards has not expired.
6. Equilibrate the standards and the conductivity sensor to the temperature of the sample.
  - Put bottles of standards in a minnow bucket, cooler, or large water bath that is being filled with ambient water.
  - Allow 15 to 30 minutes for thermal equilibration. Do not allow water to dilute the standard.
7. Rinse the conductivity sensor, the thermometer (liquid-in-glass or thermistor), and a container large enough to hold the dip-type sensor and the thermometer.
  - **First**, rinse the sensor, the thermometer, and the container three times with deionized water.
  - **Next**, rinse the sensor, the thermometer, and the container three times with the standard to be used.
8. Put the sensor and the thermometer into the rinsed container and pour in fresh calibration standard.
9. Measure water temperature. **Accurate conductivity measurements depend on accurate temperature measurements or accurate temperature compensation.**
  - If the sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
  - If using a manual instrument without a temperature display or temperature compensation, adjust the instrument to the temperature of the standard using a calibrated liquid-in-glass or a thermistor thermometer.
10. Agitate a submersible-type conductivity sensor up and down under the solution surface to expel air trapped in the sensor. Read the instrument display. Agitate the sensor up and down under the solution surface again, and read the display. Repeat the procedure until consecutive readings are the same.

11. Record the instrument reading and adjust the instrument to the known standard value.
  - For nontemperature-compensating conductivity instruments, apply a temperature-correction factor to convert the instrument reading to conductivity at 25°C.
  - The correction factor depends to some degree on the specific instrument used—use the temperature-correction factor recommended by the manufacturer. If this is not available, use correction factors from table 6.3–3.
  - If an instrument cannot be adjusted to a known calibration standard value, develop a calibration curve. After temperature compensation, if the percentage difference from the standard exceeds 5 percent, refer to the troubleshooting guide (section 6.3.4).
12. Record in the instrument log book and on field forms:
  - The temperature of the standard solution.
  - The known and the measured conductivity of the standard solution (including  $\pm$  variation).
  - The temperature-correction factor (if necessary).
13. Discard the used standard into a waste container. Rinse the sensor, thermometer, and container thoroughly with deionized water.
14. Repeat steps 7 through 13 with the second conductivity standard.
  - The purpose for measuring a second standard is to check instrument calibration over the range of the two standards.
  - The difference from the standard value should not exceed 5 percent.
  - If the difference is greater than 5 percent, repeat the entire calibration procedure. If the second reading still does not come within 5 percent of standard value, refer to the troubleshooting guide in section 6.3.4 or calibrate a backup instrument.
  - **Switching instrument calibration scales could require recalibration.**
15. Record in the instrument log book and on field forms the calibration data for the second standard.

**Do not use expired standards.  
Never reuse standards.**

**Table 6.3-3.** Correction factors for converting non-temperature-compensated values to conductivity at 25 degrees Celsius, based on 1,000 microsiemens potassium chloride solution

[Use of potassium-based constants on non-potassium-based waters generally does not introduce significant errors for general purpose instruments used to measure conductivity]

Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor
0.5	1.87	10.5	1.39	20.5	1.09
1.0	1.84	11.0	1.37	21.0	1.08
1.5	1.81	11.5	1.35	21.5	1.07
2.0	1.78	12.0	1.33	22.0	1.06
2.5	1.76	12.5	1.32	22.5	1.05
3.0	1.73	13.0	1.30	23.0	1.04
3.5	1.70	13.5	1.28	23.5	1.03
4.0	1.68	14.0	1.27	24.0	1.02
4.5	1.66	14.5	1.26	24.5	1.01
5.0	1.63	15.0	1.24	25.0	1.00
5.5	1.60	15.5	1.22	25.5	0.99
6.0	1.58	16.0	1.21	26.0	0.98
6.5	1.56	16.5	1.19	26.5	0.97
7.0	1.54	17.0	1.18	27.0	0.96
7.5	1.52	17.5	1.16	27.5	0.95
8.0	1.49	18.0	1.15	28.0	0.94
8.5	1.47	18.5	1.14	28.5	0.93
9.0	1.45	19.0	1.13	29.0	0.92
9.5	1.43	19.5	1.12	29.5	0.91
10.0	1.41	20.0	1.11	30.0	0.90

To extend the temperature range shown in table 6.3-3, consult the manufacturer's guidelines. If these are unavailable, use the following equation:

$$C_{25} = \frac{C_m}{1 + 0.02 (t_m - 25)}$$

where,

$C_{25}$  = corrected conductivity value adjusted to 25°C;

$C_m$  = actual conductivity measured before correction; and

$t_m$  = water temperature at time of  $C_m$  measurement.

## 6.3.3 MEASUREMENT

In situ measurement generally is preferred for determining the conductivity of surface water; downhole or flowthrough-chamber measurements are preferred for ground water. Be alert to the following problems if conductivity is measured in an isolated (discrete) sample or subsample:

- ▶ The conductivity of water can change over time as a result of chemical and physical processes such as precipitation, adsorption, ion exchange, oxidation, and reduction—Do not delay making conductivity measurements.
- ▶ Field conditions (rain, wind, cold, dust, direct sunlight) can cause measurement problems—Shield the instrument to the extent possible and perform measurements in a collection chamber in an enclosed vehicle or an on-site laboratory.
- ▶ For waters susceptible to significant gain and loss of dissolved gases, make the measurement within a gas-impermeable container (Berzelius flask) fitted with a stopper—Place the sensor through the stopper and work quickly to maintain the sample at ambient surface-water or ground-water temperature.
- ▶ Avoid contamination from the pH electrode filling solution—Measure conductivity on a separate discrete sample from the one used for measuring pH; in a flowthrough chamber, position conductivity sensor upstream of the pH electrode.

### Conductivity must be measured in the field.

**Document the precision of your measurements.** Precision should be determined about every tenth sample or more frequently, depending on study objectives. Successive measurements should be repeated until they agree within 5 percent at conductivity  $\leq 100 \mu\text{S}/\text{cm}$  or within 3 percent at conductivity  $> 100 \mu\text{S}/\text{cm}$ .

**The conductivity measurement reported must account for sample temperature.** If using an instrument that does not automatically temperature compensate to  $25^\circ\text{C}$ , record the uncompensated measurement in your field notes, along with the corrected conductivity value. Use correction factors supplied by the instrument manufacturer if available; otherwise, refer to table 6.3-3.

## SURFACE WATER 6.3.3.A

Surface-water conductivity should be measured in situ, if possible; otherwise, determine conductivity in discrete samples collected from a sample splitter or compositing device. Filtered samples may be needed if the concentrations of suspended material interfere with obtaining a stable measurement.

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### In situ measurement

Conductivity measurements in flowing surface water should represent the cross-sectional mean or median conductivity at the time of observation (see step 7, below). Any deviation from this convention must be documented in the data base and with the published data.

#### *First:*

- ▶ Take a cross-sectional conductivity profile to determine the degree of system variability. A submersible sensor works best for this purpose.
- ▶ Refer to NFM 6.0 for criteria to help decide which sampling method to use.

#### *Next, follow the 7 steps listed below:*

1. Calibrate the conductivity instrument system at the field site after equilibrating the buffers with stream temperature.
2. Record the conductivity variation from a cross-sectional profile on a field form and select the sampling method.
  - **Flowing, shallow stream**—wade to the location(s) where conductivity is to be measured.
  - **Stream too deep or swift to wade**—lower a weighted conductivity sensor from a bridge, cableway, or boat. Do not attach weight to the sensor or the sensor cable.
  - **Still-water conditions**—measure conductivity at multiple depths at several points in the cross section.

3. Immerse the conductivity and temperature sensors in the water to the correct depth and hold there (no less than 60 seconds) until the sensors equilibrate to water conditions.
4. Record the conductivity and corresponding temperature readings without removing the sensors from water.
  - Values should stabilize quickly to within 5 percent at conductivity  $\leq 100 \mu\text{S}/\text{cm}$  and within 3 percent at conductivity  $> 100 \mu\text{S}/\text{cm}$ .
  - Record the median of the stabilized values on field forms.
  - If the readings do not meet the stability criterion after extending the measurement period, record this difficulty in the field notes along with the fluctuation range and the median value of the last five or more readings.
5. For EWI or EDI measurements, proceed to the next station in the cross section and repeat steps 3 and 4. Record on field forms the mean (or median, if appropriate) value for each subsection measured.
6. When the measurement is complete, remove the sensor from the water, rinse it with deionized water, and store it.
7. Record the stream conductivity on the field forms:
  - **In still water—median** of three or more sequential values.
  - **EDI—mean** value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
  - **EWI—mean or median** of all subsections measured (see NFM 6.0).

---

## Subsample measurement

Representative samples are to be collected and split or composited according to approved USGS methods (Wells and others, 1990). Measure the conductivity of samples as soon as possible after collection. If the sample cannot be analyzed immediately, fill a bottle to the top, close it tightly, and maintain the sample at stream temperature until measurement.

Reported conductivity values normally are determined on an unfiltered sample. Large concentrations of suspended sediment can be a source of measurement error—record such conditions in the field notes.

- ▶ If sediment concentrations are heavy, measure conductivity on both unfiltered and filtered subsamples and record both values on the field form.
- ▶ If the conductivity value differs significantly between the filtered and unfiltered samples, report the filtered value as sample conductivity and identify it as a “filtered sample.”
  1. Calibrate the conductivity instrument system at the field site.
  2. Select the sampling method (see NFM 6.0) and collect a representative sample.
  3. Withdraw a homogenized subsample from a sample splitter or compositing device. Rinse the sample bottles three times with the sample—rinse them with sample filtrate, for filtered samples.
  4. Rinse the conductivity sensor, the thermometer (liquid-in-glass or thermistor), and a container large enough to hold the dip-type sensor and the thermometer.
    - a. First, rinse the sensor, the thermometer, and the container three times with deionized water.
    - b. Next, rinse the sensor, the thermometer, and the container using sample water.
  5. Allow the sensors to equilibrate to sample temperature, then discard the used sample water. Pour fresh sample water into a container holding the sensor and the thermometer. **When using a dip-type sensor, do not let the sensor touch the bottom or sides of the measuring container.**
  6. Measure water temperature.
    - If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
    - If the instrument is not temperature compensating, use a calibrated thermistor or a liquid-in-glass thermometer.
    - Adjust the instrument to the sample temperature (if necessary) and remove the thermometer.
  7. Measure conductivity.
    - a. Remove any air trapped in the sensor by agitating the sensor up and down under the water surface.
    - b. Read the instrument display.
    - c. Agitate the sensor up and down under the water surface, and read the display again.
    - d. Repeat the procedure until consecutive readings are the same.

8. Record the conductivity and the sample temperature on field forms.
  - If the instrument is not temperature compensating, record the raw data and convert the values to conductivity at 25°C using temperature-correction factors provided by the manufacturer.
  - Report the median of the readings to three significant figures on the field forms.
  - Discard the sample into a waste container and dispose according to regulations.
9. **Quality control—**
  - Repeat steps 3 through 8 with at least two fresh subsamples, rinsing the instruments once only with sample water.
  - Subsample values should be within  $\pm 5$  percent for conductivity  $\leq 100 \mu\text{S}/\text{cm}$ , or  $\pm 3$  percent for conductivity  $> 100 \mu\text{S}/\text{cm}$ .
  - If criteria cannot be met: filter the samples, report the median of 3 or more samples, and record this difficulty in field notes.
10. Rinse the sensor, the thermometer, and the container with deionized water. If another measurement is to be made within the next day or two, store the sensor in deionized water. Otherwise, store the sensor dry.

## GROUND WATER 6.3.3.B

Measurements of ground-water conductivity must represent aquifer conditions. Temperature changes resulting from transporting a well sample to land surface can affect conductivity.

- ▶ To minimize the effect from temperature changes, measure conductivity as close to the source as possible, using either a downhole or flowthrough-chamber sampling system (refer to NFM 6.0 for details).
- ▶ Bailed or other methods for collecting discrete samples isolated from the source are not recommended as standard practice, although such methods are sometimes called for owing to site characteristics or other study requirements.

---

### Downhole and flowthrough-chamber measurement

1. Calibrate the conductivity instrument system on site.
  - Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.
    - a. Check the temperature of the water flowing into the bucket against that of standards.
    - b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.
  - After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.
2. Install the conductivity and temperature sensors.
  - **Downhole system**—Lower the conductivity and temperature sensors to sampling point, followed by pump.
    - a. Remove any air from the system by agitating the conductivity sensor up and down under the water; read the instrument display.
    - b. Repeat this procedure until rapid consecutive readings are approximately the same.

- **Flowthrough-chamber system**—Install the chamber system as close to the well as possible and shield the system from direct sunlight.
  - a. Position the conductivity sensor upstream from the pH electrode.
  - b. Direct flow to the chamber after an initial discharge to waste to clear sediment from sample line.
  - c. Release any air trapped in the chamber.
  - d. Agitate the conductivity sensor up and down under the water to remove air from system. Rapid consecutive readings should be about the same.
- 3. During purging (table 6.0–1 in NFM 6.0):
  - Keep flow constant and laminar.
  - Allow the sensors to equilibrate with ground-water temperature for 5 minutes or more at the flow rate to be used for collecting all other samples.
- 4. Measure conductivity and associated temperature at regular intervals throughout purging; record the conductivity values and the associated temperature in the field notes.
  - If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
  - If the instrument is not temperature compensating, install a calibrated thermometer in the flowthrough chamber, record raw data, and apply correction factors.
- 5. Check the variability of the conductivity values toward the end of purging.
  - The stability criterion is met when five readings taken at regularly spaced intervals of 3 to 5 minutes or more are within
    - ±5 percent for conductivity  $\leq 100 \mu\text{S}/\text{cm}$
    - ±3 percent for conductivity  $> 100 \mu\text{S}/\text{cm}$
  - When readings fluctuate rapidly, record the median of three or more readings within about 60 seconds as the value for a specific time interval.
  - If the criterion is not met, extend the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals. Record this difficulty on the field forms.

6. Report conductivity.
  - Record the final five values on field forms.
  - Report the median value of the final five measurements as the sample conductivity.
  - If values exceed the stability criterion, report the range of values observed for the time interval, along with the median of the final five or more values.

---

## Subsample measurement

Conductivity measurements reported from bailed or other discrete samples need to be identified in the data base, indicating the sampling method used. Refer to 6.0.3.B in NFM 6.0 for use of bailers and the subsample method.

1. Calibrate the conductivity instrument system onsite.
  - Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.
    - a. Check the temperature of the water flowing into the bucket against that of standards.
    - b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.
  - After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.
2. Draw off subsamples for measurement.
  - **Quality control—Collect three subsamples to check precision.**
  - If samples need to be stored for a short time, or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles—fill to the brim, cap tightly, and maintain at ambient ground-water temperature. Measure conductivity as soon as possible.

3. Follow procedures described in steps 4 through 10 for “Subsample measurement” of surface water (6.3.3.A).

TECHNICAL NOTE: If the sample is measured in an open container and readings do not stabilize within several minutes, the cause may be CO<sub>2</sub> degassing—use a closed system to measure the sample. Filter the conductivity sample if the settling of clay particles appears to interfere with the stability of the readings.



## TROUBLESHOOTING 6.3.4

Contact the instrument manufacturer if the actions suggested in table 6.3–4 fail to resolve the problem.

- ▶ If available, use a commercial, electronic calibrator to check the function of conductivity instruments.
- ▶ Check the voltage of batteries. Always have good batteries in instruments and carry spares.

**Table 6.3–4.** Troubleshooting guide for conductivity measurement  
[HCl, hydrochloric acid; °C, degrees Celsius]

Symptom	Possible cause and corrective action
Will not calibrate to standards	<ul style="list-style-type: none"> <li>• Standards may be old or contaminated—use fresh standards.</li> <li>• Electrodes dirty—clean with a detergent solution, then with 5 percent HCl. Before using any acid solution to remove resistant residues, check manufacturer's guidelines.</li> <li>• Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air.</li> <li>• Weak batteries—replace.</li> <li>• Temperature compensation incorrect—ensure that thermometer is operating properly and is calibrated.</li> <li>• Sensor constant incorrect—replace sensor.</li> </ul>
Erratic instrument readings	<ul style="list-style-type: none"> <li>• Loose or defective connections—tighten or replace.</li> <li>• Broken cables—repair or replace.</li> <li>• Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air.</li> <li>• Rapid changes in water temperature—measure in situ.</li> <li>• Outgassing of ground-water sample—use a downhole instrument; if unavailable, use a flowthrough chamber.</li> <li>• Broken sensor—replace.</li> </ul>
Instrument requires frequent recalibration	<ul style="list-style-type: none"> <li>• Temperature compensator not working—measure conductivity of a solution. Place solution in a water bath and raise solution temperature to about 20°C. Measure conductivity again, allowing sufficient time for temperature of conductivity sensor to equilibrate to temperature of solution. If the two values differ by 5 percent or more, replace conductivity sensor.</li> </ul>

## 6.3.5 REPORTING

Report routine conductivity measurements to three significant figures, whole numbers only, in microsiemens per centimeter at 25°C.

- ▶ Record the accuracy range of the instrument system in the data base, if possible, and always report it with published values.
- ▶ Enter field-determined conductivity measurements on NWQL Analytical Services Request form using the correct parameter code.



## 6.4 pH

By D.B. Radtke, Eurybiades Busenberg,  
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# pH 6.4

The pH of an aqueous solution is controlled by interrelated chemical reactions that produce or consume hydrogen ions (Hem, 1985). Water pH is a useful index of the status of equilibrium reactions in which water participates (Hem, 1985). The pH of water directly affects physiological functions of plants and animals, and it is, therefore, an important indicator of the health of a water system.

- ▶ pH is reported on a scale that most commonly ranges from 0 to 14 and that is directly related to the ratio of hydrogen ( $H^+$ ) and hydroxyl ( $OH^-$ ) ion activities at a given temperature.
- ▶ A solution is considered acidic if  $H^+$  activity is greater than  $OH^-$  activity (pH less than 7 at 25°C); a solution is considered basic, or alkaline, when  $OH^-$  activity is greater than  $H^+$  activity.
- ▶ Carbon dioxide ( $CO_2$ )-free water at 25°C is considered neutral because activities of  $H^+$  and  $OH^-$  are equal.

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**pH: a measure representing the negative base-ten logarithm of hydrogen-ion activity of a solution, in moles per liter.**

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## 6.4.1 EQUIPMENT AND SUPPLIES

The instrument system that is used to measure pH must be tested before each field trip, and it must be cleaned soon after use. Because of the variety of pH meters and electrodes available, read thoroughly the instruction manual provided by the manufacturer. Every pH instrument must have a log book in which its manufacturer make and model, serial or property number, and all repairs and calibrations are recorded.

pH can be measured either electrometrically or colorimetrically.

- ▶ **The electrometric measurement method uses a hydrogen ion electrode. This is the only technique which is approved for measuring pH values that are to be reported or entered into the USGS data base.**
- ▶ The colorimetric method uses pH “litmus” indicators that change color with a change in pH. The colorimetric method is suitable only when rough estimates of pH are needed; for example, when assessing the volume of acid or base needed to preserve samples; or, when checking that equipment-cleaning solutions have been adequately neutralized prior to disposal.

pH meters are sophisticated electronic instruments that require care in handling and operation. pH instrument systems and buffers must be protected from dirt and extreme heat or freezing conditions while they are in the field and during storage. Keep instrument systems clean and dry when they are not in use. During field travel, protect pH meters and electrodes from being jostled or from sudden impacts.

**Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer’s instructions.**

**Table 6.4-1.** Equipment and supplies used for measuring pH<sup>1</sup>

[Except for the multiparameter instrument, this equipment is required also for ANC or alkalinity determinations (see NFM 6.6); mL, milliliters; °C, degrees Celsius; mV, millivolt;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees Celsius]

- ✓ pH meter and pH electrodes
  - Battery powered, solid state, with automatic temperature and slope compensation, or multiparameter instrument (possible alternative to separate pH meter and electrode)
  - Range of at least 2 to 12 pH, preferably 0 to 14 pH
  - Accuracy of at least  $\pm 0.1$  units
  - Temperature range of at least 0 to  $+45^\circ\text{C}$
  - Millivolt readout with accuracy of  $\pm 1.0$  mV or better for instrument resolution of 0.1 mV
  - Bayonet nut connector (BNC) is recommended
- ✓ pH electrodes, gel-filled or liquid-filled, as appropriate for study objectives and site conditions
- ✓ pH electrode filling solution of appropriate composition and molarity (for liquid-filled electrode)
- ✓ Thermometer, calibrated
- ✓ Buffer solutions, 500 mL each of pH 4, 7, and 10; temperature correction chart(s) for buffers
- ✓ Stand for holding pH electrode (or stand for holding multiparameter instrument system)
- ✓ Bottle, delivery (squeeze), for deionized water
- ✓ Deionized water, maximum conductivity of  $1 \mu\text{S}/\text{cm}$
- ✓ Beakers or measurement vessels, polyethylene or Teflon™ preferable, assorted, 50 to 150 mL, clean but not acid rinsed
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Flowthrough chamber for ground-water measurements (used with meter and electrode equipment)
- ✓ Minnow bucket with tether or equivalent, used for temperature equilibration of buffer solutions
- ✓ Antistatic spray or polish
- ✓ Waste disposal container
- ✓ Stirrer, magnetic with thin insulating pad; or stirrer, mechanical with Teflon™ coated impeller
- ✓ Stirrer bar, magnetic, Teflon™ coated
- ✓ Instrument log book for recording calibrations, maintenance, and repairs

<sup>1</sup>Modify this list to meet the specific needs of the field effort.

**CAUTION: Before handling pH buffers or other chemicals, refer to Material Safety Data Sheets (MSDS) for safety precautions. Wear eye guards and protective clothing.**

### 6.4.1.A pH BUFFER SOLUTIONS

pH measurements are only as accurate as the buffers used for calibration. Use buffers that have been certified traceable to the NIST Standard Reference Material; buffers with a pH of 4, 7, and 10 are available from QWSU.

- ▶ Note that the routine buffers obtained for measurement of pH from 4 to 10 have a high ionic strength. For pH measurements of dilute waters, obtain low ionic-strength buffers.
- ▶ Label buffer and reagent containers with the date when they are received.
- ▶ Label every buffer with its expiration date. Copy this date onto any container into which the buffer is transferred.
- ▶ **Discard buffers on their expiration dates.** The pH of the buffers may have changed substantially because of carbon dioxide absorption, mold growth, or evaporation.

*Take the following precautions to maximize the accuracy of pH measurement (modified from Busenberg and Plummer, 1987):*

1. Always cap buffer bottles to prevent evaporation and contamination from atmospheric carbon dioxide. (In order of greatest to least sensitivity to CO<sub>2</sub> contamination, pH buffer 10 > 7 > 4. Buffers are stable for the short exposure time during electrode calibration.)
2. Never pour used buffer back into stock solution bottles. Never insert an electrode or other material into stock solution bottles containing buffers—always pour the buffer into a separate container.
3. Be very careful not to contaminate the buffer with another buffer or with other fluids (pH 4 buffer is least resistant to contamination).
4. Do not dilute buffer—for example, with water dripping from sensors (more important for pH 7 buffer).
5. Before using buffers, bring them to the temperature of the sample solution, and check with the buffer manufacturer for temperature-correction factors. (In order of greatest to least pH variation with temperature, buffer of pH 10 > 7 > 4.)

## pH ELECTRODES: MAINTENANCE, RECONDITIONING, CLEANING, AND STORAGE 6.4.1.B

The slope and the measured potential of a new electrode should be monitored daily for about 1 week before use (Busenberg and Plummer, 1987). The latest instruments have microprocessors that automatically calculate and display the slope. Some older instruments have a percent-slope readout or (and) millivolt readout. For instruments with a millivolt readout, the measured electrode potential is calculated as the difference between millivolts measured at the known pH of two buffers. Because the theoretical Nernst response is known, slope can be calculated from measured potentials as follows:

$$E = E^0 - S(pH)$$

where

$S$  = slope, and

$E$  = electrode pair potential in mV.

Using two buffers of known pH (1, 2),

$$E_1 = E^0 - S(pH_1)$$

and

$$E_2 = E^0 - S(pH_2)$$

or

$$S = \frac{E_2 - E_1}{pH_1 - pH_2}$$

and

$$E^0 = E_2 + S(pH_2).$$

The theoretical slope is temperature dependent; the slope in mV can be calculated as follows:

$$S_t = 0.19841(273.15 + t)$$

where

$t$  = temperature in degrees Celsius, and

$S_t$  = slope at a given temperature.

Normally, electrodes drift from day to day and  $E^0$  typically varies by  $\pm 2$  mV; the slope remains fairly constant to within  $\pm 0.2$  percent Nernst slope after the new electrode has been conditioned. Follow the procedures recommended by the manufacturer. Properly working electrodes commonly drift from about 0.1 to 0.2 mV per hour.

## *Electrode maintenance*

Electrodes with gel-filled references require less maintenance than electrodes with liquid-filled references. Follow manufacturer's instructions.

Deterioration of the electrode is normal, and proper maintenance requires that electrode performance be monitored before every water-quality field trip and again at each site. Electrodes can give years of reliable service if maintained by following steps 1–8:

1. Do not handle the glass bulb with fingers. Oily film or scratches on the bulb will interfere with pH measurement. Fingers leave a protein film on the glass that decreases electrode sensitivity.
2. Inspect the electrode and electrode cable for physical damage; for example, check for
  - Scratched or broken bulb.
  - Cut, frayed, or broken cable.
  - Bent or broken connector.
3. **Rinse electrode thoroughly with deionized water before use. Do not wipe electrodes with paper towels or wipes—these scratch the glass bulb. Gently blot** droplets from a wet glass electrode bulb with lens paper or soft tissue by contacting only the droplets to soak up excess solution.

TECHNICAL NOTE: Wiping glass with paper causes a static charge (polarization) that results in drifting, sluggish, and erratic pH readings. It can take many minutes for the electrode to return to normal operation. Clothing also can produce a static charge that affects electrode response.

**Gel-filled electrodes** do not require filling, but should not be left in dilute water for long periods of time. (Salt can leach from the gel into the dilute water and produce a large junction potential, resulting in errors in pH measurement.)

### **For liquid-filled electrodes:**

- a. Remove salt crystal deposits from the electrode, membranes, and junctions. Check that the reference junction is not blocked.
  - Rinse off salt buildup with deionized water.
  - Check that you can observe seepage of the filling solution through the junction.
- b. Always unplug the fill hole before making pH measurements, and replug it after use. If using an electrode after it has been in a storage solution, uncap the fill hole and suspend the elec-

trode in air for about 15 minutes. This will allow the filling solution to flush residual storage solution through the porous reference junction and thoroughly wet it.

- c. Check the filling solution level and replenish it if necessary—it should reach the bottom of the fill hole. Filling solutions differ in molarity and composition—always check that you are using the correct filling solution required by the manufacturer for a particular electrode.
  - d. Drain and flush the reference chamber of refillable electrodes, and routinely refill them with the correct filling solution (see manufacturer's recommendations).
4. **Monitor electrode response.** Keep a record of electrode operation in the pH meter log book. Record the Nernst slope reading and the millivolt readings at pH 7 and pH 4 after calibration.
- Properly working glass electrodes should give approximately 98.0 to 99.5 percent response of that expected from the theoretical Nernst relation (Busenberg and Plummer, 1987). The theoretical Nernst response is 59.16 mV/pH unit at 25°C.
  - A slope of less than 94 percent signals possible electrode deterioration and the need to monitor closely any further decline in slope percent. If possible, replace or recondition the electrode at this point.
  - **Do not use an electrode with a slope of 90 percent or less.**
5. Keep the electrode bulb moist and capped when not in use. Keep a moist piece of cotton or lint-free tissue in the cap to prevent the bulb from drying out.

### *Reconditioning liquid-filled electrodes*

Before beginning a field trip, if you are unsure of an electrode's condition or have persistent problems during calibration, use the following procedures to recondition the electrode.

1. Remove the old filling solution from the electrode—
  - a. Place the needle of a 1- or 3-mL syringe into the electrode filling hole (or use other methods of removing the filling solution, such as vacuum extraction or draining).
  - b. Tilt the pH electrode until the filling solution is near the filling hole and the needle tip is covered with the filling solution.
  - c. Pull back on the syringe plunger until the syringe is full.
  - d. Discharge the solution from the syringe into a waste container and repeat steps 1(a) through (d) until all of the filling solution has been removed from the pH electrode chamber.

2. Flush the pH electrode chamber with deionized water—
  - a. Use a syringe or squeeze bottle to partially fill the pH electrode chamber with deionized water.
  - b. With a syringe, remove the deionized water from the pH electrode chamber.
  - c. As a result of changes in pressure, temperature, and evaporation, crystals may form in the pH electrode chamber. If they form, repeat steps 2(a) and (b) until all crystals have been dissolved and removed from the pH electrode chamber.
3. Fill the electrode chamber with new filling solution—
  - a. Flush the electrode chamber with fresh filling solution using a syringe or a plastic squeeze bottle.
    - Partially fill the pH electrode chamber with filling solution.
    - Tilt the pH electrode so that the filling solution will contact all of the internal electrode surfaces.
    - Remove and discard the filling solution to a waste container.
  - b. Fill the electrode chamber with fresh filling solution until the filling-solution level is just below the fill hole. Be sure to use the correct molarity filling solution.
  - c. Rinse any excess filling solution from the outside of the electrode with deionized water.

**Filling solutions might not be interchangeable for different electrodes—  
check manufacturer's instructions.**

## *Electrode cleaning*

Electrodes must be kept clean and the liquid junction free flowing in order to produce accurate pH values. Because of the variety of electrodes available, check the manufacturer's cleaning instructions.

- ▶ Rinse the outside of the electrode thoroughly with deionized water after each use. In general, this should be the only routine cleaning needed.
- ▶ Rejuvenation procedures described by the manufacturer should be used if an electrode becomes clogged or extremely dirty.
  - After completing rejuvenation procedures on a liquid-filled electrode, drain, clean and refill the reference electrode chamber with fresh filling solution. Replace the fill-hole plug, and soak the electrode in storage solution overnight. Retest the electrode. If the procedures fail to remedy the problem, discard the electrode. Document electrode reconditioning or replacement in the instrument log book.
  - Gel-filled electrodes can be rejuvenated in some instances by placing the electrode in warm water (approximately 60°C) for about one minute or less. This procedure rejuvenates the junction by liquifying the salt gel.

### ***Electrode storage***

Electrodes must be clean before they are stored for any length of time.

**Short-term storage.** Short-term storage methods are appropriate only for in-service electrodes (those used daily or weekly). Storage solutions for short-term storage of electrodes differ with the type of electrode; follow the manufacturer's recommendations. Storage solutions can have a limited shelf life. Unless otherwise instructed by the manufacturer, avoid storing glass hydrogen-ion electrodes in deionized water or concentrated KCl solutions. In the latter case, absorbed potassium reduces the glass sensitivity to hydrogen ions.

- ▶ Store liquid-filled pH electrodes upright.
- ▶ Keep liquid-filled electrodes wet to maximize their accuracy and response time. Store them so that the bulb is fully immersed in proper electrode storage solution between uses at a field site. Before moving to the next field site, replace the plug on the fill hole, fill the protective cap with storage solution, and cover the electrode bulb with the cap.
- ▶ Gel-filled electrodes must only soak in a solution for short periods during measurements. Follow the manufacturer's instructions for storage of gel-filled electrodes.
- ▶ Clean the connector ends and store them in a plastic bag.

**Long-term storage.** pH measuring systems must be stored in an area that is clean, dry, and protected from extremely hot or cold temperatures. For long-term storage of liquid-filled electrodes, drain the filling solution from the electrode, rinse the outside of the electrode with deionized water, and store the electrode dry with a protective cap covering the bulb (put either storage or filling solution in the cap before placing the cap on the bulb if the manufacturer recommends that the bulb be kept moist). Clean the electrode connector ends (with alcohol, if necessary), and store them dry in a sealed plastic bag.

## CALIBRATION 6.4.2

Calibrate and check the operation of a pH instrument system at the field site. Two pH buffers are needed to properly calibrate the pH instrument system (pH 7 buffer and either the pH 4 or 10 buffer, depending on the anticipated sample pH). A third buffer can be used to check instrument system performance over a larger range. The pH of the buffer solution is temperature dependent: pH 10 buffers change more per unit change in temperature than do pH 4 buffers. The temperature of buffer solutions must be known, and temperature-correction factors must be applied before calibration adjustments are made. Calibration and operating procedures differ with instrument systems—check the manufacturer's instructions.

**Meters with microprocessors have reliable autocalibration functions and will automatically compensate for buffer temperatures and indicate Nernst slope. For such meters, follow the manufacturer's calibration instructions precisely—do not take shortcuts.**

- ▶ Check the records of electrode performance before each calibration and field trip (see 6.4.1). Electrode response is optimum between approximately 98 percent and 99.5 percent. A slope of 94 percent indicates possible electrode deterioration. **At 90 percent slope, the electrode cannot be used.**
- ▶ Calibrate or check the temperature sensor at least three times per year, and tag the sensor with the date of District certification. Do not use the automatic temperature compensating function of a pH meter if it has not been District certified within the past 4 months.
- ▶ Record calibration in the instrument log book and on field forms at the time of instrument calibration.

*Next, follow the 10 steps listed below:*

1. Temperature equilibration of equipment (this is not needed if using an automatic compensating meter).
  - a. Bring the pH buffers, thermometer (if necessary), container, and electrode to the temperature of the sample.
  - b. Allow 15 to 30 minutes for the buffers to adjust to the sample temperature. When making temperature corrections, use the correction factors provided by the buffer manufacturer (temperature coefficients can vary with buffer manufacturer).

- To equilibrate to stream temperature, place the buffer bottles in a minnow bucket or mesh bag and suspend them in the stream.
  - To equilibrate to ground-water temperature, place the buffer bottles in a mesh bag and suspend them in a bucket or other large container (an ice chest works well) overflowing with water being pumped from the well.
2. Inspect the pH electrode.
    - a. Check for damage to the electrode bulb, body, or cables.
    - b. Rinse any precipitate off of the electrode with deionized water (the measurement can be affected if precipitate falls into the buffer or sample).
    - c. Slide the protective sleeve up or down to uncover the filling hole.
    - d. Gently shake or tap the electrode to dislodge and remove air bubbles trapped in the sensing tip of the electrode and to remove excess deionized water. Do not wipe the electrode.
  3. Calibration rinse.
    - a. Rinse (with pH 7 buffer) the electrode, thermometer or automatic temperature compensating (ATC) sensor, and a container large enough to hold the sensors and buffer. Discard the used pH buffer into a waste container.
    - b. Pour fresh pH 7 buffer into the buffer-rinsed container that holds the electrode and thermometer. Allow the instruments to equilibrate for 1 minute (if necessary), then discard the buffer into a waste container.
  4. Calibration. Steps c, d, e are not needed for autocompensating meters.
    - a. Pour fresh pH 7 buffer into the container that holds the electrode and thermometer or ATC sensor.
      - The bulb of the pH electrode must not touch the bottom or side of the container.
      - Add enough pH buffer to cover the reference junction.
    - b. Swirl the sample gently or stir carefully with the electrode. If using a magnetic stirrer, stir slowly enough so that a vortex is not created. Place a thin piece of insulating material (styrofoam or cardboard) between the magnetic stirrer and beaker to prevent transfer of heat to the buffer solution.
    - c. Measure the temperature of the buffer solution; remove the thermometer (it is not necessary to remove the ATC sensor).

- d. Determine the theoretical pH of the buffer from the temperature-correction tables.
  - e. Note and record the pH temperature readings. Adjust the meter reading to the pH value using the "standardize" function on the meter (usually a knob or pressure pad). Record the adjusted pH value for the 7.0 buffer and associated millivolt reading.
  - f. Remove the electrode and ATC sensor (some instruments require that the meter be switched to the standby or off position before removing the electrode from the solution).
    - Repeat the calibration steps using fresh portions of reference buffer solution until two successive readings are obtained at the adjusted pH value for pH 7 buffer without further adjustment to the system.
    - Discard the used pH 7 buffer into a waste container.
5. Slope adjustment rinse.
- a. Rinse the electrode and thermometer or ATC sensor thoroughly with deionized water.
  - b. Rinse a clean container, electrode, and thermometer with a second buffer (usually pH 4 or 10) that brackets the expected pH value of the sample; discard the used buffer into a waste container.
  - c. Pour the second buffer into a container holding the electrode and thermometer or ATC sensor. Allow the temperature to equilibrate for 1 minute, then discard the used buffer into a waste container.
6. Slope adjustment. This step is automated in modern meters.
- a. Pour a fresh portion of the second pH buffer into a container holding the electrode and thermometer or ATC sensor.
  - b. Stir slowly (no vortex) or swirl manually. Follow the directions in 4b, above.
  - c. Measure the temperature and pH of the buffer solution and check the pH value of the buffer on temperature coefficient tables. Record the pH and temperature readings.
  - d. Adjust the slope to the value of the second pH buffer at known temperature. (Some meters have separate slope-adjustment knobs, pressure pads, or other devices, whereas others have to be adjusted by use of a temperature knob.) Record the adjusted pH value and associated millivolt reading.

- e. Discard the used buffer into a waste container.
  - f. Repeat steps 6(a) through 6(e) using successive portions of the buffer solution until two successive readings are obtained without further adjustment.
7. Rinse the electrode and thermometer or ATC sensor thoroughly with deionized water.
8. If using a noncompensating or nonautomated meter, repeat the calibration rinse (step 3) and calibration procedures [steps 4(a) through 4(d)] to ensure that the slope adjustments did not affect the calibration adjustment.
- This step is a check only; no adjustment should be needed, but the result should be recorded. If adjustment is needed, repeat the entire calibration procedure.
  - If adjustment is still needed, a systematic problem is likely (see 6.4.4). Inspect the instrument system, clean the electrode or add filling solution, or use a spare electrode or meter.
9. Calibration check rinse.
- a. Rinse the electrode and thermometer or ATC sensor with deionized water.
  - b. Rinse another clean container, electrode, and thermometer with a third buffer (pH 4 or 10) and discard the used buffer into a waste container.
  - c. Pour the third buffer into a container holding the electrode and thermometer or ATC sensor. Allow the temperature to equilibrate for 1 minute (if necessary), then discard the used buffer into a waste container.
10. Calibration range check.
- a. Pour a fresh portion of third pH buffer into a container holding the electrode and thermometer or ATC sensor.
  - b. Stir without forming a vortex or swirl slowly (see step 4b).
  - c. Measure the temperature of the buffer solution (remove the liquid-filled thermometer and check the temperature-adjusted pH value), if necessary for the meter being used.
  - d. The pH instrument system should read the value of the third buffer at a known temperature within  $\pm 0.1$  pH units.
    - Meters reading to three or more places to the right of the decimal may not provide better accuracy than  $\pm 0.05$  units, and their accuracy must be verified.
    - If it checks, the instrument system is calibrated over a range of pH 4 to 10 and is ready for ANC or alkalinity titrations as well as pH measurement.

- If the instrument system does not check over the entire range, recalibrate before measuring the sample pH. Recalibrate before an alkalinity/ANC titration if the sample has a pH greater than 7.0.
- e. Discard the used buffer into a waste container.
  - f. Rinse the electrode and thermometer (or ATC sensor) with deionized water.

**Never reuse buffers or put used buffer solution back into stock container.**

### *Calibration for low-conductivity water:*

Proper calibration of pH instrument systems with standard buffers does not guarantee accurate pH measurement in water with conductivity less than 100  $\mu\text{S}/\text{cm}$ . The following recommendations for pH measurement in low-conductivity water are taken from Busenberg and Plummer (1987).

1. After calibration with pH 4, 7, and 10 buffers, check electrode performance daily in appropriate sulfuric acid standard solution with conductivity less than 20  $\mu\text{S}/\text{cm}$ . (For solution preparation and handling, refer to Busenberg and Plummer, 1987).
  - Before using the sulfuric acid standard solution, check for contamination by measuring conductivity.
2. Check electrode performance with deionized water saturated with an analyzed nitrogen-carbon dioxide gas mixture having a carbon dioxide mole fraction of less than 0.5 percent.
  - Addition of KCl is not recommended because of the potential for contamination and other complications.
3. Rinse the electrode at least three times, preferably with a portion of the sample to be measured.
4. Cap the Lazaran™ reference electrode of retrofitted Hydrolab™ units with saturated KCl solution when not in use.
5. Calibrate and measure pH in quiescent (unstirred) solutions after the sample has been homogenized by stirring.
6. Check the electrode performance (slope) before using the percent Nernst slope and (or) millivolt readings at pH 7 and pH 4. Keep a record of the electrode slope and millivolt readings—they can signal electrode deterioration.

## 6.4.3 MEASUREMENT

The pH of a water sample can change significantly within hours or even minutes after sample collection as a result of degassing (such as loss of carbon dioxide, hydrogen sulfide, and ammonia); mineral precipitation (such as formation of calcium carbonate); temperature change; and other chemical, physical, and biological reactions. The electrometric method of pH measurement described below applies to filtered or unfiltered surface water and ground water, from fresh to saline.

**The pH of a water sample must be measured immediately in the field; laboratory-measured pH should not be relied on in place of field-measured pH.**

Field conditions, including rain, wind, cold, dust, and direct sunlight can cause measurement problems. To the extent possible, shield the instrument and measurement process from the effects of harsh weather.

- ▶ In dry, windy climates, a static charge can build up on the face of a pH meter and cause erratic readings on the display.
- ▶ Polish the face of the display with a soft, absorbent tissue treated with several drops of antistatic solution (such as plastic polish) to minimize this interference.

**TECHNICAL NOTE:** Temperature has two effects on pH measurement of a sample: it can affect electrode potential (Nernstian slope effect), and it can change hydrogen-ion activity (chemical effect). The electrode-potential problem can be solved by using an automatic or manual temperature compensator. The change in hydrogen-ion activity resulting from temperature changes in the sample can be minimized if the electrodes, buffers, and container are allowed to equilibrate to the same temperature.

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**SURFACE WATER 6.4.3.A**

It is generally preferable to measure pH in situ rather than on a sample taken from a splitter or compositing device. If stream conditions are such that water would pass the in situ pH sensor at a very high rate of flow, however, streaming-potential effects could affect the accuracy of the measurement. For such conditions, it is preferable to withdraw a discrete sample directly from the stream or compositing device and use the subsample measurement procedures described below. The pH instrument system should be set up on board the boat so that pH is measured at the time of sample collection.

Standard pH measurement in flowing surface water represents the cross-sectional mean hydrogen ion activity or median pH at the time of observation.

**To compute a mean pH for the stream:** (1) Sum the products of each subsection area, using the logarithm of the median pH determined for each subsection; (2) divide the sum by the total area of the cross section; and (3) convert back to pH by taking the antilogarithm of the quotient.

---

**In situ measurement**

*Follow the 7 steps listed below for in situ pH measurement:*

1. Calibrate a pH system on site (after equilibrating the buffers with the stream temperature, if necessary). Check the electrode performance (see "Electrode Maintenance," in 6.4.1) and the calibration date of the thermometer being used.
2. Record the pH variation from a cross-sectional profile, if possible, to determine if pH is uniform at any given discharge, and select the sampling method (NFM 6.0.2) appropriate for study objectives.
  - **Flowing, shallow stream**—Wade to the location(s) where pH is to be measured.
  - **Stream too deep to wade**—Lower a weighted pH sensor with a calibrated temperature sensor from a bridge, cableway, or boat. Do not attach the weight to sensor or sensor cables.
  - **Still-water conditions**—Measure pH at multiple depths at several points in the cross section.

3. Immerse the pH electrode and temperature sensor in the water to the correct depth and hold them there for at least 60 seconds to equilibrate them to water temperature.
4. Measure the temperature.
  - If the pH instrument system contains an automatic temperature compensator (ATC), use the ATC to measure water temperature.
  - If the instrument system does not contain an ATC, use a separate calibrated thermometer, adjust the meter to the sample temperature (if necessary), and remove the thermometer.
5. Record the pH and temperature values without removing the sensor from the water.
  - Values generally stabilize quickly within  $\pm 0.05$  to 0.1 standard pH unit, depending on the instrument system.
  - Record the median of the observed values.
  - If readings do not stabilize after extending the measurement period, note this difficulty on the field forms along with the pH readings, and record the median value of the last five or more readings.
6. EWI or EDI measurements—Proceed to the next station in the cross section. Repeat steps 3 through 5. After all stations in the cross section have been measured, rinse the sensors with deionized water and store them.
7. Record the stream pH on the field forms:
  - **In still water—median** of three or more sequential values.
  - **EDI—mean** value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
  - **EWI—mean or median** of all subsections measured. (Note that pH values must be converted to a logarithm before calculating a mean value.)

---

## Subsample measurement

When streams are fast-flowing or the water contains much sediment or algae, pH measurement of a discretely collected subsample might be preferable to in situ measurement. Representative samples are to be collected and split or composited according to approved USGS methods (Wells and others, 1990). pH measurement in fast-flowing streams should be made at the time of collection from a boat that has been set up for such measurements.

- ▶ Measure pH as soon as possible after compositing the EDI or EWI sample.
- ▶ Filter the sample if the pH continues to drift: measure pH in the field on both unfiltered and filtered subsamples and record both values on the field form.
- ▶ If the filtered sample provides the only stable pH value, report this value as sample pH.

TECHNICAL NOTE: Reported pH values are normally determined on an unfiltered sample. However, large concentrations of suspended sediment or algae can be a source of measurement error; slow settling of clay particles or algal respiration can cause "drift" of an observed pH value.

**Throughout collection and processing, avoid excess aeration to prevent losses and gains of dissolved gases (especially CO<sub>2</sub>) from solution.**

1. Calibrate the pH system on site (after equilibrating buffer temperature with stream temperature, if necessary). Check the electrode performance (see 6.4.1).
2. Select the appropriate sampling method (see NFM 6.0) and collect a representative sample.
3. Withdraw properly homogenized sample(s) from the compositing device.
  - Rinse the collection bottles three times with the sample (use filtrate, if a filtered sample is used).
  - If the samples need to be stored for a short time or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles, fill them to the brim, cap them tightly, maintain them at ambient stream temperature, and measure pH in the field as soon as possible.
4. Rinse thoroughly with deionized water—the pH electrode, thermometer or ATC sensor, stir bar, and a measurement container.
  - For pH, follow the deionized water rinse of equipment with a rinse using sample water.
  - For ANC or alkalinity, rinse with deionized water only; do not rinse with the sample when using this equipment (see NFM 6.6).

5. Immerse electrode and temperature sensor in sample water for at least 60 seconds to equilibrate to sample temperature.
6. Pour fresh aliquot of the sample water into a container holding the electrode and thermometer. **Do not let the electrode touch the bottom or sides of container during measurement.**
7. Measure and record the initial temperature. Use the ATC, if it is available and calibrated, or use a separate calibrated thermometer and adjust the meter manually to the sample temperature (if necessary).
8. Establish equilibrium between the electrode(s) and sample by stirring **slowly** (no vortex) or by manual swirling.
  - Do not stir if a vortex is formed that affects the electrode performance.
  - Do not use a magnetic stirrer for samples with low conductivity (less than 100  $\mu\text{S}/\text{cm}$ ).
  - Before recording a pH value, allow the sample to reach quiescence.
9. Record the pH and temperature measurements on the field forms, along with the sampling, processing, and measurement methods used and any observed anomalies.
10. **Quality control**—Repeat steps 6 through 9 with at least two fresh subsamples to check measurement precision. Subsample values should agree within  $\pm 0.1$  pH unit (or study-determined criterion). Report the median of the values measured.
11. Rinse the electrode and temperature sensor thoroughly with deionized water. Replace the plug on the fill hole of refillable electrodes and follow the recommended storage procedure.
12. Discard the used sample into a waste container and dispose of it according to regulations.

### 6.4.3.B GROUND WATER

Measurements reported as ground-water pH must represent aquifer conditions (consult NFM 6.0 for guidance). Measure pH as close to the source as possible, either downhole or within a flowthrough chamber.

- ▶ Use equipment that minimizes aeration and operate equipment in a manner to help mitigate losses and gains of dissolved gases in solution (for example, carbon dioxide).

- ▶ Although downhole measurements are likely to be most representative of ground-water pH, proper use of pH instruments with flowthrough chambers can yield comparable values.
- ▶ The downhole system is not practical if samples will be collected after field measurements, because the instrument should not be left in the well during sampling and the pump should not be turned off between purging and sample collection—use a flowthrough-chamber system.
- ▶ Streaming potentials in the flowthrough chamber can result in biased pH values. Make the final (the reported sample pH) measurement in quiescent water.

Bailed or other methods for collecting discrete samples isolated from their source are not recommended for the determination of pH, although such methods are sometimes used owing to site characteristics or study requirements. Record the method used to obtain the sample for pH measurements on the field forms and in the data base.

---

### Downhole and flowthrough-chamber measurements

1. Calibrate the pH instrument system on site.
  - a. If necessary, bring the buffer solutions to the temperature of the water to be measured (discharge the well water into a bucket while suspending the standards in a net bag; allow at least 15 minutes for temperature equilibration; check temperature of the water flowing into the bucket against that of the buffers).
    - Check that the thermometer has been District certified within at least the past 4 months.
    - Check electrode performance (see 6.4.1 and 6.4.2).
  - b. After calibration, rinse the pH electrode thoroughly with deionized water and blot it to remove excess water. Do not wipe the electrode.
2. Install the pH monitoring system for sample measurement (see 6.0.3 in NFM 6.0).
  - **Downhole system**—Lower sensors to the measuring point, followed by the pump, to monitor pH variation during purging.

- **Flowthrough system**—Install the chamber system as close to the well as possible and shield the chamber and tubing from direct sunlight. Check that the electrode fill hole is open to the atmosphere and that the reference junction is entirely submerged. Check for and eliminate a backpressure condition.
3. During purging (see table 6.0–1 and fig. 6.0–3 in NFM 6.0):
    - Keep the flow constant and laminar.
    - Allow the sensors to equilibrate with the ground water for 5 minutes or more at the flow rate to be used for collecting all of the other samples.
  4. Record pH values at regularly spaced time intervals throughout purging. Compare the variability of the pH values toward the end of purging with the stability criterion:
    - The stability criterion is met when five readings made at regularly spaced intervals of 3 to 5 minutes or more are within 0.1 standard pH unit or less (depending on the equipment). Routine measurement must fall within the  $\pm 0.1$  unit criterion. When readings fluctuate rapidly, select the median of three or more readings within about 60 seconds as the value recorded for the specific time interval.
    - If the criterion is not met, extend the purge period in accordance with study objectives, and continue to record measurements at regularly spaced time intervals. Record any difficulty on the field forms.
  5. Measure and report the pH:
    - If using a flowthrough system, divert the flow from passing into the flowthrough chamber after recording the other field measurements. Measure the sample pH in the chamber as soon as the water is still. Take several readings to be sure that the system has stabilized.
    - If using a downhole method, measure the sample pH after pumping has ceased. This entails installing the downhole sensors in the well after sample collection. If field measurements only are being monitored, stop the pump (after recording the other field-measurement values) and allow the pH to stabilize before recording the pH value.
    - Report the final value measured on a quiescent (no-flow) sample, if the values are stable. If the stability criterion is not met, record the range of values observed for the time interval monitored, and report the median of the final five or more values observed.



## Subsample measurement

pH measurements reported from bailed or other discrete samples need to be identified in the data base by a description of the sampling method used. Refer to 6.0.3.B in NFM 6.0 for use of bailers and the subsample method.

**Do not use a subsample method  
if waters are reducing.**

1. Calibrate the pH system on site (after equilibrating the buffers with the ground-water temperature, if necessary). Check the electrode performance (see sections 6.4.1 and 6.4.2).
2. Draw off a subsample through a bottom-emptying device that fits tightly over the bottle opening.
  - **Quality control**—Collect three subsamples to check precision.
  - Rinse the sample bottles three times with sample; use filtrate if filtered sample is used. Cap the bottles until they are ready for use.
  - If the samples need to be stored for a short time or if several subsamples will be measured, collect the sample aliquots in separate field-rinsed bottles, fill them to the brim, cap them tightly, maintain them at ambient ground-water temperature, and measure the pH as soon as possible.
3. Follow the procedures described in steps 4 through 12 for subsample measurement of surface water (6.4.3.A).

**TECHNICAL NOTE:** An alternative method is to pour the sample into an open container instead of measuring it in a closed system. If this method is used and readings do not stabilize within several minutes, the cause may be out-gassing of carbon dioxide—measure the sample in a closed system. Filter the sample if settling of charged clay particles interferes with the stability of readings.

## 6.4.4 TROUBLESHOOTING

Contact the instrument manufacturer if the suggestions in table 6.4–2 fail to resolve the problem.

- ▶ If available, use a commercial pH electronic calibrator to check the pH meter function.
- ▶ A large percentage of all problems encountered during pH calibration and measurement can be attributed directly to problems with the pH electrode—refer to 6.4.1.B.
- ▶ New electrodes are susceptible to some of the problems listed in table 6.4–2, and they may need reconditioning before they can be used.
- ▶ Check the voltage of the batteries. Always have good batteries in instruments and carry spares.

**Table 6.4–2.** Troubleshooting guide for pH measurement

[M, molar; HCl, hydrochloric acid; KCl, potassium chloride; °C, degrees Celsius; ~, about]

Symptom	Possible cause and corrective action
Instrument system will not calibrate full scale	<ul style="list-style-type: none"> <li>• Buffers may be contaminated or old—use fresh buffers.</li> <li>• Faulty electrode—recondition electrode (see discussion in section 6.4.1 on electrode maintenance, cleaning, and storage).</li> <li>• Weak batteries—replace.</li> </ul>
Slow response time	<p>For liquid-filled electrodes:</p> <ul style="list-style-type: none"> <li>• Weak filling solution—change filling solution (section 6.4.1).</li> <li>• No filling solution—add fresh solution (section 6.4.1).</li> <li>• Dirty tip—clean with soap solution. <b>Do not scratch electrode tip.</b></li> <li>• Chemical deposits—place electrode in a 0.1 M HCl solution for about 30 minutes.</li> <li>• Clogged or partially clogged junction—unclog by placing electrode tip in 0.1 M KCl solution at 90°C for about 15 minutes. <b>Do not boil calomel electrodes</b> (section 6.4.1).</li> <li>• Water is cold or of low ionic strength—longer equilibration time is needed (be patient).</li> <li>• Weak batteries—replace with new batteries.</li> </ul> <p>For gel-filled electrodes:</p> <ul style="list-style-type: none"> <li>• Dirty bulb—rinse with deionized water.</li> <li>• Clogged junction—liquify gel by placing electrode into warm (~60°C) water for one minute or less.</li> </ul>
Erratic readings	<ul style="list-style-type: none"> <li>• Loose or defective connections—tighten, clean, or replace connections.</li> <li>• Broken or defective cable—repair or replace cable.</li> <li>• Static charge—polish face of meter with antistatic solution.</li> <li>• Loose battery connection—tighten.</li> <li>• Air bubbles in the electrode bulb—shake gently.</li> <li>• Too much pressure in flowthrough chamber—reduce pressure.</li> <li>• Weak batteries—replace with new batteries.</li> </ul>

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## REPORTING 6.4.5

Report pH measurements in the data base to the nearest 0.1 standard pH unit.

- ▶ pH values to the nearest 0.05 unit can be published provided the instrument system has been calibrated at the required precision and accuracy.
- ▶ Report the instrument accuracy range with the published values and record the accuracy range in the data base, if possible.
- ▶ Enter the field-determined pH under the correct parameter code on the NWQL analytical services request form and on field forms.



# 6.5 REDUCTION- OXIDATION POTENTIAL (ELECTRODE METHOD)

By D.K. Nordstrom and F.D. Wilde

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# REDUCTION- 6.5

## OXIDATION POTENTIAL (ELECTRODE METHOD)

In contrast to other field measurements, the determination of the reduction-oxidation potential of water (referred to as redox) should not be considered a routine determination. Measurement of redox potential, described here as Eh measurement, is not recommended in general because of the difficulties inherent in its theoretical concept and its practical measurement (see "Interferences and Limitations," section 6.5.3.A).

- ▶ Eh measurement may show qualitative trends but generally cannot be interpreted as equilibrium values.
- ▶ Determinations of redox using the platinum (or other noble metal) electrode method (Eh) are valid only when redox species are (a) electroactive, and (b) present in the solution at concentrations of about  $10^{-5}$  molal and higher. Redox species in natural waters generally do not reach equilibrium with metal electrodes.

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**Reduction-oxidation potential (as Eh): a measure of the equilibrium potential, relative to the standard hydrogen electrode, developed at the interface between a noble metal electrode and an aqueous solution containing electroactive redox species.**

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Procedures for equipment calibration (test procedures) and Eh measurement are described in this section for the platinum electrode only. Although the general guidance given here applies to other types of redox electrodes (such as gold and glassy carbon electrodes), it is necessary to consult the manufacturer's instructions for correct use of the specific electrode selected. Concentrations of redox species can be determined by direct chemical analysis instead of using the electrode method (Baedecker and Cozzarelli, 1992).

## 6.5.1 EQUIPMENT AND SUPPLIES

The equipment and supplies needed for making Eh measurements using the platinum electrode method are listed in table 6.5–1. Eh equipment must be tested before each field trip and cleaned soon after use. Every instrument system used for Eh measurement must have a log book in which all the equipment repairs and calibrations or equipment tests are recorded, along with the manufacturer make and model numbers and serial or property number.

**Electrodes.** Select either a redox-sensing combination electrode or an electrode pair (a platinum and reference electrode). **Use of the correct electrolyte filling solution is essential to proper measurement and is specified by the electrode manufacturer.** Orion Company, for example, recommends selection of a filling solution to best match the ionic strength of the sample solution, in order to minimize junction potentials.

**Table 6.5–1.** Equipment and supplies used for Eh measurements<sup>1</sup>

[mV, millivolt; ±, plus or minus;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees Celsius]

- ✓ Millivolt meter or pH meter with millivolt reading capability, preferably with automatic temperature compensator; 0.1-mV sensitivity; scale to at least  $\pm 1,400$  mV; BNC connector (see instrument specifications for pH meters, 6.4.1 in NFM 6.4)
- ✓ Redox electrodes, either (a) platinum and reference electrode (calomel or silver:silver-chloride) or (b) combination electrode
- ✓ Electrode filling solutions (refer to manufacturer's specifications)
- ✓ Thermometer (liquid-in-glass or thermistor type), calibrated (see NFM 6.1 for selection and calibration criteria)—for use with millivolt meters without temperature compensator
- ✓ Flowthrough cell with valves, tubing, and accessories impermeable to air (for use with pump system)
- ✓ Sampling system: (1) in situ (downhole) measurement instrument, or (2) submersible pump (used with closed-system flowthrough cell). Pump tubing must be "impermeable" to oxygen.
- ✓ ZoBell's solution
- ✓ Aqua regia or manufacturer's recommended electrode-cleaning solution
- ✓ Liquid nonphosphate laboratory-grade detergent
- ✓ Mild abrasive: crocus cloth or 400- to 600-grit wet/dry Carborundum™ paper
- ✓ Deionized water (maximum conductivity of 1.0  $\mu\text{S}/\text{cm}$ )
- ✓ Bottle, squeeze dispenser for deionized water
- ✓ Safety equipment: gloves, glasses, apron, chemical spill kit
- ✓ Paper tissues, disposable, lint free
- ✓ Waste-disposal container

<sup>1</sup>Modify this list to meet specific needs of the field effort.

**CAUTION: The standard hydrogen reference electrode (SHE) can be dangerous and is not recommended for field use.**

- ▶ Silver:silver-chloride or calomel reference electrodes are the redox electrodes in common use.
- ▶ The Orion™ combination electrodes are platinum redox and silver:silver-chloride reference electrodes in one body (the Orion™ brand is used for purposes of illustration only).

**ZoBell's solution.** ZoBell's is the standard solution for testing redox instruments. ZoBell's solution can be obtained from the QWSU in Ocala, Fla., or it can be prepared fresh (see below). Quinhydrone solution is sometimes used but is not recommended because it is significantly less stable above 30°C and its temperature dependence is not as well defined as that of ZoBell's.

ZoBell's solution consists of a 0.1 molal KCl solution containing equimolal amounts of  $K_4Fe(CN)_6$  and  $K_3Fe(CN)_6$ . ZoBell's is reported stable for at least 90 days if kept chilled at 4°C. To prepare ZoBell's solution:

1. Weigh the chemicals (dry chemicals should be stored overnight in a desiccator before use).
  - 1.4080 g  $K_4Fe(CN)_6 \cdot 3H_2O$  (Potassium ferrocyanide)
  - 1.0975 g  $K_3Fe(CN)_6$  (Potassium ferricyanide)
  - 7.4557 g KCl (Potassium chloride)
2. Dissolve these chemicals in deionized water and dilute solution to 1,000 mL.
3. Store the solution in a dark bottle, clearly labeled with its chemical contents, preparation date, and expiration date. Keep the solution chilled.

**CAUTION: ZoBell's solution is toxic—handle with care.**

**Aqua regia.** Aqua regia can be used for cleaning the Eh electrode (check the electrode manufacturer's recommendations). Prepare the aqua regia at the time of use—do not store it. To prepare the aqua regia, mix 1 volume concentrated nitric acid with 3 volumes of concentrated hydrochloric acid.

### 6.5.1.A MAINTENANCE, CLEANING, AND STORAGE

Refer to 6.4.1 of NFM 6.4 on pH for general guidelines on meter and electrode maintenance, cleaning, and storage. Follow the manufacturer's guidelines on the operation and maintenance of the meters and electrodes, and keep a copy of the instruction manual with each instrument system. Keep the meters and electrodes clean of dust and chemical spills, and handle them with care.

#### *Maintenance*

Keep the surface of noble electrodes clean of coatings or mineral deposits. A brightly polished metal surface prevents deterioration of electrode response. The billet tip is more easily cleaned than the wire tip on the platinum electrode. Condition and maintain the Eh electrodes as recommended by the manufacturer.

#### *Cleaning*

Keep the O-ring on electrodes moist during cleaning procedures.

- ▶ To remove precipitate that forms on the outside wall or tip of the reference or combination electrode, rinse the outside of the electrode with deionized water.
- ▶ If particulates or precipitates lodge in the space between the electrode sleeve and the inner cone of sleeve-type electrode junctions, clean the chamber by flushing out the filling solution (the precise procedure to be followed must come from the electrode manufacturer).
- ▶ To remove oily residues, use a liquid nonphosphate detergent solution and polish the surface with mild abrasive such as coarse cloth, a hard eraser, or 400- to 600-grit wet/dry Carborundum™ paper (Bricker, 1982).
- ▶ To recondition the Eh electrode, immerse the electrode in warm aqua regia (70°C) for about 1 minute. **Do not immerse the electrode for longer than 1 minute** because aqua regia dissolves the noble metal as well as foreign matter and leads to an erratic electrode response (Bricker, 1982). Soak the electrode several hours in tap water before use.

TECHNICAL NOTE: Disassembly of the electrode is not recommended for routine cleaning and should only be used when absolutely needed. Additional cleaning and reconditioning procedures are discussed in NFM 6.4 and in American Public Health Association and others (1992), American Society for Testing and Materials (1990), Edmunds (1973), Adams (1969), and Callame (1968).

### *Storage*

For short-term storage, immerse the electrode in deionized water to above the electrode junction and keep the fill hole plugged to reduce evaporation of the filling solution. The recommended procedures for long-term storage of electrodes vary with the type of electrode and by manufacturer. The Orion™ combination electrodes are stored dry after rinsing precipitates from outside of the electrode, draining the filling solution from the chamber, and flushing it with water (consult the manufacturer's cleaning instructions). The electrode connector ends must be kept clean. Clean them with alcohol, if necessary. Store the connector ends in a plastic bag when not in use.

**Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.**

## 6.5.2 EQUIPMENT TEST PROCEDURE

Eh measuring systems can be tested for accuracy but they cannot be adjusted. Eh equipment must be tested, either in the laboratory or in the field, against a ZoBell's standard solution before making field measurements. In general, field testing with ZoBell's is not required, but the protocol used will depend on study needs.

- ▶ Before using, check that the ZoBell's solution has not exceeded its shelf life.
- ▶ Test the Eh equipment using the ZoBell's solution **before and after** field use.
- ▶ Be aware that:
  - ZoBell's is toxic and needs to be handled with care.
  - ZoBell's reacts readily with minute particles of iron, dust, and other substances, making field use potentially difficult and messy.

The Eh measurements are made by inserting a platinum electrode coupled with a reference electrode into the solution to be measured. The resulting potential, read directly in millivolts from a potentiometer (such as a pH meter), is corrected for the difference between the standard potential of the reference electrode being used at the solution temperature and the potential of the standard hydrogen electrode (table 6.5–2).

TECHNICAL NOTE:  $E_{\text{ref}}$  is the whole-cell potential of the reference electrode in ZoBell's solution.

$E_{\text{ref}} = 238$  mV (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the silver:silver-chloride (Ag:AgCl) electrode;

$E_{\text{ref}} = 185.5$  mV (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the calomel (Hg:HgCl<sub>2</sub>) electrode;

$E^{\circ} = 430$  mV is the standard electrode potential of ZoBell's solution measured against the hydrogen electrode at 25°C.

Half-cell potentials for the calomel, silver:silver chloride, and combination electrodes are shown in table 6.5-2. Table 6.5-3 provides the theoretical Eh of ZoBell's solution as a function of temperature. For those temperatures not shown on tables 6.5-2 and 6.5-3, interpolate the values. Add the value corresponding to the solution temperature to the measured potential electromotive force (emf measurement).

**Table 6.5-2.** Standard half-cell potentials of selected reference electrodes as a function of temperature and potassium chloride reference-solution concentration, in volts

[Liquid-junction potential included—multiply volts by 1,000 to convert to millivolts; KCl, potassium chloride; Temp °C, temperature in degrees Celsius; M, molar; —, value not provided in reference]

Temp °C	Silver:silver chloride			Calomel <sup>1</sup>				Orion™ 96-78 combination electrode <sup>3,4</sup>
	3M KCl <sup>1</sup>	3.5M KCl <sup>2</sup>	Saturated KCl <sup>2</sup>	3M KCl <sup>2</sup>	3.5M KCl <sup>2</sup>	4M KCl <sup>2</sup>	KCl saturated <sup>2</sup>	
10	0.220	0.215	0.214	0.260	0.256	—	0.254	0.256
15	0.216	0.212	0.209	—	—	—	0.251	0.253
20	0.213	0.208	0.204	0.257	0.252	—	0.248	0.249
25	0.209	0.205	0.199	0.255	0.250	0.246	0.244	0.246
30	0.205	0.201	0.194	0.253	0.248	0.244	0.241	0.242
35	0.202	0.197	0.189	—	—	—	0.238	0.238
40	0.198	0.193	0.184	0.249	0.244	0.239	0.234	0.234

<sup>1</sup>Modified from Langmuir (1971).

<sup>2</sup>Modified from Bates (1973).

<sup>3</sup>Nordstrom (1977) and D.K. Nordstrom, U.S. Geological Survey, written commun., 1995; the half-cell potentials calculated from Nordstrom (1977) are recommended rather than the values from Chateau (1954) cited in the instrument manual provided by the Orion Company because Nordstrom's values were developed specifically for the Orion™ 96-78 redox electrode and provide greater accuracy and precision.

<sup>4</sup>Orion™ manufacturer recommends that for sample solutions with total ionic strength exceeding 0.2 molar (for example, seawater), use a 4M KCl-saturated filling solution (usually supplied with the Orion™ model 97-78 electrode) and the half-cell potentials shown above for the silver:silver chloride saturated KCl reference electrode.

**Table 6.5-3.** Eh of ZoBell's solution as a function of temperature

[From Nordstrom (1977); °C, degrees Celsius; mV, millivolts]

Temperature °C	Eh (mV)	Temperature °C, (continued)	Eh (mV), (continued)
10	467	26	428
12	462	28	423
14	457	30	418
16	453	32	416
18	448	34	407
20	443	36	402
22	438	38	397
24	433	40	393
25	430		

*To test Eh equipment, complete the following 7 steps and record results on the Eh data record form for the equipment test procedure (fig. 6.5–1):*

1. Follow the manufacturers' recommendations for instrument warm up and operation.
  - Set the scale to the desired millivolt range.
  - Record the type of reference electrode being used.
2. Unplug the fill hole. Shake the electrode gently to remove air bubbles from the sensing tip of the electrode. Check the level of the filling solution and replenish to the bottom of the fill hole.
  - The filling solution level must be at least 1 in. above the level of solution being measured.
  - Use only the filling solution specified by the manufacturer.
3. Rinse the electrode, thermometer, and measurement beaker with deionized water. **Blot (do not wipe) excess moisture from the electrode.**
4. Pour ZoBell's solution into a measurement beaker containing the electrode and temperature sensor.
  - The Eh electrode must not touch the bottom or side of the container.
  - Add enough solution to cover the reference junction.
  - Allow 15 to 30 minutes for the solution and sensors to equilibrate to ambient temperature.
5. Stir slowly with a magnetic stirrer (or swirl manually) to establish equilibrium between the electrode(s) and solution. Switch the meter to the millivolt function, allow the reading to stabilize ( $\pm 5$  mV), and record the temperature and millivolt value.
6. Look up the half-cell reference potential for the electrode being used (table 6.5–2). Add this value to the measured potential to obtain the Eh of ZoBell's at ambient temperature.
  - If the value is within 5 mV of the ZoBell Eh given on table 6.5–3, the equipment is ready for field use. (See the example below.)
  - Refer to section 6.5.4 if the value is not within 5 mV of the ZoBell Eh.
7. Rinse off the electrodes and the thermometer thoroughly with deionized water. Store the test solution temporarily for possible verification.

**EXAMPLE:**

Example of the equipment test procedure using a silver:silver chloride-saturated KCl (Ag:AgCl) electrode.

$$E_h = emf + E_{ref}$$

where:

$E_h$  is the potential (in millivolts) of the sample solution relative to the standard hydrogen electrode,

$emf$  or  $E_{measured}$  is the electromotive force or potential (in millivolts) of the water measured at the sample temperature,

$E_{ref}$  is the reference electrode potential of the Zobell's solution corrected for the sample temperature (table 6.5-2).

- a. Follow steps 1-5 (above). For this example,
  - Measured temperature = 22°C
  - $emf = 238$  mV.
- b. Check table 6.5-2. The interpolated reference potential = 202 mV for Ag:AgCl-saturated KCl at 22°C.
- c. From  $E_h = emf + E_{ref}$

$$E_h \text{ (Zobell's)} = 238 \text{ mV} + 202 \text{ mV} = 440 \text{ mV.}$$

- d. Check table 6.5-3. The test value of 440 mV is within  $\pm 5$  mV of 438 mV from table 6.5-3. Thus, the equipment is functioning well and ready for field use.

**Check the date on Zobell's solution—do not use solution past its expiration date.**

### Eh Data Record

#### Equipment Test Procedure

Equipment description and identification (model and serial and/or W number): \_\_\_\_\_

Meter \_\_\_\_\_

Eh electrode \_\_\_\_\_ Reference electrode \_\_\_\_\_

ZoBell's solution: Lot # \_\_\_\_\_ Date: prepared \_\_\_\_\_ expired \_\_\_\_\_

Before sample Eh:    After sample Eh:

1. Temperature of ZoBell's solution:                      T = \_\_\_\_\_  
(after equilibration to ambient temperature)
  
2. Observed potential (in millivolts) of ZoBell's  
relative to measuring electrode, at  
ambient temperature ( $E_{\text{measured}}$  or *emf*):    *emf* = \_\_\_\_\_
  
3. Reference electrode potential (in millivolts)  
at ambient temperature from table 6.5-2  
( $E_{\text{ref}}$ ):     $E_{\text{ref}}$  = \_\_\_\_\_
  
4. Calculate Eh of ZoBell's:  $Eh = emf + E_{\text{ref}}$               Eh = \_\_\_\_\_
  
5. Theoretical potential (in millivolts)  
of ZoBell's at ambient temperature  
from table 6.5-3:    Eh (theoretical) = \_\_\_\_\_
  
6. Subtract calculated Eh from Eh theoretical  
(ZoBell's)(step 4 minus step 5)                       $\Delta Eh =$  \_\_\_\_\_
  
7. Check: is  $\Delta Eh$  within  $\pm 5$  mV?              Observations: \_\_\_\_\_

**Figure 6.5-1.** Eh data record: equipment test procedure.

## MEASUREMENT 6.5.3

To obtain accurate results, it is necessary to prevent losses and gains of dissolved gases in solution. Consult NFM 6.0 for information on precautions and general procedures used in sample collection and NFM 6.2 for a description of the flowthrough cell used in dissolved-oxygen determination (the spectrophotometric method).

- ▶ Chemical, physical, and biological reactions can cause the Eh of water to change significantly within minutes or even seconds after the collection of a sample.
- ▶ Water samples cannot be preserved and stored for the Eh measurement.
- ▶ Use equipment that eliminates sample aeration and operate the equipment to meet this goal. If using a flowthrough chamber or cell:
  - Use tubing that is impermeable (relatively) to oxygen.
  - Channel the sample flow through an airtight cell (closed system) constructed specifically to accommodate redox or ion-specific electrodes, temperature, and other sensors.
  - Connections and fittings must be airtight.
  - Purge atmospheric oxygen from the sample tubing and associated flow channels before measuring Eh.

**Do not use pumping systems in which inert gas contacts and lifts the sample to the surface: the gas could strip gaseous redox species from the water.**

Measure Eh in situ with a submersible instrument or use an airtight flowthrough system.

*First:*

1. Record the type of reference-electrode system being used (fig. 6.5-1).
2. Check for the correct electrode filling solution. If working in very hot or boiling waters, change the reference electrode filling solution daily.
3. Keep the electrode surface brightly polished.

TECHNICAL NOTE: Temperature determines the Eh reference potential for a particular solution and electrode pair, and may affect the reversibility of the redox reactions, the magnitude of the exchange current, and the stability of the apparent redox potential reading. The observed potential of the system will drift until thermal equilibrium is established. **Thermal equilibrium can take longer than 30 minutes but it is essential before beginning the measurements.**

*Next, measure the Eh and complete the field form (fig.6.5–2):*

1. Select an in situ or closed-system sampling method. Immerse the electrodes and temperature sensors in the sample water.
  - **In situ (or downhole)**—Lower the sensors to the depth desired and follow the manufacturer's recommendations.
  - **Closed-system flow cell**—Check that the connections and sensor grommets do not leak, and that the water being pumped fills the flowthrough cell.
2. Allow the sensors to reach thermal equilibrium with the aqueous system being measured and record the time lapsed.
  - It is essential that platinum electrodes be flushed with large volumes of sample water to obtain reproducible values.
  - Record the pH and temperature of the sample water.
3. Switch the meter to the millivolt function.
  - Allow the reading to stabilize ( $\pm 5$  mV).
  - Record the value and temperature (see the TECHNICAL NOTE that follows step 7, below).
  - **Stabilization should occur within 30 minutes.**
4. Take readings of the sample temperature and potential (in millivolts) every few minutes for the first 15 to 20 minutes.
  - It is best to stop the flow of the sample while the reading is being taken to prevent streaming-potential effects.
  - After 15 to 20 minutes, begin to record the time, temperature, and potential in plus or minus millivolts about every 10 minutes. Continue until 30 minutes have passed from the initial measurement and until the measurements indicate a constant potential.

5. After the measurements have been completed for the day, rinse the electrode(s) thoroughly with deionized water.

If field calibration is required for a study,

- a. Place the electrode(s) and other sensors in ZoBell's solution that has been equilibrated to the temperature of the aqueous system to be measured. The electrode(s) must not touch the container, and the solution must cover the reference junction.
  - b. Allow the electrode to reach thermal equilibrium (15 to 30 minutes).
  - c. Record the potential reading.
  - d. Follow steps 5–7 of the equipment test procedure in section 6.5.2.
6. Record all data and calculate Eh (see EXAMPLE, section 6.5.2). Fill out the Eh data record form for field measurements (fig. 6.5–2).

<b>Eh Data Record</b>		
<b>Field Measurements</b>		
	Field Eh	Field Eh <sup>1</sup>
1. Temperature and pH of system measured: T = _____	_____	_____
pH = _____	_____	_____
2. Time to thermal equilibration:		
Measurement began at _____	_____	_____
Measurement ended at _____	_____	_____
3. Measured potential of water system (mV): <i>emf</i> = _____	_____	_____
4. Reference electrode potential mV of ZoBell's at sample temperature: $E_{ref}$ = _____	_____	_____
5. Calculate sample Eh: $emf + E_{ref}$ (add step 3 + step 4): Eh = _____	_____	_____
6. Field measurements should agree within about 10 mV. Observations: _____		

<sup>1</sup>The second measurement is necessary for quality control.

**Figure 6.5–2.** Eh data record: field measurements.

### 7. Quality control—Repeat the measurement.

TECHNICAL NOTE: The response of the Eh measurement system may be considerably slower than that of the pH system and that response also may be asymmetrical: the time required for stabilization may be longer when moving from an oxidizing to reducing environment or vice versa. If the readings do not stabilize within about 30 minutes, record the potential and its drift; assume a single quantitative value is not possible. If an estimate of an asymptotic final (hypothetical) potential in such a drifting measurement is desired, refer to the method used by Whitfield (1974) and Thorstenson and others (1979).

## 6.5.3.A INTERFERENCES AND LIMITATIONS

Measurements should not be carried out without an awareness of the interferences and limitations inherent in the method.

- ▶ Organic matter and sulfide may cause contamination of the electrode surface, salt bridge, or internal electrolyte, which can cause drift or erratic performance when reference electrodes are used (American Public Health Association and others, 1992).
- ▶ Hydrogen sulfide can produce a coating on the platinum electrode that interferes with the measurement if the electrode is left in sulfide-rich water for several hours (Whitfield, 1974; Sato, 1960).
- ▶ The platinum single and combination redox electrodes may yield unstable readings in solutions containing chromium, uranium, vanadium, or titanium ions and other ions that are stronger reducing agents than hydrogen or platinum (Orion Research Instruction Manual, written commun., 1991).
- ▶ Do not insert redox electrodes into iron-rich waters directly after electrode(s) contact with ZoBell's. An insoluble blue precipitate coats the electrode surface because of an immediate reaction between ferro- and ferricyanide ions in ZoBell's with ferrous and ferric ions in the sample water, causing erratic readings.

Many elements with more than one oxidation state do not exhibit reversible behavior at the platinum electrode surface and some systems will give mixed potentials, depending on the presence of several different couples (Barcelona and others, 1989; Bricker, 1982, p. 59–65; Stumm and Morgan, 1981, p. 490–495;

Bricker, 1965, p. 65). Methane, bicarbonate, nitrogen gas, sulfate, and dissolved oxygen generally are not in equilibrium with platinum electrodes (Bernier, 1981).

TECHNICAL NOTE: Misconceptions regarding the analogy between Eh (pe) and pH as master variables and limitations on the interpretation of Eh measurements are explained in Hostettler (1984), Lindberg and Runnells (1984), Thorstenson (1984), and Bernier (1981). To summarize:

(1) Hydrated electrons do not exist in meaningful concentrations in most aqueous systems—in contrast, pH represents real activities of hydrated protons. Eh may be expressed as pe, the negative logarithm of the electron activity, but conversion to pe offers no advantage when dealing with measured potentials.

(2) Do not assume that redox species coexist in equilibrium. Many situations have been documented in which dissolved oxygen coexists with hydrogen sulfide, methane, and ferrous iron.

- The practicality of Eh measurements is limited to iron in acidic mine waters and sulfide in waters undergoing sulfate reduction.
- Other redox species are not sufficiently electroactive to establish an equilibrium potential at the surface of the conducting electrode.

(3) A single redox potential cannot be assigned to a disequilibrium system, nor can it be assigned to a water sample without specifying the particular redox species to which it refers. Different redox elements (iron, manganese, sulfur, selenium, arsenic) tend not to reach overall equilibrium in most natural water systems; therefore, a single Eh measurement generally does not represent the system.

## 6.5.3.B INTERPRETATION

A rigorous quantitative interpretation of a measurement of Eh requires interactive access to an aqueous speciation code. Exercise caution when interpreting a measured Eh using the Nernst equation. The Nernst equation for the simple half-cell reaction ( $M^I_{(aq)} = M^{II}_{(aq)} + e^-$ ) is

$$Eh = E^o + 2.303RT/nF \log (a^{II}_{M(aq)} / a^I_{M(aq)})$$

where:

$R$  = gas constant;

$T$  = temperature, in degrees kelvin;

$n$  = number of electrons in the half-cell reaction;

$F$  = Faraday constant; and

$a^I_{M(aq)}$  and  $a^{II}_{M(aq)}$  = thermodynamic activities of the free ions  $M^I_{(aq)}$  and  $M^{II}_{(aq)}$  and not simply the analytical concentrations of total  $M$  in oxidation states I and II, respectively.

Measurements of Eh are used to test and evaluate geochemical speciation models, particularly for suboxic and anoxic groundwater systems. Eh data can be useful for gaining insights on the evolution of water chemistry and for estimating the equilibrium behavior of multivalent elements relative to pH for an aqueous system. Eh can delineate qualitatively strong redox gradients; for example, those found in stratified lakes and rivers with an anaerobic zone, in an oxidized surface flow that becomes anaerobic after passing through stagnant organic-rich systems, and in mine-drainage discharges.

## TROUBLESHOOTING 6.5.4

Contact the instrument manufacturer if the suggestions in table 6.5-4 fail to resolve the problem.

- ▶ Check the voltage of the batteries.
- ▶ Always start with good batteries in the instruments and carry spares.

**Table 6.5-4.** Troubleshooting guide for Eh measurement

[ $\pm$ , plus or minus; mV, millivolts; *emf*, electromotive force]

Symptom	Possible corrective action
Eh of ZoBell's solution exceeds theoretical by $\pm 5$ mV	<p style="text-align: center;"><u>Check meter operation:</u></p> <ul style="list-style-type: none"> <li>• Use shorting lead to establish meter reading at zero mV.</li> <li>• Check/replace batteries.</li> <li>• Check against backup meter.</li> </ul>
Excessive drift	
Erratic performance	
Poor response when using paired electrodes	<p style="text-align: center;"><u>Check electrode operation:</u></p> <ul style="list-style-type: none"> <li>• Check that electrode reference solution level is to the fill hole.</li> <li>• Plug questionable reference electrode into reference electrode jack and another reference electrode in good working order of the same type into the indicator electrode jack of the meter; immerse electrodes in a potassium chloride solution, record mV, rinse off and immerse electrodes in ZoBell's solution. The two mV readings should be <math>0 \pm 5</math> mV. If using different electrodes (Ag:AgCl and Hg:HgCl<sub>2</sub>), reading should be <math>44 \pm 5</math> mV for a good reference electrode.</li> <li>• Polish platinum tip with mild abrasive (crocus cloth, hard eraser, or a 400–600-grit wet/dry Carborundum™ paper), rinse thoroughly with deionized water. Use a Kimwipe™ if these abrasives are not available.</li> <li>• Drain and refill reference electrolyte chamber.</li> <li>• Disconnect reference electrode. Drain and refill electrolyte chamber with correct filling solution. Wipe off connectors on electrode and meter. Use backup electrode to check the <i>emf</i>.</li> <li>• Read <i>emf</i> with fresh aliquot of ZoBell's solution; prepare fresh ZoBell's solution if possible.</li> <li>• Recondition electrode by cleaning with aqua regia and renewing filling solution—<b>this is a last resort.</b></li> </ul>

## 6.5.5 REPORTING

Report the calculated Eh in mV to two significant figures.

Potentials are reported to the nearest 10 mV, along with the temperature at which the measurement was made, the electrode system employed, and the pH at time of measurement.



## 6.6 ALKALINITY AND ACID NEUTRALIZING CAPACITY

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

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# ALKALINITY AND ACID NEUTRALIZING CAPACITY 6.6

Alkalinity and the acid neutralizing capacity (ANC) are determined using identical electrometric procedures involving the acidimetric titration of a sample; the only difference is that the alkalinity sample is filtered, but the ANC sample remains unfiltered. The terms alkalinity, ANC, and carbonate alkalinity are used in this manual as follows:

- ▶ **Alkalinity** applies to the acid neutralizing capacity of solutes in a water sample, reported in equivalents per liter (or milliequivalents or microequivalents). Alkalinity, thus, consists of the sum of titratable carbonate and noncarbonate chemical species in a **filtered water sample** (filter membrane of 0.45- $\mu\text{m}$  or less pore size).
- ▶ ANC applies to the acid-neutralizing capacity of solutes plus particulates in an **unfiltered water sample**, reported in equivalents per liter (or milliequivalents or microequivalents). (The ANC value would be equivalent to alkalinity for samples without titratable particulate matter.)
- ▶ **Carbonate alkalinity** represents the acid-neutralizing capacity of carbonate solutes ( $\text{HCO}_3^- + 2m\text{CO}_3^{2-}$ , where  $m$  is moles), reported either in equivalents per liter (or milliequivalents or microequivalents) 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 ( $\text{HCO}_3^-$ ) and less frequently to carbonate ( $\text{CO}_3^{2-}$ ).

---

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

**Acid Neutralizing Capacity (ANC): the equivalent sum of all bases or base-producing materials in an aqueous system that can be titrated with a strong acid to an equivalence point.**

---

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

### **Alkalinity is determined on a filtered sample.**

Any substance in the water sample that reacts with the strong titrant acid can contribute to the water's acid neutralizing capacity.

- ▶ Important noncarbonate contributors include organic ligands (especially acetate and propionate) and ions of hydroxide, phosphate, ammonium, silicate, sulfide, borate, and arsenate (Hem, 1985).
- ▶ Except for unusual natural waters and waters significantly 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 filtered from samples to be titrated for the alkalinity determination.

**TECHNICAL NOTE:** Alkalinity and ANC are independent of exchange with carbon dioxide and other atmospheric gases. However, atmospheric gas exchange can alter concentrations of individual species, such as bicarbonate. Also, aeration of a sample during filtration can cause mineral precipitation on the filter—this alters alkalinity, especially in water systems closed to the atmosphere under ambient conditions.

## EQUIPMENT AND SUPPLIES 6.6.1

Equipment and supplies for the electrometric method to determine alkalinity and ANC are listed in table 6.6-1. The equipment must be tested before each field trip and cleaned immediately after each use.

### *Buret, micrometer buret, digital titrator*

The buret provides good accuracy and precision when used by a trained operator.

- ▶ Micrometer burets provide better accuracy and precision than burets—they can deliver acid increments to 0.0001 mL and are available commercially (for example, Gilmont™ micrometer burets).
- ▶ The digital titrator is not as accurate as a buret because it was designed for endpoint titrations. The digital titrator is popular because it is more convenient and less fragile than a buret and keeps the acid in a virtually closed system. (The Hach brand is used as an example in this document.) **Delivery tubes of clear (instead of red) plastic are recommended. Empty titrant cartridges are available.**

### *Volumetric pipet, graduated cylinder, digital balance*

The volumetric pipet is used for dispensing the correct volume of filtered sample only.

- ▶ Use only class A “TD” pipets. TD is a calibration designation meaning “To Deliver” (TD is distinguished from “TC” or “To Contain” pipets).
- ▶ Class A pipets should not be used to aspirate or dispense solutions containing suspended particles—the small bore of this pipet tends to reject particles during aspiration and retain them during delivery (C.J. Patton, U.S. Geological Survey, written commun., 1995).

The graduated cylinder and digital balance are used for dispensing the correct volume of unfiltered (ANC) sample only. The digital balance yields higher precision than the graduated cylinder.

**Table 6.6–1.** Equipment and supplies used for alkalinity or ANC titrations<sup>1</sup>

[mL, milliliters; ANC, acid neutralizing capacity; g, gram;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25°Celsius; N, normal]

**Equipment and supplies common for using either a digital titrator or a buret**

- ✓ pH meter, preferably with automatic temperature compensator (see NFM 6.4 for selection and associated supplies)
- ✓ pH electrode, calibrated, combination or equivalent, and appropriate filling solution, if required
- ✓ Thermometer, calibrated (see NFM 6.1 for selection and calibration criteria)
- ✓ Stirrer, magnetic (battery operated) or glass stir rods
- ✓ Stirring bars, Teflon™ coated, smallest size (always carry spare bars)
- ✓ Volumetric pipets, class A—25 mL, 50 mL, and 100 mL (for alkalinity)
- ✓ Graduated cylinder (for ANC). For higher precision, use a digital balance, 0.1-g accuracy, 200-g capacity, pocket-sized (available from Acculab Company)
- ✓ Pipet squeeze bulb or pipet pump
- ✓ Sample bottle, 500 mL, acid rinsed or deionized-water rinsed
- ✓ Beakers, glass—50 mL, 100 mL, and 150 mL
- ✓ Beaker, Berzelius, 300 mL, tall form, spoutless, with two- or three-hole stopper
- ✓ Deionized water (DIW) (maximum conductivity of 1  $\mu\text{S}/\text{cm}$ )
- ✓ Dispenser bottle, squeeze, for deionized water
- ✓ Filtration unit, in-line capsule or pressure unit with inert gas (for alkalinity)
- ✓ Sodium carbonate standard solution
- ✓ Safety gloves, glasses, acid spill kit, and apron
- ✓ Titrant solution, sulfuric acid solution, 0.1600*N*, 1.600*N*, and 0.01639*N* (pre-filled cartridges for use with the Hach system are available for 0.1600*N* and 1.600*N* solutions)
- ✓ Paper tissues, disposable, soft and lint free

**Equipment and supplies for using a digital titrator**

- ✓ Digital titrator and mounting assembly
- ✓ Delivery tubes, bent-stem, colorless, transparent
- ✓ Titrant cartridges, empty or prefilled according to study needs (used with Hach system)

**Equipment and supplies for using a buret**

- ✓ Calibrated buret, 25-mL capacity with 0.05-mL graduations and Teflon™ stopcock
- ✓ Calibrated buret, 10-mL capacity with 0.02-mL graduations and Teflon™ stopcock
- ✓ Micrometer buret (alternative to standard burets, for greater accuracy)
- ✓ Titrant solution, sulfuric acid solution, 0.01639*N*
- ✓ Buret stand and clamp
- ✓ Wire pen cleaner (for cleaning buret tip)
- ✓ Buret cap
- ✓ Buret meniscus reader
- ✓ Acid bottle, pump (for filling buret)

<sup>1</sup>Modify this list to meet the specific needs of the field effort.

## *Sulfuric acid titrant*

Sulfuric acid is the titrant used routinely by USGS. The normality of sulfuric acid titrant is subject to change with time.

- ▶ 0.1600N or 1.600N solutions in prefilled cartridges for the Hach digital titrator are available from the QWSU (USGS, Ocala, Fla.). Normality of sulfuric acid in prefilled Hach titrant cartridges is monitored by the QWSU for 1 year after date of purchase; the QWSU notifies USGS personnel if a change in normality occurs. The lot number indicates the date of preparation (QWSU will translate lot numbers upon request). **QWSU recommends that Hach titrant cartridges be used within 3 months of purchase.**
- ▶ 0.01639N solution for the buret is available from the QWSU. Normality of 0.01639N titrant is not monitored by the QWSU after preparation and standardization. **Check the normality of this titrant each month.**
- ▶ Acid solutions of other normalities may be needed, depending on the sample chemistry or the ionic strength. Prepare under a fume hood. Check the normality monthly.

TECHNICAL NOTE: For samples vulnerable to precipitation reactions, a Berzelius beaker can help minimize gas exchange. Select a size of Berzelius beaker that fits the sample volume and associated titrating equipment and yet minimizes headspace above the sample. Fit the Berzelius beaker with a two- or three-hole stopper to accommodate the electrode(s), the thermometer, and the digital or buret titrator. Another option is to work in a glove box filled with an inert gas atmosphere. Oceanographers use a closed cell with an expanding plunger to avoid gas exchange (Almgren and others, 1977).

**CAUTION: Use the safety precautions outlined on the Material Safety Data Sheets (MSDS) when handling chemicals—wear safety glasses, gloves, and protective clothing.**

### 6.6.1.A MAINTENANCE, CLEANING, AND STORAGE

Proper maintenance, cleaning, and storage of the pH instrument is critical for ensuring the accuracy of alkalinity or ANC determinations, and guidance is provided in NFM 6.4.

Clean the volumetric pipets, beakers, bottles, burets, and stirring bars with hot water and nonphosphate detergent; rinse them copiously with tap water followed by deionized water. If oily or chemical residues are difficult to remove, soak the glassware and nonmetal equipment in a mild (5 percent by volume) hydrochloric acid or nitric acid solution (see Horowitz and others, 1994), and repeat the detergent wash. Store cleaned equipment wrapped or bagged in plastic until ready for use.

Reagents must not exceed their shelf life. Store reagents, as appropriate, in a dust-free cabinet, desiccator, or refrigerator. When chemicals to be used for preparation of reagents are received, mark the dates of receipt and expiration on container. When a reagent is prepared, label the container with the contents, date of preparation, expiration date, and preparer's initials. Store the 0.01639*N* standard sulfuric acid solution and filled Hach titrant cartridges in a cool, dark place (a storage cabinet or frost-free refrigerator). Seal the filled cartridges in plastic bags to avoid moisture loss or gain.

**Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.**

## CALIBRATION AND STANDARDIZATION 6.6.2

Calibration is required for the pH instrument—follow instructions in NFM 6.4.

Alkalinity and ANC determinations require standardization if the 0.01639N sulfuric acid titrant (buret method) is used. In the procedure that follows (Fishman and Friedman, 1989), the reagent concentrations were selected so that the titrant volume would correspond exactly to the bicarbonate equivalent in milligrams per liter of sample.

### *Prepare fresh carbon dioxide-free deionized water (DIW):*

1. Boil the DIW in a beaker for 15 minutes.
2. Cool the DIW to room temperature. Cover the beaker to minimize atmospheric contamination while the DIW cools.

An alternative to the method in steps 1 and 2 is to infuse the DIW with compressed helium or nitrogen gas for about 10 minutes.

### *Prepare a fresh standard solution of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) (1.00 mL = 1.00 mg $\text{HCO}_3^-$ ):*

1. Dry 1.0 g primary standard  $\text{Na}_2\text{CO}_3$  at 150 to 160°C for 2 hours.
2. Cool in a desiccator; weigh out 0.8686 g  $\text{Na}_2\text{CO}_3$ ; add to a 1-L volumetric flask.
3. Dilute with carbon dioxide-free DIW to the 1-L mark.

### *Prepare sulfuric acid titration solution:*

1. Add 0.5 mL concentrated  $\text{H}_2\text{SO}_4$  (specific gravity 1.84 g/mL) to 950 mL DIW.
2. Mix thoroughly.

To standardize the sulfuric acid, follow steps 1 through 9 below. To check the normality of a sulfuric acid titration solution, follow steps 3 through 6 below.

1. Calibrate the pH system (follow the instructions in NFM 6.4).
2. Prepare a sodium carbonate standard solution as outlined above.
3. Pipet 25 mL of sodium carbonate standard solution into a 100-mL beaker.
4. Titrate with the sulfuric acid solution to pH 4.5.
5. Record the volume of titrant used.
6. Determine the normality of acid by use of the following equation:

$$N = (25) (0.01639) / mL_a$$

where

$N$  = normality, and

$mL_a$  = volume of sulfuric acid added in milliliters to reach pH 4.5.

7. Adjust the concentration of sulfuric acid to exactly 0.01639*N* by dilution with deionized water or by the addition of dilute acid, as indicated by the first titration.
8. Confirm the exact normality by restandardization.
9. Keep the solution in a tightly sealed 1-L glass bottle until used.
10. If the sulfuric acid titrant solution is not exactly 0.01639*N*, divide the actual normality of the H<sub>2</sub>SO<sub>4</sub> titrant by 0.01639*N* to obtain the correction factor.

**CAUTION: Wear appropriate safety gloves, glasses, and apron when working with corrosive and oxidizing solutions.**

## COLLECTION AND PROCESSING 6.6.3

Collect and process the samples in a manner that ensures that they represent environmental concentrations at the time of collection. Minimize the effects of wind, rain, cold, dust, and sun on the samples. Collect and process the samples in a chamber to protect them from airborne particulates.

Before collecting or processing the sample, clean the samplers, compositing and splitting devices, sample bottles, measurement vessels, and other equipment that contacts the sample (for detailed procedures refer to Horowitz and others, 1994).

- ▶ Prerinse the sample bottles with deionized water and store in sealable plastic bags until ready for field sampling (acid-rinsed sample bottles are recommended, especially for samples with low alkalinity or ANC). Field rinse the bottle(s) three times with sample (sample filtrate for alkalinity).
- ▶ Do not field rinse the measurement vessels. Volumetric pipets and graduated cylinders should be clean and dry before use.

### *To collect and process the sample:*

1. Filter the samples along with other anion samples, if making alkalinity determination. The 0.45- $\mu\text{m}$  flowthrough disposable filter capsule is the standard unit used by USGS. Record on field forms if a different unit or membrane is used, as this can affect the determination.
2. Fill and securely cap two 250-mL sample bottles with the sample (filtrate for alkalinity) to ensure there is enough sample to repeat the titration, to preserve the integrity of the second aliquot after the first has been opened, and to avoid losing the volume of sample needed to spillage.

3. Prevent agitation of the sample or prolonged exposure to air in order to avoid oxidation of hydrogen sulfide, ferrous iron, manganous manganese, and prevent precipitation of mineral phases.
  - Loss of carbon dioxide (CO<sub>2</sub>) from the sample will not change the alkalinity or ANC determination, but chemical or physical reactions can cause concentrations of bicarbonate and carbonate to change within minutes.
  - Begin the titration as soon as possible, as there is less chance of chemical precipitation once acidification begins. If the titration is delayed, maintain the samples at the temperature of their ambient environment.
  - If there is a tendency for mineral precipitation, collect and process the sample in an inert gas atmosphere.

### *Surface water*

Collect and process a representative sample according to USGS-approved methods (see Horowitz and others, 1994).

- ▶ NASQAN, BENCHMARK, and NAWQA programs require filtration of alkalinity samples through a 0.45- $\mu$ m membrane.
- ▶ To collect and process samples from anoxic lake or reservoir depth intervals, adapt procedures described for ground water.

### *Ground water*

Collect the sample as close to the source as possible; minimize aeration of the sample; take the precautions described in step 3 above.

- ▶ Purge the well (NFM 6.0) and connect the filter unit in-line with the pump.
- ▶ Flush and fill the lines and filter unit with sample water so as to exclude air.

## MEASUREMENT 6.6.4

Alkalinity, ANC, and concentrations of bicarbonate, carbonate, and hydroxide species are determined using either the inflection point titration (IPT) method or the Gran function plot (Gran) method to analyze the titration data. Be familiar with the information in 6.6.4.B (IPT method) and 6.6.4.C (Gran method) before selecting the method to be used and before starting the sample titration.

- ▶ **The inflection point titration (IPT) method** is adequate for most waters and study needs. Difficulty in identifying the inflection points using an IPT method increases as the ratio of organic acids to carbonate species increases.
- ▶ **The Gran method** is recommended for water in which the alkalinity or ANC is expected to be less than about 0.4 meq/L (20 mg/L as  $\text{CaCO}_3$ ), or in which conductivity is less than 100  $\mu\text{S}/\text{cm}$ , or if there are appreciable noncarbonate contributors or measurable concentrations of organic acids.

The IPT and Gran methods require electrometric titration of a sample with incremental additions of  $\text{H}_2\text{SO}_4$  of specified normality. Suggested combinations of titrant normality and sample volume for various ranges of alkalinity or ANC values are given in table 6.6–2. Generally, 1.600*N* acid is too strong for most samples and is used at alkalinity or ANC greater than 4.0 meq/L (200 mg/L as  $\text{CaCO}_3$ ).

**Table 6.6–2.** Suggested sample volume and titrant normality (*N*) for use with digital titrator or at various ranges of alkalinity or ANC [meq/L, milliequivalents per liter; mg/L, milligrams per liter;  $\text{CaCO}_3$ , calcium carbonate; mL, milliliter; >, greater than]

ANC or alkalinity (meq/L)	Alkalinity (mg/L as $\text{CaCO}_3$ )	Sample volume (mL)	Titrant normality (N)
0–1.0	0–50	100	0.1600 (or lower)
1.0–4.0	50–200	50	.1600
4.0–20	200–1,000	100	1.600
>20	>1,000	50	1.600

**Titrate a filtered sample if you will check the charge balance or will report the results as carbonate alkalinity.**

## 6.6.4.A TITRATION PROCEDURES

Titration procedures are identical for surface-water and ground-water determinations on filtered or unfiltered aliquots of fresh to saline water samples. Become familiar with the information and detailed instructions for the buret and digital titration systems and the IPT and Gran methods before proceeding with the titration.

**TECHNICAL NOTE:** Fixed endpoint titration to pH 4.5 is no longer used by the USGS for reported alkalinity values because it can be less accurate than the IPT and Gran methods, particularly at small concentrations of total carbonate species and in water with significant organic and other noncarbonate contributors to alkalinity or ANC.

Before beginning titration, select the titration system to be used.

- ▶ The digital system is convenient but tends to be less precise or accurate than the buret system because of mechanical inadequacies. Good technique is requisite to produce acceptable results.
- ▶ The buret system can be cumbersome and fragile in the field, and requires experience to execute with precision and accuracy.
- ▶ A micrometer buret can achieve accuracy to one-tenth of a mg/L (routine determinations are reported to whole numbers).

Select the size of the volumetric pipet (for alkalinity sample) or the graduated cylinder or digital balance (for unfiltered ANC sample) and the measurement vessel, according to the volume of sample needed.

- ▶ 50 mL of a sample in a 100-mL beaker is selected for most routine work.
- ▶ Use 100 mL of a sample in a 150-mL beaker for low concentration of alkalinity or ANC. If the total sample volume is small, you may need to use a sample volume of 25 mL or less, although concentration is low.
- ▶ Use 25 mL or less of a sample and a 50-mL beaker for high concentration of alkalinity or ANC.

To achieve greater accuracy, use lower normality titrant, decrease the volume of acid increments, and increase the number of increments. Figure 6.6–1 provides a general summary of the electrometric titration procedures for alkalinity or ANC.

When pipetting the sample, a small amount of contents remains in the tip of class A “TD” volumetric pipets—do not blow it out, but use the following procedure:

1. Suspend the pipet tip vertically in a beaker, touching neither the walls nor the contents of the receiving vessel.
2. Allow the sample to drain freely until the liquid it contains reaches the bottom of the bulb.
3. Touch the pipet tip to the beaker wall until the flow from the pipet stops—leave the tip in contact with the beaker wall for an additional 10 seconds after the flow stops.

**The buret system yields better accuracy  
than the digital titrator.**

Calibrate pH system.

Collect representative sample; filter subsamples for alkalinity.



- Field rinse sample bottles with sample (or filtrate).
- Fill bottles completely and cap tightly; maintain sample at ambient water temperature until titration.
- Rinse with DIW only: electrodes, sensors, beaker, stir bar, delivery tube.
- Place small-size stir bar in beaker.



Select and record titration method, subsample volume, and titrant normality.

- Digital system: Assemble titrator, bleed delivery tube, set counter to zero.
- Buret system: Fill clean, dry buret with titrant—purge trapped air bubbles.



- Pipet appropriate volume of sample into beaker.
- Place beaker on stirrer.
- Insert electrodes and temperature sensor, away from bottom or sides.
- Stir gently—do not splash; minimize vortex.
- Record initial time, pH, temperature, sample volume, normality, and counter reading if using digital system.



Add titrant, stir for 15–20 seconds, read and record pH.  
Repeat until titration is complete.



pH > 8.1

Titrate slowly (to determine carbonate species), small increments, to pH < 8.1.

pH < 8.1

Titrate rapidly, large increments, to pH ~ 5.5 (for conductivity < 100  $\mu\text{S}/\text{cm}$ ) and no less than pH 5.0 in carbonate systems. Continue titration in small increments to pH ~ 4.

pH < 5.0

Titrate cautiously, small increments: IPT to pH ~ 4.0 or less; Gran to pH ~ 3.5 or less. Titrate to lower pH if noncarbonate contribution is large.

Determine and record equivalence points.

**Figure 6.6–1.** Summary of alkalinity or ANC titration procedures.

When titrating, stirring helps to establish a uniform mixture of sample and titrant and an equilibrium between sensors and sample.

- ▶ **If using a magnetic stirrer, stir the sample slowly and continuously**, using the smallest stir bar; avoid creating a vortex and large streaming potentials. If using a digital titrator, keep the delivery tube immersed throughout the procedure but keep the aperture of the tube away from the stir bar to avoid bleeding acid from the tube to the sample between titrant additions.
- ▶ If swirling the sample to mix, make the pH measurement as the sample becomes quiescent, after each addition of titrant.
- ▶ Avoid splashing the sample out of the beaker or onto the beaker walls. Droplets on the beaker walls can be rinsed down with deionized water. If you splash the sample out of the beaker you must start over.

**If concentrations of contributing carbonate species will be determined**—Titrate to pH of about 8.1 carefully, in small increments. If concentrations of contributing carbonate species **will not** be determined—titrate rapidly at first, adding relatively large acid increments to bring pH to about 5.5; then titrate slowly in small increments.

- ▶ **IPT method.** Titrate to at least pH 4.0 (to pH 3.5 if the alkalinity or ANC range is unknown for the water sampled or if the sample contains high concentrations of noncarbonate contributors, such as organic acids).
  - Titrate cautiously at and beyond the expected equivalence points.
  - Let the pH value stabilize before the next addition of titrant.
- ▶ **Gran method.** Titrate to pH 3.5, or to pH 3.0 or less if the alkalinity or ANC range is unknown for the waters sampled.
  - It is not necessary to develop incremental points above about pH 5.5 for a Gran determination of the bicarbonate equivalence point.
  - A sufficient number of titration points beyond the equivalence are needed to ensure the accuracy of the calculation.

**To obtain the most accurate results for carbonate species, titrate at the field site without delay.**

**Quality control (QC)**—Verify your ability to reproduce the alkalinity or ANC determinations by repeating the titration periodically on duplicate or triplicate samples. The frequency and distribution of QC determinations are established by study requirements.

**Rule of thumb**—QC should be no less than every tenth sample. Determination on a filtered sample should be reproducible within  $\pm 5$  percent when titrating a duplicate aliquot from the same batch of sample filtrate.

- ▶ For filtered samples with less than 0.4 meq/L (20 mg/L as  $\text{CaCO}_3$ ), reproducibility should be between 5 and 10 percent.
- ▶ If the alkalinity is about 0.02 meq/L or less, differences between duplicate samples are likely to exceed 10 percent using the standard titration methods because of rounding error alone.

When interferences are absent, titration on an unfiltered sample often results in a determination identical to or within 5 percent of the filtered sample and can be used as the QC check. If filtered and unfiltered values fail the  $\pm 5$ -percent criterion, repeat the titration on a replicate aliquot of filtered sample.

Reproducibility of the ANC determination to within 5 percent on duplicate unfiltered samples can be problematical when the sample has large amounts of particulate matter—extend the quality-assurance criterion to  $\pm 10$  percent.

### Calculation

Use the following equation to calculate the alkalinity or ANC in milliequivalents per liter:

$$(\text{meq/L}) = \frac{\text{mL}_a \times N (\text{meq/mL}_{\text{acid}}) \times 1,000 (\text{mL/L})}{\text{mL}_{\text{sample}}}$$

where

$\text{mL}_a$  = total volume of the standard acid solution used to reach the equivalence point, in milliliters

$N$  = normality of the standard acid solution used, in milliequivalents per milliliter acid and

$\text{mL}_{\text{sample}}$  = volume of the sample titrated, in milliliters.

## Buret titrator

When using a buret, exercise caution to ensure that the acid does not evaporate or become contaminated by extrinsic matter or moisture. The titrant temperature should be equilibrated to the sample temperature before use. Always empty the buret after each use. Never reuse the titrant solution; dispose of the solution properly.

1. Fill a clean, dry buret with 0.01639*N* sulfuric acid titrant.
  - Use a 10-mL semimicroburet with 0.05-mL graduations and a Teflon™ stopcock for samples with alkalinity or ANC less than 4 meq/L (200 mg/L as CaCO<sub>3</sub>).
  - Use a 25-mL buret with 0.1-mL graduations and a Teflon™ stopcock for samples with alkalinity or ANC of 4 meq/L (200 mg/L as CaCO<sub>3</sub>) or greater and when the sample pH exceeds 8.1.
  - If greater accuracy is desired, use a Gilmont™-type micrometer buret.
2. Make sure that no air bubbles are trapped in buret or buret stopcock. Record the sulfuric acid normality and initial buret reading on field forms.
3. Pipet the selected volume of sample to a clean beaker. Do not pipet by mouth.
  - If a magnetic stirrer is used, place a clean, dry, small stir bar into the beaker before pipetting the sample to the beaker. Do not use a magnetic stirrer if sample conductivity is <100 μS/cm. Place beaker on stirrer.
4. Rinse the pH and temperature sensors with DIW. Blot water droplets adhering to the sensors with lint-free paper (residual DIW will not affect the determination).
5. Insert the sensors in the beaker.
  - Do not let the sensors touch the beaker bottom or wall.
  - Sample depth in the beaker must be sufficient to cover the junction of the reference electrode, the electrode bulb, and the temperature sensor.
6. Measure the initial pH and temperature while gently stirring or after gently swirling the sample.
  - Do not splash the sample onto the beaker wall or out of the beaker.

- Minimize the vortex caused by magnetic stirring.
  - Record on the field form the pH and temperature values, the counter reading (it should read "0000"), the titrant normality, the time, and the sample size.
7. Begin titration. If using a magnetic stirrer, stir the sample slowly and continuously. Measure pH after each addition of titrant, and after the acid and sample are mixed homogeneously. If a magnetic stirrer is not used, swirl to mix the sample and acid after each addition of titrant. Allow 15 to 20 seconds after each addition for equilibration, then record pH.
- **pH  $\geq$  8.1**—To determine the bicarbonate inflection point, add the titrant drop by drop in 0.01-mL increments with a 25-mL buret until pH is less than 8.0.
  - **pH  $<$  8.1**—Titrate rapidly to pH of about 5.0, using several large acid increments (to pH of 5.5 for sample alkalinity or ANC of 0.4 meq/L ( $<$ 20 mg/L as  $\text{CaCO}_3$ ) or conductivity of sample  $<$ 100  $\mu\text{S/cm}$ ).
  - **pH  $<$  5.0**—Cautiously add the titrant drop by drop in 0.01-mL increments from pH 5.0 to 4.0 or less (the most sensitive part of the titration curve is usually between pH 4.8 and 4.3). Extend titration to pH 3.5 or less if using the Gran method or for a sample high in organic acid concentration.

TECHNICAL NOTE: 0.01 mL of a standard 0.05-mL drop of titrant tends to remain on the buret tip. To dispense this 0.01-mL titrant drop, quickly rotate the stopcock through 180 degrees (one-half turn) and then rinse the titrant from the buret tip into the filtration beaker with a small quantity of DIW (C.J. Patton, U.S. Geological Survey, written commun., 1995).

### Calculation

Use the following equations to calculate alkalinity or ANC and carbonate species from inflection points with 0.01639*N* sulfuric acid:

$$\text{Alkalinity or ANC (meq/L)} = \frac{mL_a \times N \text{ (meq/mL}_{\text{acid}}) \times 1000 \text{ (mL/L)}}{mL_{\text{sample}}}$$

$$\text{Alkalinity (mg/L as CaCO}_3\text{)} = 1000/mL_s \times (0.8202 \times mL_a) \times CF$$

$$\text{Bicarbonate (mg/L as HCO}_3^-\text{)} = 1000/mL_s \times [(mL_a \text{ from ip near pH 8.3 to ip near pH 4.5)} - (mL_a \text{ to ip near pH 8.3})] \times CF$$

$$\text{Carbonate (mg/L as CO}_3^{2-}\text{)} = 1000/mL_s \times [(mL_a \text{ at ip near pH 8.3)} \times 0.9835] - (\text{mg/L OH}^- \times 3.527) \times CF$$

$$\text{Hydroxide (mg/L as OH}^-\text{)} = 1000/mL_s \times [(mL_a \text{ to ip near pH 8.3)} - (mL_a \text{ from ip near pH 8.3 to ip near pH 4.5})] \times 0.2788 \times CF$$

where:

$mL_{\text{sample}}$  or  $mL_s$  = volume of sample, in milliliters

$mL_a$  = volume of  $\text{H}_2\text{SO}_4$  added, in milliliters

$ip$  = inflection point

$CF$  = correction factor for  $\text{H}_2\text{SO}_4$  normality (to be used if normality of  $\text{H}_2\text{SO}_4$  is not exactly 0.01639*N*;  $CF$  is determined by dividing the actual normality of the  $\text{H}_2\text{SO}_4$  by 0.01639)

$N$  = normality of acid solution used.

The presence of hydroxide is indicated when the carbonate titrant volume exceeds the bicarbonate titrant volume.

## Digital titrator

It is necessary to be thoroughly familiar with the operation of the digital titrator before field use. A plunger in the digital titrator forces acid in the titrant cartridge into the delivery tube. The plunger is controlled by a main-drive screw, which in turn is controlled by rotation of the delivery knob. The delivery knob controls the volume of titrant delivered through the delivery tube, as indicated by a digital counter.

1. Record the sample volume to be titrated and the titrant normality. Equilibrate titrant temperature to sample temperature.
2. Assemble the digital titrator.
  - a. Depress the plunger-release button and retract the plunger.
  - b. Insert the titrant cartridge into the titrator and twist the cartridge one-quarter turn to lock it into position.
  - c. Carefully depress the plunger-release button and push the plunger forward until it makes contact with the Teflon™ seal inside the cartridge.
3. Remove the vinyl cap from the cartridge (save the cap) and insert the straight end of the delivery tube into the cartridge.
  - Do not push the delivery tube beyond the cartridge tip.
  - Do not alter the delivery tube.
  - Tag the delivery tube to avoid cross contamination. Do not interchange delivery tubes between cartridges with different titrant normality.
4. Purge the titrant through the delivery tube to ensure that no air bubbles or water are in the tube by holding the titrator with the cartridge tip up and turning the delivery knob to force a few drops of titrant through the end of the delivery tube. Rinse tube exterior with DIW and blot off acid or water droplets before inserting it into the sample.
5. Set the digital counter to zero using the counter-reset knob, taking care not to turn the delivery knob.
6. Pipet the selected volume of the sample to a clean beaker. If a magnetic stirrer is used, place a clean, dry, small stir bar into the beaker before pipetting the sample to the beaker. Do not use a magnetic stirrer for sample conductivity <math><100 \mu\text{S}/\text{cm}</math>.

7. Insert sensors into the beaker.
  - Rinse the pH and temperature sensors with DIW. Blot off water droplets adhering to the sensors.
  - Do not let sensors touch the bottom or wall of the beaker.
  - The amount of sample in the beaker must be sufficient to cover the junction of the reference electrode, the electrode bulb, and the temperature sensor.
8. Measure the initial pH and temperature while gently stirring or after gently swirling the sample.
  - Do not splash sample onto beaker wall or out of the beaker.
  - Minimize the vortex caused by magnetic stirring.
  - Record the pH and temperature values, the counter reading (it should read "0000"), the titrant normality, the time, and the sample size on field forms.
9. Immerse the end of the titrant delivery tube in the sample. To prevent bleeding of the titrant from the delivery tube, keep the aperture of the delivery tube away from the stir bar.
10. **Begin titration.** If using a magnetic stirrer, stir the sample slowly and continuously. Measure pH after each addition of titrant, and after the acid and sample are mixed homogeneously. If a magnetic stirrer is not used, swirl to mix the sample and acid after each addition of the titrant. Allow 15 to 20 seconds after each addition for equilibration, then record pH.
  - **pH  $\geq$  8.1**—Slowly add the titrant in replicate increments no greater than two to three digital counts until pH of the sample is about 8.0, to determine the carbonate inflection point. Record the pH and digital counter reading after each addition of the titrant. Larger increments can be used for samples containing high carbonate concentrations.
  - **pH  $<$  8.1**—Titrate rapidly with several large acid increments to pH of about 5.0 (to pH 5.5 for sample alkalinity at 0.4 meq/L ( $<$ 20 mg/L as  $\text{CaCO}_3$ ) or sample conductivity  $<$ 100  $\mu\text{S/cm}$ ).
  - **pH  $<$  5.0**—Add titrant cautiously, in increments of one to three digital counts, from pH 5.0 to 4.0 or less. (The most sensitive part of the titration curve is between pH 4.8 and 4.3 for many natural waters.) If using the Gran method, extend the titration to pH 3.5 or less and to pH 3.0 or less for samples high in organic acids and other noncarbonate contributors, or when the alkalinity or ANC range is unknown.

11. After completing the titration, depress the plunger release, retract the plunger, and remove the titrant cartridge. Immediately replace the vinyl cap on the cartridge tip. Discard the delivery tube after each use.
12. **Calculate alkalinity/ANC in the field—**

$$\text{Alkalinity or ANC (meq/L)} = \frac{mL_a \times N(\text{meq/mL}_{\text{acid}}) \times 1000 \text{ (mL/L)}}{mL_{\text{sample}}}$$

- To determine carbonate alkalinity concentrations and concentrations of contributing species, plot change in pH divided by change in digital counts against digital counts of the titrant or tabulate change in pH divided by change in digital counts.
- Refer to table 6.6–3 for digital titration factors.
- The factors and equations used for the 0.1600*N* or 1.600*N* titrant cartridges are as follows (these calculations are based on the same equations described under the buret titration procedures, except that milliliters of acid used is shown as digital counts for the Hach™ titrator; 800 counts = 1 mL):

$$\text{Alkalinity or ANC (meq/L)} = B(D3)(C_a)/mL_s$$

$$\text{Carbonate (mg/L as CO}_3^{2-}) = A(D1)/mL_s$$

$$\text{Bicarbonate (mg/L as HCO}_3^-) = (B-2A)(D2)/mL_s$$

$$\text{Hydroxide (mg/L as OH}^-) = (A-C)(D4)/mL_s$$

$$\text{Alkalinity (mg/L as CaCO}_3) = B(D3)/mL_s$$

where:

$mL_s$  = volume of the sample, in milliliters

$A$  = digital count from the initial pH to the inflection point near 8.3

$B$  = digital count from the initial pH to the inflection point near 4.5

$C$  = digital count from the inflection point near 8.3 to the inflection point near 4.5

$D$  = digital titration factor

$C_a$  = concentration of acid.

**Table 6.6–3.** Digital titration factors  
[ $N$ , acid normality]

Factors	0.01600 <i>N</i> titrant	0.1600 <i>N</i> titrant	1.600 <i>N</i> titrant
D1	1.20	12.0	120
D2	1.22	12.2	122
D3	1.00	10.0	100
D4	.34	3.4	34

## INFLECTION POINT TITRATION METHOD 6.6.4.B

The IPT method uses the inflection points of plotted values to select equivalence points instead of assuming equivalence points to be at pH 8.3 and 4.5 (as in the fixed endpoint method). Inflection points are points of maximum rate of change in pH per volume of titrant added. **Near equivalence points, rapid pH changes occur with small additions of titrant. For this reason, titration as you near and pass the expected equivalence points must be slow and cautious, using small incremental additions of titrant.** Relative error of the determinations can be within  $\pm 4$  percent if the equivalence point is recognizable within  $\pm 0.3$  pH unit of the true equivalence point.

**Use either the buret or digital titrator.** To determine the inflection point, you can either construct a titration curve by plotting the change in pH divided by the change in titrant volume against the incremental volumes of the titrant added to the sample, or tabulate a titration. Figures 6.6–2 and 6.6–3 represent the titration of a sample that has both a carbonate and a bicarbonate inflection point, whereas tables 6.6–4 and 6.6–5 represent a titration that resulted only in a bicarbonate inflection point.

- ▶ More than one inflection point in close proximity indicates that the true inflection point has been missed. If this occurs, titrate a duplicate sample using smaller acid increments near the inflection point or use a Gran plot.
- ▶ If no clear point or points can be determined easily, interferences from weak organic acids are likely—use the Gran method.

### EXAMPLES:

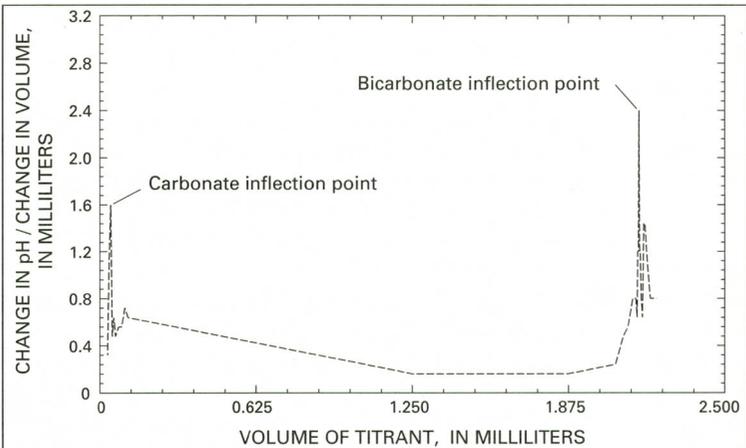
**IPT method using the buret system.** Referring to table 6.6–4, pH 4.51 at a titrant volume of 8.95 mL is the point of maximum rate of change of pH per volume titrant. The actual inflection point is before the titrant volume corresponding to the maximum change in pH per unit volume of acid added; therefore, the correct value lies between 8.95 mL and the previous value, 8.90 mL. In this example, the calculated titrant volume 8.93 mL would be the correct inflection point.

**IPT method using the digital titrator.** Referring to table 6.6–5, pH 4.51 is the point of maximum rate of change of pH per volume of titrant. The actual inflection point, however, is between the digital-counter value (454) representing the maximum change in pH per unit volume of acid added and the previous digital-counter value (452). The correct (calculated) digital-counter value for the inflection point would be 453. The error in computing concentration from the digital-counter value 454 instead of the digital-counter value 453 is considered insignificant. Note, however, that the larger the increments used, the greater the significance of the error. Calculation of the correct inflection point is recommended.

**Table 6.6-4.** Results of typical inflection point titration using a buret  
[mL, milliliter]

pH	Change in pH	Titrant volume (mL)	Change in volume	Change in pH per change in volume
7.28	—	0.00	—	—
7.00	0.28	2.00	2.00	0.140
6.70	.30	4.00	2.00	.150
6.33	.37	6.00	2.00	.185
5.73	.60	8.00	2.00	.300
5.24	.49	8.50	.50	.980
4.93	.31	8.70	.20	1.55
4.81	.12	8.80	.10	1.20
4.72	.09	8.85	.05	1.80
4.62	.10	8.90	.05	2.00
<b>4.51<sup>a</sup></b>	<b>.11</b>	<b>8.95</b>	<b>.05</b>	<b>2.20</b>
4.42	.09	9.00	.05	1.80
4.34	.08	9.05	.05	1.60
4.22	.12	9.12	.07	1.71
3.92	.30	9.22	.20	1.50
3.62	.30	9.32	.20	1.50

<sup>a</sup>pH 4.51 is the point at which the maximum rate of change of pH per volume of titrant occurs.

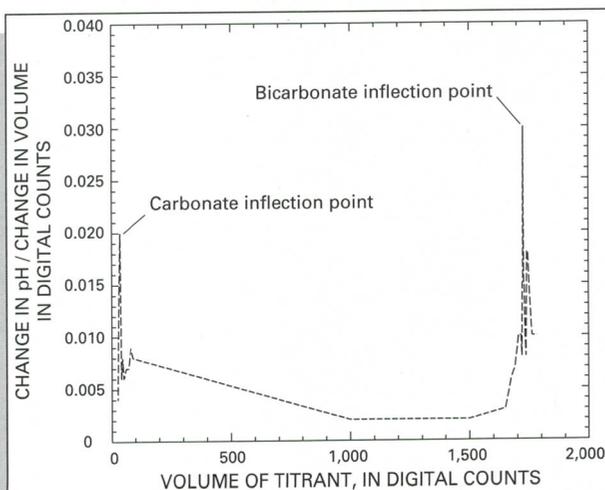


**Figure 6.6-2.** Example of an inflection point titration using a buret.

**Table 6.6-5.** Results of typical inflection point titration using a digital titrator

pH	Change in pH	Counter reading (mL)	Change in counter	Change in pH per change in counter
7.28	—	0	—	—
7.00	0.28	100	100	0.0028
6.70	.30	200	100	.0030
6.33	.37	300	100	.0037
5.73	.60	400	100	.0060
5.24	.49	435	35	.0140
4.93	.31	445	10	.0310
4.81	.12	448	3	.0400
4.72	.09	450	2	.0450
4.62	.10	452	2	.0500
<b>4.51<sup>a</sup></b>	<b>.11</b>	<b>454</b>	<b>2</b>	<b>.0550</b>
4.42	.09	456	2	.0450
4.34	.08	458	2	.0400
4.22	.12	461	3	.0400
3.92	.30	471	10	.0300
3.62	.30	481	10	.0300

<sup>a</sup>pH 4.51 is the point of maximum rate of change of pH per digital count.

**Figure 6.6-3.** Example of inflection point titration using a digital titrator.

### 6.6.4.C GRAN FUNCTION PLOT METHOD

Gran function plots commonly are used to determine alkalinity and ANC in sea water, low ionic-strength water, water with low carbonate concentrations, and water with measurable concentrations of organic compounds. The Gran function plot method also is used for calculations of the base neutralizing capacity in waters of low ionic strength such as atmospheric deposition.

The Gran function plot method uses functions that linearize titration curves, making it possible to determine alkalinity or ANC with a few points rather than relying on the inflection point from an entire titration curve (Baedecker and Cozzarelli, 1992). Four Gran functions can be calculated over the entire titration curve. The  $F_1$  function, described below, is the most commonly applicable Gran function.

- ▶ The  $F_1$  function requires titration data beyond the equivalence point, usually to pH between 3.0 and 3.5. For systems with measurable concentrations of organic acids, titrate to pH 2.5 (Baedecker and Cozzarelli, 1992).
- ▶ The buret titration system is recommended to achieve the accuracy desired when using the Gran method: substitute the equivalence points determined by the Gran function plot into the equations given in the discussion of the buret system. The digital titration system also is used under some circumstances (illustrated on table 6.6–6 and fig. 6.6–4): refer to table 6.6–3 to calculate concentrations.

*To construct a Gran function plot:*

1. Titrate incrementally to about pH 3.5. It is not necessary to develop incremental points above about pH 5.5 for a Gran determination of the bicarbonate equivalence point.
2. Plot  $(V_o + V_t) 10^{-\text{pH}}$  against the titrant volume (fig. 6.6–4 and table 6.6–6) using the  $F_1$  function for the bicarbonate equivalence point,

where:

$V_o$  = volume of the sample

$V_t$  = volume of the titrant added

$V_s$  = volume of the titrant needed to reach the bicarbonate equivalence point

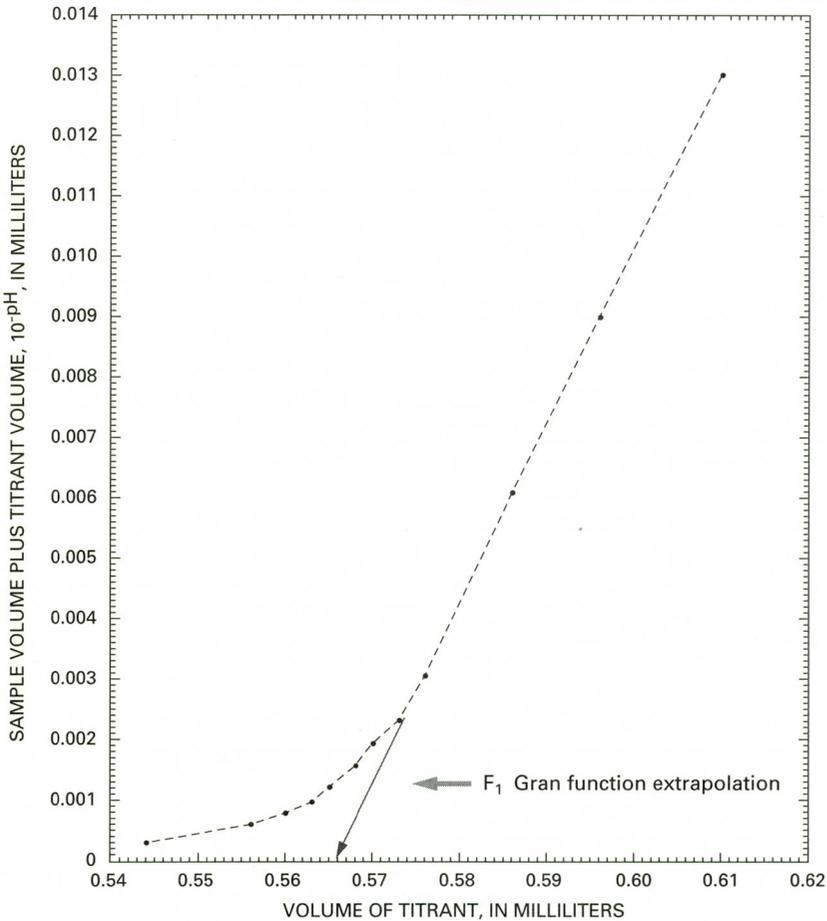
$V_w$  = volume of the titrant needed to reach the carbonate equivalence point.

3. Extrapolate the straight line in the region beyond the equivalence point to  $(V_o + V_t) 10^{-\text{pH}} = 0$  or  $V_t = V_s$ .
- ▶ **Carbonate equivalence point.** Plot  $(V_t - V_s) 10^{-\text{pH}}$  against the titrant volume (in mL or digital counts). To locate the equivalence point, extrapolate the straight line in the region beyond the equivalence point to  $(V_t - V_s) 10^{-\text{pH}} = 0$  or  $V_t = V_w$ .
  - ▶ **Hydroxide equivalence point.** Plot  $(V_o - 2V_w + V_t) 10^{-\text{pH}}$  against the titrant volume (in mL or digital counts). To locate the equivalence point, extrapolate the straight line in the region beyond the equivalence point to  $(V_o + V_t) 10^{-\text{pH}} = 0$  or  $V_t = V_w$ .

TECHNICAL NOTE: During alkalinity titration (carbonate system), the hydrogen ions added convert carbonate to bicarbonate and then bicarbonate to carbonic acid. The titration continues until no more species are reacting. When this process is complete, additional hydrogen ions will be in excess in the solution. The Gran function plot identifies the point at which all alkalinity has been titrated and hydrogen ions begin to be in excess. Beyond the equivalence point, the shape of the curve is determined by hydrogen ions in excess of all hydronium ion acceptors in the sample. The curvature results from the logarithmic relation between pH and hydrogen-ion activity.

## EXAMPLE:

**Gran function plot method using the digital titrator.** Refer to figure 6.6-4 and table 6.6-6. In the region beyond the equivalence point in figure 6.6-4, a straight line results. Extrapolation of this straight line to  $(V_o + V_t)10^{-\text{pH}} = 0$  or  $V_t = V_s$  locates the equivalence point. The extrapolated straight line intercept at  $(V_o + V_t) 10^{-\text{pH}} = 0$  on figure 6.6-4 is 0.566 mL of titrant added and corresponds to an equivalence point at approximately pH of 4.58.



**Figure 6.6-4.** Example of Gran function plot of a bicarbonate titration using a digital titrator.

**Table 6.6-6.** Example of information needed for a Gran function plot

[Data shown in columns 1, 2, 6, and 7 are results of an incremental titration using a digital titrator—remaining columns show calculations used for the Gran function plot (fig. 6.6-4); V, volume of sample; v, volume of titrant; mL, milliliters; cts, digital counts; e-, base 10 logarithm to the negative exponent]

pH	Change in pH	$10^{-\text{pH}}$	(V+v) in mL	$\frac{(V+v)}{10^{-\text{pH}}}$ in mL	Counter reading cts/mL	Change in counter	Change in pH/change in counter
7.28	0.00	5.248e-8	50.000	2.624e-6	0/0.00	0	0
7.00	.28	1.000e-7	50.125	5.012e-6	100/.125	100	.0028
6.70	.30	1.995e-7	50.250	1.003e-5	200/.250	100	.0030
6.33	.37	4.677e-7	50.375	2.356e-5	300/.375	100	.0037
5.73	.60	1.862e-6	50.500	9.404e-5	400/.500	100	.0060
5.24	.49	5.754e-6	50.544	2.908e-4	435/.544	35	.0140
4.93	.31	1.175e-5	50.556	5.940e-4	445/.556	10	.0310
4.81	.12	1.549e-5	50.560	7.831e-4	448/.560	3	.0400
4.72	.09	1.906e-5	50.563	9.635e-4	450/.563	2	.0450
4.62	.10	2.399e-5	50.565	1.213e-3	452/.565	2	.0500
4.51	.11	3.090e-5	50.568	1.563e-3	454/.568	2	.0550
4.42	.09	3.802e-5	50.570	1.923e-3	456/.570	2	.0450
4.34	.08	4.571e-5	50.573	2.312e-3	458/.573	2	.0400
4.22	.12	6.026e-5	50.576	3.048e-3	461/.575	3	.0400
3.92	.30	1.202e-4	50.589	6.082e-3	471/.586	10	.0300
3.75	.17	2.399e-4	50.601	8.998e-2	477/.596	6	.0280
3.59	.16	2.399e-4	50.610	1.301e-2	487/.610	10	.0160

## 6.6.5 TROUBLESHOOTING

The major difficulties with equipment for alkalinity or ANC are the same as for pH measurement—refer to NFM 6.4. Particulate materials, including algae or other biota, can interfere with the stability and reproducibility of pH readings. Such difficulties normally are eliminated by filtering the sample.

When the sample has low ionic strength, or when dissolved organic compounds or noncarbonate inorganic species are present that can interfere with the titration (note color, odor, or previous chemical analysis), follow the procedures for a Gran function determination.

## REPORTING 6.6.6

Report alkalinity and ANC to three significant figures. Only the value from filtered samples is to be published as alkalinity. Titration values from unfiltered samples are to be entered and published as ANC (the NWIS parameter code dictionary uses the term "alkalinity, unfiltered" instead of ANC).

Alkalinity and ANC should be reported in milliequivalents per liter (or microequivalents per liter), if possible. If this option is not available in the data base, calculate alkalinity and ANC in milligrams per liter, assigning all neutralizing capacity to the carbonate system.

If calculating ANC, alkalinity, bicarbonate, or carbonate in milligram units, then report: less than 1,000 mg/L, to whole numbers; 1,000 mg/L and above, to three significant figures. Carbonate alkalinity usually is reported in the data base in milligrams per liter as calcium carbonate.

Conversion factors listed below are taken from Hem (1985).

Multiply	By	To obtain
Alkalinity (mg/L as $\text{HCO}_3^-$ )	0.8202	Alkalinity (mg/L as $\text{CaCO}_3$ )
Alkalinity (mg/L as $\text{HCO}_3^-$ )	0.4917	Alkalinity (mg/L as $\text{CO}_3^{2-}$ )
Alkalinity (mg/L as $\text{CaCO}_3$ )	0.08332	Alkalinity (meq/L as $\text{CaCO}_3$ )
Bicarbonate (mg/L as $\text{HCO}_3^-$ )	0.01639	Bicarbonate (meq/L as $\text{HCO}_3^-$ )
Bicarbonate (mg/L as $\text{HCO}_3^-$ )	16.388	Bicarbonate ( $\mu\text{eq/L}$ as $\text{HCO}_3^-$ )
Carbonate (mg/L as $\text{CO}_3^{2-}$ )	0.03333	Carbonate (meq/L as $\text{CO}_3^{2-}$ )
Hydroxide (mg/L as $\text{OH}^-$ )	0.05880	Hydroxide (meq/L as $\text{OH}^-$ )

Report the average value for duplicate samples or the median when more than two replicate samples are used for quality control and the value falls within the appropriate quality-assurance criterion for variability.

Use the correct parameter code to indicate (1) the method of titration or calculation and (2) a filtered or unfiltered sample.



# 6.7 TURBIDITY

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## TURBIDITY 6.7

Turbidity measures the scattering effect that suspended solids have on light: the higher the intensity of scattered light, the higher the turbidity.<sup>1</sup> Primary contributors to turbidity include clay, silt, finely divided organic and inorganic matter, soluble colored organic compounds, plankton, and microscopic organisms (American Public Health Association and others, 1992). The measurement is qualitative and cannot be correlated directly as micrograms per liter of suspended solids.

---

**Turbidity: a measure of the collective optical properties of a water sample that cause light to be scattered and absorbed rather than transmitted in straight lines.**

---

Determination of turbidity is a common component of water-quality assessments.

- ▶ In surface water, the clarity of a natural body of water is used routinely as an indicator of the condition and productivity of the aqueous system.
- ▶ In ground water, turbidity commonly is measured during well development and well purging to indicate the extent to which particulates occurring as a result of well installation and sampling activities have been removed.

Turbidity measurements reported for regulatory purposes require a true nephelometric measurement using turbidimeter instruments that meet U.S. Environmental Protection Agency (USEPA) specifications (see 6.7.1).

---

<sup>1</sup>Turbidity measurements have not been systematically researched, tested, compared, or quality assured within the U.S. Geological Survey (USGS). Recommendations in this section were compiled from the references cited, instrument handbooks, field experience, and a limited series of tests on available instruments conducted by the USGS Hydrologic Instrumentation Facility (HIF).

Turbidity is measured in nephelometric turbidity units (NTU) or Formazin turbidity units (FTU), depending on the method and equipment used. Turbidity measured in NTU uses nephelometric methods that depend on passing specific light of a specific wavelength through the sample. FTU is considered comparable in value to NTU and is the unit of measurement when using absorptometric methods (spectrophotometric equipment). Jackson turbidity unit (JTU) values also approximate NTU but the JTU is no longer in common use. Turbidity values are entered into the USGS National Water Information System (NWIS) database only if the measurement is made in NTU and with instruments that are operated using USEPA-approved methods—not all turbidimeters that display NTU values meet these criteria.

**Visible turbidity is found at greater than 5 NTU (Strausberg, 1983). The legal limit of turbidity in drinking water is 0.5 NTU.**

**Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.**

## EQUIPMENT AND SUPPLIES 6.7.1

Equipment and supplies commonly used for field measurement of turbidity are listed in table 6.7-1. Before field use of water-quality instruments, become familiar with the manufacturer's instructions for calibration, operation, and maintenance. **Test field instruments before use.**

**Table 6.7-1.** Equipment and supplies used for measuring turbidity<sup>1</sup>

[≤, equal to or less than; μm, micrometer; mL, milliliters; in., inch]

- ✓ Turbidimeter or spectrophotometer or submersible-sensor instrument (such as a multiparameter instrument with a turbidity sensor).<sup>2</sup>
- ✓ Turbidity stock solutions and standards:
  - Formazin stock suspension, commercially obtained or prepared with hydrazine sulfate and hexamethylenetetramine chemicals.
  - Manufacturer-provided secondary standards.
- ✓ Sample cells (cuvettes), clear colorless glass (supplied from instrument manufacturer).
- ✓ Debubbler (degassing apparatus, commercially available or self-made).
- ✓ Inert (dry) gas (for example, nitrogen) and gas delivery apparatus; tanks must be fitted with regulators and filter.
- ✓ Sample bottle (preferably a bottle that does not sorb suspended material; if the sample will be stored temporarily, use an amber bottle).
- ✓ Silicon oil, optical grade (with same index of refraction as sample cells; supplied by instrument manufacturer).
- ✓ Paper tissues, extra lint free.
- ✓ Turbidity-free water, deionized water filtered through a ≤0.2-μm filter membrane with precision-sized pores.
- ✓ Bottle to hold turbidity-free water, cleaned and rinsed three times with filtered water.
- ✓ Volumetric flask, Class A, 100 mL or 500 mL.
- ✓ Volumetric pipet, Class A, 5.0 mL and pipet filler.
- ✓ Filter flask, 500 mL; filter holder; filter pump, aspirator.
- ✓ Rubber stopper, one-hole, No. 7; tubing, 5/16-in. inside diameter.

<sup>1</sup> Modify this list to meet the specific needs of the field effort.

<sup>2</sup> See text for description of USEPA-approved instrumentation.

**Turbidity instruments.** Three basic types of instrumentation are used to measure turbidity: turbidimeters (nephelometers), spectrophotometers, and multiparameter instruments with submersible sondes that can accommodate a turbidity sensor (commonly referred to as a turbidity probe). Choice of turbidity instrument depends on site characteristics and intended use of the data in addition to instrument specifications, performance, and reliability.<sup>2</sup>

- ▶ If measuring turbidity for regulatory or compliance purposes, the only method approved by the USEPA employs Method 180.1 (STORET NO. 00076) (USEPA, 1979).<sup>3</sup>
- ▶ For nonregulatory monitoring purposes, either a submersible sensor that measures turbidity using a near-infrared light source or a spectrophotometer in absorbance mode may be used.
  - Turbidity probes (submersible sensors) are available for multiparameter instruments with pH, temperature, conductivity, and other sensors; this is convenient for monitoring turbidity along with other field measurements. For ground-water studies, multiparameter instruments are available with sondes that can be used in 2-in. diameter wells.
  - Field spectrophotometers can be convenient for qualitative turbidity measurements if additional sample properties will be measured spectrophotometrically.

#### USEPA-approved specifications for turbidity instruments

- The light source should be a tungsten lamp operated at a color temperature between 2,200 to 3,000 Kelvin.
- The maximum distance traversed by incident and scattered light within the sample tube is 10 centimeters.
- The detector and any filter system are to have a spectral peak response between 400 and 600 nanometers.
- The detector should be centered at an angle of 90 degrees to the incident light path and must not exceed  $\pm 30$  from 90 degrees.
- Instrument sensitivity should permit detection of a turbidity difference of 0.02 NTU or less in water with less than 1 NTU.

<sup>2</sup>Turbidity instruments are being developed and improved by several companies; investigate instrument performance and reliability before making an equipment selection.

<sup>3</sup>The USEPA also approves the GLI-2 method turbidity instrument system (a microprocessor-based turbidity system using a pulsed-light, four-beam sensor); the GLI-2 provides stable and reproducible turbidity readings to 0.5 NTU but it is not a portable instrument.

Selected turbidity instruments were tested by the Hydrologic Instrumentation Facility. Referring to table 6.7–2, field tests of the Hach DR 2000™ indicated consistently higher FTU values compared with NTU values measured with the Analite 152™, Hach 2100P™, Hydrolab DataSonde 3™, and YSI 3800™. Not available at the time of testing were either the Hydrolab H20™ or YSI 6000™ multiparameter instruments with turbidity probe or the Analite 156™. Refer to Hydrologic Instrumentation Facility (1994) for test details.

**Table 6.7–2.** Measurement range and laboratory test results of selected turbidity instruments

[This table is meant to serve as a guide by which study criteria for turbidity instruments can be developed. Instruments listed were tested by the USGS Hydrologic Instrumentation Facility (HIF) unless otherwise noted. Turbidity instruments are being improved and new instruments are in development. NTU, nephelometric turbidity units; <, less than; ±, plus or minus; >, greater than; ~, approximately; %, percent; FTU, Formazin turbidity units; ≤, less than or equal to; YSI, Yellow Springs Instrument Company, Inc.; ISO, International Standards Organization]

Instrument	Measurement range	Percent difference from NTU standards
Hach 2100P™. (Handheld portable turbidimeter; 0.01 NTU resolution.) <sup>1</sup>	<10 to 1,000 NTU	~5%, 20 to 950 NTU
Hach Ratio/XR™. (Flowthrough cell, bench turbidimeter—can be adapted for field with a generator; 0.001 NTU resolution on 0–2 scale.) <sup>1</sup>	0 to 2,000 NTU	<5%, 20 to 950 NTU
Hydrolab DataSonde 3™ (DS-3) <sup>2</sup> . (Multiparameter, submersible instrument with internal logging and electronic communications capabilities.)	0 to 1,000 NTU	<2%, 40 to 950 NTU >10%, 20 NTU
YSI 3800™. (Multiparameter, submersible; 1 NTU resolution.)	0 to 1,000 NTU	≤3%, 40 to 950 NTU > 10%, 20 NTU
YSI 6000™. (Multiparameter, submersible instrument with internal logging and electronic communications capabilities; probe equipped with mechanical wiper.) <sup>2</sup>	0 to 1,000 NTU	Manufacturer specifications (not tested by HIF): ±5% of reading or 2 NTU (whichever is greater)
Analite 152™ and 156™. (Fiber optic portable nephelometer with wand-type sensor, 1-foot long.) <sup>2</sup>	<10 to >30,000 NTU	~5% or less, 400 to 950 NTU
Hach DR2000™. (Spectrophotometer; readings in FTU.)	0 to 450 NTU	5% or less, 20 to 400 NTU

<sup>1</sup>Meets USEPA regulatory specifications for turbidity measurements, has 90-degree hatchure and visible radiation.

<sup>2</sup>Hydrolab DataSonde3™, Analite 152™ and 156™, YSI 6000™ (not tested), and Hydrolab H20™ (not tested) use infrared technology. Instruments that conform to ISO 7027 criteria for backscatter angle of 90 degrees include the YSI 6000™, Hydrolab DS-3™, and Hydrolab H20™.

The method used for sample handling falls into three general categories, as dictated by instrument capabilities: (1) manual (discrete) sample, using a cuvette-based instrument, with sample decanted into a sample cell (cuvette); (2) pumped sample, in which a sample is pumped through a “flowthrough cell,” which is a turbidity-sensor-containing cuvette that is an internal part of the instrument; and (3) direct determination, by positioning a turbidity probe either in situ or into a flowthrough chamber that receives pumped sample (see NFM 6.0).

**Turbidity-free water.** Turbidity-free water is used for preparation of turbidity standards and is prepared by filtering either sample water or deionized water (DIW) through a 0.2- $\mu\text{m}$  or smaller pore-sized membrane. Turbidity-free water is recommended instead of unfiltered DIW for preparation of standards.

**Turbidity standards.** USEPA (1979) guidelines recommend monthly preparation of the stock turbidity suspension for the calibration standard, and daily preparation of the standard turbidity suspension at the dilutions needed (see 6.7.2). Formazin stock solution is available commercially.

**Debubbler/degassing system.** Bubbles in the sample will give false turbidity readings. A debubbler or degassing system is required if sample contains effervescing gases. The equipment plumbing must be set up to maintain a constant head, resulting in constant velocity through the turbidimeter’s flowthrough cell. When using a turbidity probe within a flowthrough chamber, it might be necessary to direct debubbled water through the chamber.

- ▶ Obtain a debubbler from the instrument manufacturer, or construct one as shown on figure 6.7–2 in section 6.7.3.
- ▶ Probe-based instruments are available with a wiper mechanism that clears bubbles from the optical surface of the submersible sensor (probe).

**Instruments with gas-sweep capacity.** Condensation must be removed or reduced throughout turbidity determination. Some flowthrough-cell instruments have the capacity to continuously sweep the sample compartment with dry gas, reducing condensation on the sample cell; otherwise, condensation is to be removed manually every few minutes.

## MAINTENANCE, CLEANING, AND STORAGE 6.7.1.A

Check manufacturer's instructions for instrument maintenance, cleaning, and storage. **Test equipment before each field trip and record all repairs in the instrument log book.** Manufacturer's instructions and the log book should accompany the instrument at all times.

**Turbidity instruments.** Protect instruments from extreme temperatures. Shield the instrument LED display panel from direct sunlight. If a bench-top turbidimeter gets wet, allow it to dry thoroughly before the next use (field turbidimeters are constructed to withstand moisture). Check and replace batteries routinely.

**Sample cells (cuvettes).** Handle and store sample cells in a manner to prevent dirt, scratches, or other damage. Follow instrument manufacturer instructions for the maintenance of sample cells. Keep sample cells scrupulously clean, inside and out. After each use, (1) wash with nonphosphate laboratory detergent, (2) rinse repeatedly with deionized water until all detergent residue is removed, and (3) allow cells to air dry in a dust-free environment.

**Submersible turbidity probe.** Exercise care that optical surfaces of probes are not scratched during cleaning, operation, or storage. Scratched or damaged probes must be replaced. Keep optical surfaces free of all foreign material by wiping with moist lens-cleaning paper or cloth.

**Standard solutions.** Discard turbidity standards with elapsed expiration dates. Protect turbidity standards from extreme temperatures. Never pour used standard or a portion of unused standard back into its original (stock) container.

**Keep sample cells scrupulously clean and free of scratches.**

## 6.7.2 CALIBRATION

Follow the manufacturer's instructions for instrument calibration and record calibration readings and adjustments in the instrument log book.

- ▶ Calibration of turbidity instruments against a Formazin or other approved primary standard usually is done in the laboratory, with instrument checks performed in the field. **Use standards that bracket the range of turbidity anticipated in environmental samples, if possible.**
- ▶ For instruments that are factory calibrated in standard turbidity units, the calibration procedure checks the accuracy of calibration scales provided by the manufacturer.
- ▶ Periodically check the accuracy and precision of your instrument against that of another instrument.
- ▶ Consult the manufacturer if the precision of your instrument deviates 5 percent or more from the manufacturer's specifications.

The USEPA specifies that the turbidimeter must be calibrated with a primary standard (a Formazin or a styrene divinylbenzene polymer standard such as Amco AEPA-1 Polymer™) (U.S. Environmental Protection Agency, 1994). A solid scattering standard provided by the manufacturer for setting overall instrument sensitivity for all ranges should not be relied on unless the turbidimeter is demonstrated to be free of drift on all ranges (U.S. Environmental Protection Agency, 1979).

Temperature changes affect Formazin turbidity standards and the performance of the turbidity instrument.

- ▶ Turbidity instruments are not currently available with an automatic temperature-compensating function.
- ▶ Standards and instruments should be at the same and constant temperature during calibration to achieve stable and accurate results.
- ▶ To avoid the effects of thermal fluctuations on the calibration, perform the Formazin calibration and calibration of the secondary standard (for example, Gelex™) against the primary standard in the office laboratory at room temperature instead of at the field site. At the field site, check instrument calibration using a secondary standard.

### *Preparation of the stock turbidity suspension and standard dilutions*

Prepare the stock turbidity suspension monthly and standard dilutions on the day of instrument calibration. To prepare and dilute a 400 NTU Formazin stock suspension<sup>4</sup>:

1. Dissolve 1.000 g hydrazine sulfate  $[(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4]$  in filtered water and dilute to 100 mL in a volumetric flask.
2. Dissolve 10.00 g hexamethylenetetramine  $[(\text{CH}_2)_6\text{N}_4]$  in filtered water and dilute to 100 mL in a volumetric flask.
3. Mix 5.0 mL of hydrazine sulfate and 5.0 mL of hexamethylenetetramine solutions in a 100-mL volumetric flask and let stand 24 hours at  $25 \pm 3^\circ\text{C}$ ; dilute to the mark and mix. To prepare 500 mL of 400 NTU standard, mix 25 mL of the reagent solutions in a 500-mL flask, dilute to the mark, and mix.
4. For a 40 NTU standard, dilute 10.00 mL of the 400 NTU stock suspension to 100 mL with turbidity-free water (sample or deionized water passed through a filter media of  $\leq 0.2 \mu\text{m}$ ).
  - Dilute stock suspension on the day the standard is needed, use it immediately after preparation, and discard unused standard.
  - Inconsistent techniques used to dilute standards can add as much as 5 percent measurement error.

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## TURBIDIMETER CALIBRATION 6.7.2.A

The calibration instructions and procedures that follow are general and should be modified to apply to the instrument being used—check manufacturer's instructions:

1. Prepare Formazin suspensions as described above.
  - Calibrate each instrument range using at least three standard concentrations. Use standards that bracket the range of turbidity anticipated in the sample solution.
  - Prepare dilute standards fresh from the stock at the time of use—after dilution, the stock suspension is stable only for 4 to 6 hours.
  - For turbidity greater than 40 NTU, use undiluted stock solution.
  - **Do not use standards with flocculated suspensions.**

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<sup>4</sup> Refer to American Public Health Association and others (1992) for detailed instructions.

2. Switch the turbidimeter on and allow it to warm up. Put on disposable gloves.
3. Check instrument focus: insert template in the cell holder. The lamp image should just fill the inside circle. Adjustment is required if the image is off center, too large, or too small.
4. Field rinse a clean, dry, scratch-free, index-marked cell with the highest concentration of the standard for the instrument range setting or range of interest.
  - a. Hold the sample cell by the rim (top lip), not beneath the lip.
  - b. Pour standard into the sample cell to the fill mark.
  - c. Wipe the exterior of the cell using a soft, lint-free cloth or tissue to remove moisture (condensation) on cell walls.
  - d. Apply a thin layer of silicon oil (table 6.7–1) onto the exterior of the cell to reduce condensation on the cell and mask slight scratches and nicks. Apply silicon oil uniformly onto the blank cell if it will be used on the cell filled with standard (check manufacturer's recommendations).
5. Select the desired NTU range.
  - Set the calibration adjustment to equal the high value of standard for the range of interest.
  - Before inserting the standard, ensure that no air bubbles are present.
6. Orient the standard cell in the cell holder—the calibration cell and sample cell must have identical orientation when in the instrument measurement chamber.
7. In the instrument log book, record and graph the instrument value for each standard (instrument reading versus standard value—see fig. 6.7–1).
8. Adjust standardization control until the value on the meter equals the NTU value of the standard used.
9. Remove the sample cell and discard the first turbidity standard.
  - a. Rinse and fill a clean cell with the second turbidity standard and orient the cell in the instrument.
  - b. Take a reading without adjusting the calibration.
  - c. Plot this instrument NTU reading against the NTU value of the turbidity standard (fig. 6.7–1).

10. Repeat step (9) for at least one more turbidity standard with NTU value to cover the turbidity range of interest. The greater the number of turbidity standard values used, the greater the reliability of the calibration.
11. Prepare a calibration curve for each range of values to be used if a precalibrated scale is not supplied by the manufacturer. (The accuracy of calibration scales provided with the instrument must be verified by using a precalibrated instrument and appropriate standards.)
  - The plot of instrument reading versus turbidity standard value is a range calibration curve.
  - Verify that any instrument reading (dial setting) within the range calibrated is correct and agrees with correlative points on the calibration curve.
12. Calculate the NTU of a diluted sample:

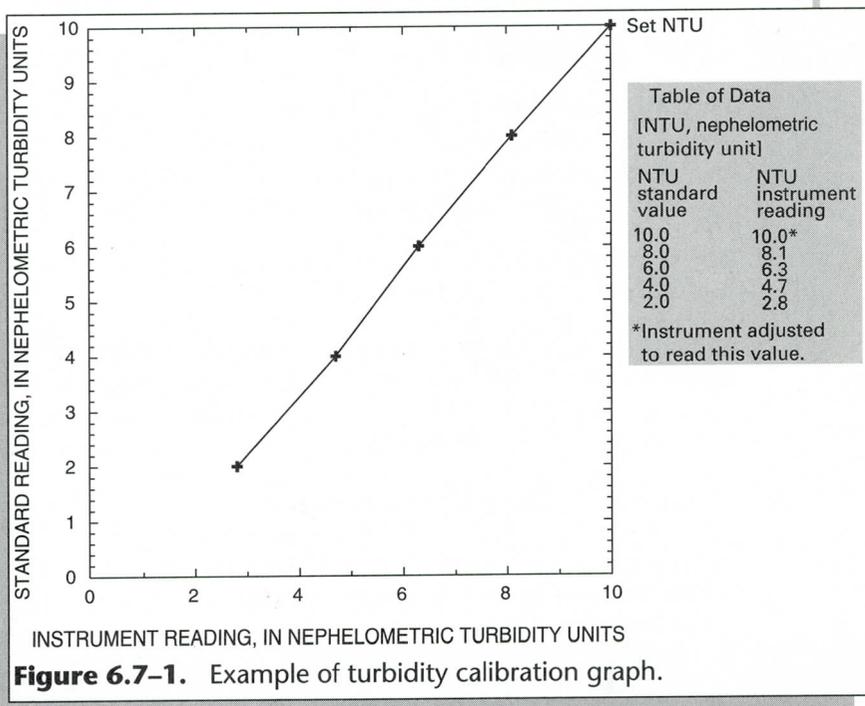
$$NTU = A \times (B+C) / C$$

where

A = NTU found in diluted sample,

B = volume of dilution water, in milliliters, and

C = sample volume taken for dilution, in milliliters.



## 6.7.2.B SUBMERSIBLE TURBIDITY SENSOR CALIBRATION

Most multiparameter instruments with turbidity probe capability are microprocessor-based, with the calibration parameters stored in instrument memory. Turbidity values of the standards are user-selectable in some instruments, but some instruments have internally established standard values that cannot be changed. Low-level check standards in the 1–5 NTU range will allow the user to assess the actual performance of the instrument near the detection limit; **instrument reliability generally decreases at NTU less than 5**—consult manufacturer's specification for the expected accuracy of the measurement.

Monitor digital output carefully to assure that turbidity readings are stable before confirming the calibration. Note that if the instrument uses signal averaging to smooth instrument output, output response to changes in turbidity readings can be slowed.

**Calibrate the instrument before leaving for the field site.** While in the field, check instrument performance periodically using turbidity standard and turbidity-free water. The optical surface of the probe must be clean before beginning the calibration procedure. Modify the general instructions that follow as necessary so that they are compatible with the manufacturer's instructions:

1. Prepare a sufficient volume of the Formazin standard, as described previously. Volume of standard required could be 500 mL for some instruments, particularly if the entire sonde bundle instead of just the turbidity probe will be immersed.
2. **Select Procedure (A) or (B).** The same procedure, once tested and selected, also should be used in future studies.

**Procedure A.** Immersion of entire sonde (bundle of field-measurement sensors, including the turbidity sensor)—requires larger volumes of standard; standard is vulnerable to contamination and dilution. The sonde sensor guard may need to be removed.

**Procedure B.** Immersion of turbidity probe only—depending on sonde configuration, isolation of the turbidity probe and achieving a bubble-free optical surface could be difficult. This technique minimizes the volume of standard required for calibration.

3. Using a zero NTU standard (turbidity-free water):
  - a. Rinse sonde/probe with deionized water, followed by a portion of turbidity-free water.
  - b. Immerse entire surface of sonde/probe in turbidity-free water.
  - c. Agitate the sonde/probe repeatedly to remove bubbles from the optical surface (activate mechanical wiper, if present).
  - d. Monitor turbidity readings for 1 to 2 minutes or longer to ensure that readings are stable (consult manufacturer's recommendations and signal-averaging information).
  - e. Confirm the zero NTU calibration point using manufacturer's instructions.
  - f. Remove sonde/probe and dry thoroughly to minimize dilution or contamination of the next standard.
  - g. Discard first standard (turbidity-free water).
  
4. Using the second standard (Formazin suspension):
  - a. Rinse sonde/probe surfaces with a portion of standard. Discard rinsate.
  - b. Immerse entire surface of sonde/probe in a container filled with standard.
  - c. Agitate the sonde/probe repeatedly to remove bubbles from the optical surface (activate mechanical wiper, if present).
  - d. Monitor turbidity readings for 1 to 2 minutes or longer to ensure that readings are stable (consult manufacturer's recommendations and signal-averaging information).
  - e. Confirm the NTU calibration point for the standard used, according to manufacturer's instructions.
  - f. Remove sonde/probe and rinse surfaces thoroughly with deionized water followed by turbidity-free water. Dry sonde/probe thoroughly.
  - g. Discard used standard.
  
5. Repeat steps 4(a–g) using a different Formazin suspension standard if increased accuracy is desired and instrument software permits use of a third calibration point.

6. By diluting the existing standards, prepare a standard with turbidity, either approximately midway between the calibration points and (or) close to the estimated turbidity of the water to be measured.
  - a. Measure the turbidity of this suspension, making certain that it is within the accuracy specification of the instrument with regard to the true value.
  - b. Repeat the calibration procedure if the measurement is not within the specification.

Once the instrument is calibrated, the accuracy of the recorded measurements can be increased by preparing a calibration graph using dilutions of the Formazin standards, as described previously for calibration of turbidimeters (6.7.2.A).

TECHNICAL NOTE: Multiparameter instruments with turbidity-probe capability use a light-emitting diode in the range of near-infrared wavelength as the radiation source and usually are microprocessor-based. The USEPA has not approved instruments using this method as of this writing, and the accuracy attainable with probe-based instrumentation is substantially less than that of USEPA-approved instruments. ISO turbidity-measurement criteria were developed to improve measurement consistency of instruments using the near infrared technology, and some of the field instruments available meet ISO 7027 recommendations (table 6.7-2).

## SPECTROPHOTOMETER CALIBRATION 6.7.2.C

Spectrophotometric turbidity measurements are useful to indicate relative values or to monitor changes in turbidity with time. Spectrophotometers are inaccurate for absolute turbidity values, and the instrument sensitivity is unrated.

Spectrophotometers commonly have a stored program for turbidity that has been factory-calibrated. This can be verified but not adjusted. Check the instrument output against that of a different instrument every few weeks while the instrument is in use. Check the relative accuracy of the turbidity measurement before leaving for the field by inserting Formazin standards covering the FTU range needed.

1. Use freshly prepared standards.
  - Be accurate in your dilution of the stock suspension.
  - Prepare standards daily and discard any unused portion after each use.
2. **Wear disposable powderless (vinyl or latex) gloves**—fingerprints or smudges on cuvettes cause false turbidity readings; oils from skin can etch the cuvette glass.
3. Hold the sample cell (cuvette) at the rim (on the top lip), not beneath the lip. Pour standard into sample cell to the fill line.
4. Wipe the exterior of the sample cell with a clean, soft, lint-free cloth or tissue after filling to remove moisture and condensation from cell walls.
  - Check periodically for condensation on the sample cell and wipe it dry.
  - After wiping condensation from cell walls, apply a light coating (two drops) of silicon oil (optical grade) using a lint-free cloth—check recommendations from the instrument manufacturer.
5. Eliminate gas bubbles from standards.
6. Check that the calibration cell and sample cell have the same orientation when placed into the instrument measurement chamber.

## 6.7.3 MEASUREMENT

Three methods for field measurement of turbidity are described in this section: the nephelometric method or “turbidimetric determination,” using a cuvette-based turbidimeter (6.7.3.A); “determination by submersible sensor” using a multiparameter water-quality instrument with a turbidity probe (6.7.3.B); and the absorptometric determination, using a spectrophotometer (6.7.3.C). Procedures are similar for use of turbidity instruments in surface water and ground water, although some applications may differ, as described below.

- ▶ **Turbidity is time sensitive**—Measure sample turbidity on site to avoid biased values that can result from (1) biodegradation, settling, or sorption of particulates in the sample; or (2) precipitation of humic acids and minerals (carbonates and hydroxides, for example) caused by changes in sample pH during transport and holding.
- ▶ Biased or erroneous readings can result from unmatched cell orientation, colored sample solutions, gas bubbles, condensation, and scratched or dirty sample cells (see TECHNICAL NOTE). Condensation on the sample cell commonly occurs on hot days when humidity is high.

TECHNICAL NOTE: Causes of low-biased readings include particulate settling or sorption on container surfaces, biodegradation, and sample solutions with true color (color from dissolved substances that absorb light—some instruments are designed with optics to eliminate bias from color). High-biased or false turbidity readings can be caused by the presence of condensation and finely-divided air or other gas bubbles in the sample or on the cell or probe surface, and scratches, fingerprints, or dirt on the surface of the sample cell or turbidity probe.

**Be sure that sample cells are marked to indicate orientation—match orientation so that cells yield the same value when light passes through.**

## *Surface Water*

Collect samples for turbidity measurement or make in situ measurements using either discharge-weighted, pumped-sample, or grab-sample procedures, as appropriate for site characteristics and for study objectives (see NFM 6.0).

- ▶ If taking discrete samples from a churn splitter or other sample-compositing device, remove samples for turbidity measurement when the water volume in the compositor is near maximum.
- ▶ Verify the turbidity determination by measuring turbidity on two or more samples, if samples are removed from a compositing device or collected as grab samples from the surface-water body. Collect turbidity sample directly into the cuvette for immediate measurement or into a clean amber glass bottle for short-term storage.
- ▶ If turbidity is measured in situ, take three or more sequential turbidity readings, until readings stabilize to within  $\pm 10$  percent (see NFM 6.0).

## *Ground Water*

Turbidity in ground water generally is less than 5 NTU. Natural ground-water turbidity of up to 19 NTU has been reported for some environmental settings (Nightingale and Bianchi, 1977; Strausberg, 1983; Puls and Powell, 1992). Contaminated ground-water systems, however, can have considerably higher turbidity (Wells and others, 1989; Gschwend and others, 1990; Puls and Powell, 1992; Backhus and others, 1993).

- ▶ **During well development**—Monitor turbidity caused by well installation, recording consecutive measurements to document decreases in turbidity as development proceeds.
- ▶ **During well purging**—Monitor changes in turbidity by taking sequential readings until purging criteria are met (NFM 6.0). The final stabilized turbidity value should be equal to or less than the value recorded at the end of well development. A decrease in turbidity values during purging indicates mitigation of subsurface disturbance caused by well installation and by deployment of data-collection equipment in the well.
- ▶ Report the median of the final five or more sequential measurements that meet the  $\pm 10$ -percent criterion for stability (NFM 6.0).

*For discrete-sample measurement using a turbidimeter or spectrophotometer:*

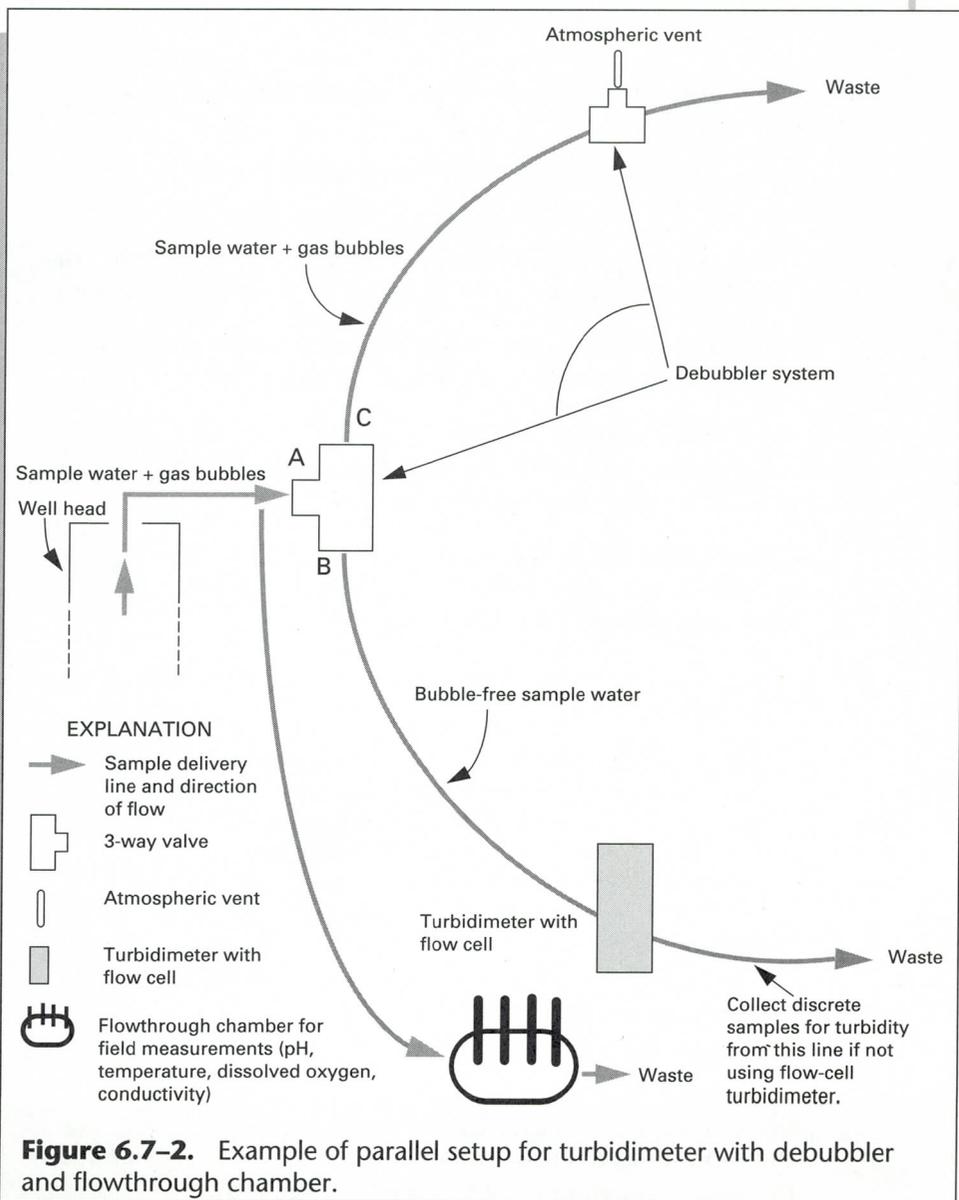
- **Pump the ground-water sample** directly from the sample discharge line into a precleaned glass or polyethylene sample-collection bottle.
- **Bailers are not recommended** for collecting turbidity samples, as bailer deployment can cause turbidity.
- Do not collect the discharge passing through the flowthrough chamber in which pH, conductivity, or other field-measurement sensors are installed.

*For turbidimeter measurement using a flowthrough cell:*

1. Split the sample flow from the well between the turbidimeter and the flowthrough chamber used for other field measurements, as illustrated in figure 6.7–2 (parallel lines are not needed if field measurements are made using a downhole or other in situ method, or when discrete samples are split from a composite). **The turbidimeter requires greater flow velocity than is appropriate for the flowthrough chamber.**
  - a. Position the sample-line split to the turbidimeter/debubbler system in front of (closer to the well) the flowthrough chamber to avoid sediment in the flowthrough chamber. (The higher velocity flow required through the turbidimeter can result in mobilizing sediment—see TECHNICAL NOTE.)
  - b. Set up the debubbler plumbing to maintain a constant head and constant velocity through the turbidimeter's flowthrough cell.
2. To construct a debubbler, use a short length of rigid plastic tubing with one perpendicular tee through which sample enters, another tee at the top end (the atmospheric vent), and hose clamps to secure the tubing. The diameter of the tubing and fittings needed for the debubbler is proportional to the rate at which sample flows through the turbidimeter. Referring to figure 6.7–2:
  - Water entering debubbler at "A" must exit at both "B" and "C."
  - Flow exiting at the top ("C") must be greater than the flow exiting at the bottom ("B").
  - The tubing extending from the debubbler bottom ("B") to the turbidimeter will probably need a smaller diameter than the top tubing to ensure a minimum velocity of 0.46 to 0.61 meters per second (1 1/2 to 2 feet per second).

- The atmospheric vent should be located at the highest point in the debubbler system to prevent siphoning.

TECHNICAL NOTE: Backpressure must not be allowed in a flowthrough chamber containing pH or dissolved-oxygen sensors, and the line to the flowthrough chamber must be disconnected or bypassed until any appreciable volume of sediment clears from the line. **Water should never discharge from the atmospheric vent.**



### 6.7.3.A TURBIDIMETRIC DETERMINATION

The nephelometric method for making turbidimetric determinations that is described in this section requires a photoelectric turbidimeter that meets USEPA specifications.<sup>5</sup> This method is applicable in the range of turbidity from 0 to 40 NTU without dilution, and from about 40 to 1,000 NTU with dilution. The method has been tested for drinking and process water and yields real values in NTU.

***Check the turbidimeter against a standard before measuring sample turbidity:***

1. Warm up the turbidimeter according to the manufacturer's instructions.
2. Rinse a clean, dry, scratch-free, index-marked cell with the turbidity standard selected at the NTU within the range of interest.
3. Shake and pour standard into the sample cell to the fill mark and dry the cell exterior with a lint-free cloth.
4. Follow manufacturer's instructions for readout of turbidity value and record the NTU of the standard used and the turbidity value measured in the turbidimeter calibration log.
5. Determine the required reading for the turbidity standard from the calibration curve for the instrument's range and adjust the calibration to the required NTU reading.
6. Measure sample turbidity as soon as sample is collected (see TECHNICAL NOTE).

TECHNICAL NOTE: Turbidity should be measured immediately. However, if temporary storage of samples becomes necessary, collect samples in clean amber glass bottles, keep out of sunlight, and keep chilled at or below 4°C to prevent biodegradation of solids. The holding time must not exceed 24 hours (American Society for Testing and Materials, 1990).

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<sup>5</sup>The nephelometric method using a calibrated slit turbidimeter is not described—refer to American Society for Testing and Materials (1990).

*Measurement of sample with turbidity less than 40 NTU:*

1. After instrument standardization check, empty the cell of turbidity standard and field rinse a freshly cleaned cell with the sample to be tested. Change gloves.
2. **Measurement of discrete sample** (skip to step 3 for flowthrough cell measurement):
  - a. Shake the sample vigorously to completely disperse the solids. Allow air bubbles to disappear before filling sample cell.
  - b. Pour the sample into a sample cell to the line marked (to the neck if there is no line). Do not touch cell walls with fingers.
  - c. Remove condensation from the cell with a clean, soft, lint-free cloth or tissue. If condensation continues, apply a thin coating of silicon oil on the outside of the cell about every third time the cell is wiped dry of moisture.
  - d. Orient the cell with standard in the turbidimeter. Go to step 4.
3. **If using an instrument with an internal flowthrough cell:**
  - a. Orient the cell in the cell chamber of the turbidity instrument.
  - b. Pump a steady stream of sample in-line from the sample source.
    - Use a constant flow rate through the turbidity instrument.
    - Flow to the turbidimeter must be sufficient to keep particulates suspended (1 1/2 to 2 feet per second).
  - c. Check periodically for condensation on flow cell—remove any moisture from cell using soft, lint-free wipe. If necessary, wipe cell walls with two drops of silicon oil and a lint-free wipe. If available, try a gas sweep of the flowthrough cell compartment using dry nitrogen gas.
    - **Make sure that the flow rate of the gas does not exceed the rate recommended by the manufacturer.**
    - Filter the gas to remove particulates and moisture—use a filter that includes desiccant (particulates or moisture in the gas stream can cause additional variability in the turbidity readings).
    - Eliminate air bubbles in sample before measurement using a debubbler device.

4. Determine the measured NTU value of the sample either by reading turbidity directly from the instrument scale or by using the instrument value and calibration curve, as is appropriate for the instrument being used (see TECHNICAL NOTE).
  - a. Record three to five separate readings at regularly spaced intervals.
  - b. Report the median of the last three or more sequential values that fall within  $\pm 10$  percent.

TECHNICAL NOTE: When using the 0.2-NTU scale only, you may need to subtract a correction factor from the reading to correct for stray light. The Hach Company reports the correction for the 0.2-NTU scale to be on the order of 0.04 NTU for the Hach 2100P™. The stray-light correction is determined by reading turbidity from an empty instrument (without cuvette).

#### 5. Quality control.

- a. Repeat discrete sample measurement on two additional samples and check that they fall within the  $\pm 10$ -percent criterion. Report the value of the first if two samples are measured, or report the median if three or more samples are measured.
- b. Using a clean sample cell, repeat the procedure, substituting turbidity-free water to run a blank. Run the blank either before or after the sample, following manufacturer's instructions.

#### *For measurement of sample with turbidity exceeding 40 NTU:*

1. Obtain discrete sample.
2. Dilute the sample with one or more equal volumes of turbidity-free water until turbidity is less than 40 NTU after mixing and degassing.
3. For 100- and 1,000-NTU ranges only—place the cell riser into the cell holder before the sample cell. This decreases the length of the light path in order to improve the linearity of measurements. **Do not use the cell riser for the lower NTU ranges.**
4. Follow procedures for samples with turbidity less than 40 NTU.
5. Based on the dilution factor and original sample volume, compute the turbidity of the original sample (see 6.7.2, "Calibration for Turbidimeter," steps 11 and 12):
  - a. Add volume of dilution water (in mL) to sample volume (in mL).

- b. Multiply by NTU of diluted sample.
- c. Divide by the volume of sample (in mL) that was diluted.

EXAMPLE: If 5 volumes of turbidity-free water were added to 1 volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample is computed as 180 units.

**Don't forget to adjust the turbidity value of diluted samples using the dilution factor.**

### DETERMINATION BY SUBMERSIBLE SENSOR 6.7.3.B

Determination of turbidity using a multiparameter instrument with submersible sensor-containing sonde is useful for water-quality studies in which the turbidity data will be used qualitatively and not for regulatory or compliance purposes. Turbidity sensors for these instruments utilize an LED with near infrared radiation as the light source and turbidity values normally are reported as NTU. Current instrumentation of this type is not approved by the USEPA.

Multiparameter instruments can be used with a flowthrough chamber, instead of being deployed in situ, for monitoring ground-water field measurements. If measurements will be made in a flowthrough chamber, the turbidity probe is part of the sonde bundle that includes other field-measurement sensors (for example, pH, conductivity, temperature, and dissolved oxygen) and a separate or parallel setup for turbidity measurement (fig. 6.7-2) is not needed.

Multiparameter instruments with internal batteries and memory can be used in surface-water studies that require long-term deployment. Guidelines for long-term instrument deployment falls under the topic of continuous monitors, and is beyond the scope of this chapter—refer to manufacturer's instructions and recommendations and to guidance documents for continuous monitors.

*The following procedures apply to in situ determination and to determination of turbidity in a flowthrough chamber:*

1. Calibrate the instrument in the laboratory or office before leaving for the field site (see 6.7.2).
2. At the field site, follow procedures for selection of surface-water and ground-water sampling locations and for in situ (Procedure A) or flowthrough-chamber (Procedure B) field measurements, as described in NFM 6.0.

**Procedure A: In situ measurement**—Immerse the sonde with turbidity and other field-measurement sensors in the water body.

**Procedure B: Flowthrough chamber**—Secure chamber cover over sonde/probe to form an air-tight and water-tight seal. Discharge first sample aliquot to waste, then open connection to flowthrough chamber and pump sample from water source to flowthrough chamber according to instructions in NFM 6.0.3.

3. Activate instrument to display turbidity values in real time.
4. Agitate the turbidity-containing sonde to remove bubbles from the optical surface: move sonde up and down or in a circular pattern and (or) activate wiper mechanism if available.
5. Monitor turbidity readings as described for other field measurements in NFM 6.0.
  - Allow at least 2 minutes before recording the required number of sequential readings.
  - Stability is reached if values for three (for in situ procedure) to five (for flowthrough-chamber procedure) or more sequential readings, spaced at regular time increments, are within 10 percent.
6. Record turbidity readings on field form and in field notes. Log the reading into instrument memory, if applicable.
7. **Surface-water sites**—Repeat steps 2–5 for in situ measurements (Procedure A) at each vertical to be measured.
8. Before leaving the field site, clean the sonde with a thorough rinse of deionized water and replace sonde in the storage vessel.
9. **Quality control.** Check instrument performance periodically by placing a check standard in the instrument storage vessel and comparing standard value with the reading displayed.

## ABSORPTOMETRIC DETERMINATION 6.7.3.C

The absorptometric method described below uses a field spectrophotometer to provide a relative measure of the sample turbidity. The spectrophotometer shoots a beam of light through the sample at a specific wavelength and measures the amount of transmitted light absorbed by solids present in the sample compared to how much of the transmitted light is absorbed by a Formazin standard.

- ▶ **This method is not approved by the USEPA.** It is a useful method, for example, if the purpose for the turbidity determination is as an indicator of ambient or “stabilized” conditions during well development or purging.
- ▶ Spectrophotometric measurement of turbidity yields readings in FTU. **Do not enter absorptometrically derived turbidity values into the data base.**
- ▶ **Turbidity values below 50 FTU—the range of most surface water and ground water—are inaccurate using this method** and the procedure is recommended only as a relative measure of sequential turbidity values.

The absorptometric method for a Hach DR/2000™ portable spectrophotometer is described below, because this is the instrument that currently is in use for most USGS field work. **Check operating instructions if using an instrument of different make, model, or manufacturer—the position on the dial for wavelength of turbidity may vary for different instruments.**

1. Enter the stored program number for turbidity and rotate the wavelength dial until the display indicates the wavelength value in nanometers (nm) for the instrument in use—450 nm for a Hach DR/2000™, for example.
2. Put on gloves. Measure standards on the instrument that bracket the range anticipated in the sample solution. This step checks the accuracy of the calibration scales. **Change gloves with each change in standard and sample.**
3. Pour 25 mL of deionized water into a clean sample cell for the blank. Hold the cell by the rim—do not touch the cell wall.
4. Place blank sample into cell holder, close the light shield, and press zero. The display should show “wait” and then “0. FTU turbidity.”

5. Shake environmental sample vigorously to suspend all solids and allow air bubbles to dissipate.
6. Pour 25 mL of sample into another clean sample cell, holding cell by the rim (top lip).
7. Carefully place sample into cell holder.
  - a. Close the light shield. Press read/enter.
  - b. The display first will show "wait" and then show the turbidity value in FTU.
  - c. Record the FTU reading.

## TROUBLESHOOTING 6.7.4

Consult instrument manufacturer for additional guidance if troubleshooting suggestions shown on table 6.7-3 do not remedy the problem encountered.

**Table 6.7-3.** Troubleshooting guide for field turbidity measurement

Symptom	Possible cause and corrective action
Erratic readings	<ul style="list-style-type: none"> <li>• Check voltage of the batteries: replace weak batteries with new batteries.</li> <li>• Condensation on cell wall: see fourth symptom.</li> <li>• Bubbles in sampling system or on optical surface of probe-based system: tap sample line to flowthrough cell or chamber systems to dislodge bubbles; adjust debubbler apparatus; remove bubbles on probe-based system by agitating the unit repeatedly or activating wiper mechanism.</li> </ul>
Unusually high or low turbidity	<ul style="list-style-type: none"> <li>• Bubbles in sampling system or on optical surface of probe-based system: see corrective action for erratic readings (first symptom).</li> </ul>
Readings first appear stable, then begin to increase inexplicably	<ul style="list-style-type: none"> <li>• Check for moisture on cell wall: see fourth symptom.</li> </ul>
Moisture or condensation on wall of cell	<ul style="list-style-type: none"> <li>• Wipe cell dry.<sup>1</sup></li> <li>• Apply a thin veneer of silicon oil.<sup>2</sup></li> <li>• Add gas sweep to system.</li> </ul>
Blank samples or reference material standards do not read accurately	<ul style="list-style-type: none"> <li>• Check that the cells are oriented as instructed.</li> <li>• Check accuracy against that of another instrument.</li> </ul>

<sup>1</sup> Use soft, lint-free cloth.

<sup>2</sup> Check with instrument manufacturer before applying silicon oil.

## 6.7.5 REPORTING

ASTM and USEPA guidelines for reporting turbidity measurements are tabled below.

- ▶ Record only NTU (not FTU) values in the data base.
- ▶ Remember to multiply sample readings by the appropriate dilution factor to obtain a final turbidity value.

**Table 6.7-4.** Guidelines for reporting nephelometric turbidity measurements (from USEPA, 1990)

NTU	Record to nearest
0-1	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1,000	50
>1,000	100

# CONVERSION FACTORS, SELECTED TERMS AND SYMBOLS, CHEMICAL SYMBOLS AND FORMULAS, AND ABBREVIATIONS

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## CONVERSION FACTORS

Multiply	By	To obtain
millimeter (mm)	0.03937	inch (in.)
centimeter (cm)	0.3937	inch
square centimeter (cm <sup>2</sup> )	0.155	square inch (in <sup>2</sup> )
meter (m)	3.281	foot
micrometer (μm)	3.3 x 10 <sup>-6</sup>	foot (ft)
kilometer (km)	0.6214	mile
square meter (m <sup>2</sup> )	10.7639	square foot (ft <sup>2</sup> )
square kilometer (km <sup>2</sup> )	0.3861	square mile
cubic meter per second (cm <sup>3</sup> /s)	35.31	cubic foot per second (ft <sup>3</sup> /s)
liter (L)	0.264	gallon (gal)
milliliter (mL)	0.0338	ounce, fluid
	2.64 x 10 <sup>-4</sup>	gallon
gram (g)	0.03527	ounce, avoirdupois
milligram (mg)	35.27 x 10 <sup>-5</sup>	ounce, avoirdupois
microgram (μg)	3.52 x 10 <sup>-8</sup>	ounce, avoirdupois
nanogram (ng)	3.52 x 10 <sup>-11</sup>	ounce, avoirdupois

**Temperature:** Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation: °F = 1.8 (°C) + 32

Use the following equation to convert temperature from degrees Celsius to degrees Kelvin (K): 0°C = 273.150 K

**Sea level:** In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

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## SELECTED TERMS AND SYMBOLS

\*The definitions identified with an asterisk were adopted by the Water Resources Division of the U.S. Geological Survey in Water Resources Division Memorandum 91.09.

\***accuracy:** The extent to which the measured value of a quantity agrees with the accepted value for that quantity.

**approximately:** ~

**approximately equal to:**  $\simeq$

\***bias:** Systematic error that is manifested as a consistent positive or negative deviation from the known or true value. It differs from random error, which shows no such deviation.

**dissolved constituent:** A solute in a water sample—often operationally defined by the method and media properties used to separate the aqueous solutes from the particulate or colloidal phase.

**District:** A water-data-collecting organizational unit of the USGS located in any of the states or territories of the United States of America.

**filtered sample:** A sample passed through a commercial filter membrane of identified media, diameter, and pore size.

**Formazin turbidity unit (FTU):** (See Nephelometric turbidity unit).

**gpm:** gallons per minute

**greater than:** >

**greater than or equal to:**  $\geq$

**less than:** <

**less than or equal to:**  $\leq$

**method detection limit (MDL):** The minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the analyte concentration is greater than zero; determined from analysis of a sample in a given matrix containing analyte.

**micrometer ( $\mu\text{m}$ ):** The millionth part of the meter; the pore diameter of filter membranes is given in micrometer units.

**micromoles per liter ( $\mu\text{moles/L}$ ):** A solution having a concentration of one million moles of a substance per liter solution (micromolar solution). A mole of substance is its atomic or molecular weight in grams.

**$\mu\text{S/cm}$ :** microsiemens per centimeter at 25 degrees Celsius.

**milliequivalents per liter (meq/L) or microequivalents per liter ( $\mu\text{eq/L}$ ):** One equivalent per liter is equal to one thousand milligram-equivalents per one thousand milliliters (meq/mL). Chemical analyses of solutes in a sample are expressed in unit concentrations that are chemically equivalent in terms of atomic or molecular weight and electrical charge.

**milligrams per liter (mg/L) or micrograms per liter ( $\mu\text{g/L}$ ):** Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million.

**millivolt (mV):** A unit of electromotive force equal to one thousandth of a volt.

**min:** minute

**minimum reporting level (MRL):** The smallest measured concentration of a constituent that may be reliably reported using a given analytical method. In many cases, the MRL is used when documentation for the method detection limit is not available.

**molal (m):** Moles per kilogram (1,000 grams) of solvent.

**molar (M):** Concentration in moles per liter of solution, where one mole of a substance is its formula weight expressed in grams.

**nanometer (nm):** The millionth part of a millimeter.

**Nephelometric turbidity unit (NTU):** A measure of turbidity in a water sample, roughly equivalent to Formazin turbidity unit (FTU) and Jackson turbidity unit (JTU).

**normality (N):** The number of equivalents of acid, base, or redox-active species per liter (equivalents/L) of solution. Examples: a solution that is 0.01 *F* in HCl is 0.01 *N* in  $\text{H}^+$ . A solution that is 0.01 *F* in  $\text{H}_2\text{SO}_4$  is 0.02 *N* in acid. Formality (*F*) is the number of atomic (formula) weights per 1,000 grams of solution.

**plus or minus:**  $\pm$

**\*precision:** The degree of similarity among independent measurements of the same quantity, without reference to the known or true value. It often is presented as the inverse of the standard deviation.

**\*quality assurance (QA):** All those planned or systematic actions necessary to provide adequate confidence that a product or service will satisfy given requirements for quality.

**\*quality control (QC):** The operational techniques and the activities used to fulfill requirements of quality.

**recommended (recommend, recommended, recommendation):** Pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given procedure or equipment selection are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints may affect the choice of recommended equipment or procedures. The recommended equipment or procedures selected must be documented and can be based on referenced research and good field judgment. Departure from or modifications to recommended procedures must be quality assured and documented.

**required (require, required, requirements):** Pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and reviewed by water-quality specialists and selected District personnel. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be quality assured and documented.

**specific electrical conductance (conductivity) (SC):** Conductivity of water is expressed in microsiemens per centimeter at 25 degrees Celsius ( $\mu\text{S}/\text{cm}$ ). This unit is equivalent to micromhos per centimeter at 25 degrees Celsius ( $\mu\text{mho}/\text{cm}$ ), formerly used by the U.S. Geological Survey.

**unfiltered sample:** Sometimes referred to as a wholewater or raw sample—pertains to a water sample collected for subsequent chemical or physical analysis without undergoing a phase-separation procedure.

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## CHEMICAL SYMBOLS AND FORMULAS

$\text{CaCO}_3$	calcium carbonate
$\text{CO}_2$	carbon dioxide
$\text{CO}_3^{2-}$	carbonate ion
$\text{H}^+$	hydrogen ion
$\text{H}_2\text{SO}_4$	sulfuric acid
$\text{HCl}$	hydrochloric acid or hydrogen chloride
$\text{HCO}_3^-$	bicarbonate ion
$\text{Hg}$	mercury
$\text{HNO}_3$	nitric acid
$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	potassium ferrocyanide
$\text{K}_3\text{Fe}(\text{CN})_6$	potassium ferricyanide
$\text{KCl}$	potassium chloride
$\text{Na}_2\text{CO}_3$	sodium carbonate
$\text{NaOH}$	sodium hydroxide
$\text{OH}^-$	hydroxide ion

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## ABBREVIATIONS

ALK	alkalinity
ANC	acid neutralizing capacity
ASTM	American Society for Testing and Materials
ATC	automatic temperature compensator
BNC	bayonet nut connector
DIW	deionized water
DO	dissolved oxygen
EDI	equal-discharge increment
EDTA	ethylene diaminetetracetic acid
emf	electromotive force
EWI	equal-width increment
FTU	Formazin turbidity unit
HIF	Hydrologic Instrumentation Facility
IPT	inflection-point titration

ISO	International Standards Organization
LS	land surface
MP	measuring point (for water level measurements)
MSDS	Material Safety Data Sheets
N	normal
NASQAN	National Stream Quality Accounting Network
NAWQA	National Water-Quality Assessment Program
NFM	<i>National Field Manual for the Collection of Water-Quality Data</i>
NIST	National Institute of Standards and Technology
NTU	Nephelometric turbidity unit
NWIS	National Water Information System of the USGS
NWQL	National Water Quality Laboratory of the USGS
OWQ	Office of Water Quality of the USGS
PAO	phenylarsine oxide
PTFE	polytetrafluoroethylene polymer (a variety of Teflon™)
QA	quality assurance
QC	quality control
QW	quality of water, or water quality
QWDATA	Water-Quality Data Processing Routine (part of the USGS NWIS system)
QWSU	Quality of Water Service Unit, USGS, Ocala, Florida
redox	reduction-oxidation potential (also referred to as oxidation-reduction potential, or ORP)
SC	specific electrical conductance (conductivity)
STORET	Storage and Retrieval (USEPA Water-Quality Data Management System)

T	temperature
TBY	turbidity
TC	to contain
TD	to deliver
TWRI	Techniques of Water-Resources Investigations
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
WRD	Water Resources Division of the U.S. Geological Survey
YSI	Yellow Springs Instrument Company

# SELECTED REFERENCES, INTERNAL DOCUMENTS, AND PUBLICATIONS ON TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS

## SELECTED REFERENCES FOR GENERAL GUIDELINES — 6.0

- American Society for Testing and Materials, 1992, Standards on ground water and vadose zone investigations: American Society for Testing and Materials publication code number 03-418192-38, 166 p.
- Edwards, T.K., and Glysson, D.G., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, 118 p.
- Edwards, T.K., and Glysson, D.G., 1998, Field methods for measurement of fluvial sediment: Techniques of Water-Resources Investigations of the United States Geological Survey, book 3, chap. C2, 80 p.
- Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: Techniques of Water-Resources Investigations of the United States Geological Survey, book 5, chap. A1, 545 p.
- Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.
- Hydrologic Instrumentation Facility, 1991, Hydrolab H<sub>2</sub>O, *in* Instrument News: Stennis Space Center, Miss., U.S. Geological Survey Hydrologic Instrumentation Facility, December 1991, p. 7-9.
- Hydrologic Instrumentation Facility, 1992, pH, *in* Instrument News: Stennis Space Center, Miss., U.S. Geological Survey Hydrologic Instrumentation Facility, March 1992, p. 7-8.
- Hydrologic Instrumentation Facility, 1992, pH, *in* Instrument News: Stennis Space Center, Miss., U.S. Geological Survey Hydrologic Instrumentation Facility, September 1992, p. 8.
- Hydrologic Instrumentation Facility, 1992, Conductivity, *in* Instrument News: Stennis Space Center, Miss., U.S. Geological Survey Hydrologic Instrumentation Facility, December 1992, p. 12-13.
- Hydrologic Instrumentation Facility, 1993, pH, *in* Instrument News: Stennis Space Center, Miss., U.S. Geological Survey Hydrologic Instrumentation Facility, March 1993, p. 10-14.
- Hydrologic Instrumentation Facility, 1992, Hydrolab's H<sub>2</sub>O, *in* Instrument News: Stennis Space Center, Miss., U.S. Geological Survey Hydrologic Instrumentation Facility, March 1993, p. 4-5.
- Hydrologic Instrumentation Facility, 1993, Dissolved oxygen, *in* Instrument News: Stennis Space Center, Miss., U.S. Geological Survey Hydrologic Instrumentation Facility, September 1993, unnumbered insert.
- Hydrologic Instrumentation Facility, 1994, Temperature measurement tests, *in* Instrument News: Stennis Space Center, Miss., U.S. Geological Survey Hydrologic Instrumentation Facility, September 1994, p. 3-7; 10-12.
- Hydrologic Instrumentation Facility, 1994, Turbidity meter tests, *in* Instrument News: Stennis Space Center, Miss., U.S. Geological Survey Hydrologic Instrumentation Facility, June 1994, p. 11-13.

- Kearl, P.M., Korte, N.E., and Cronk, T.A., 1992, Suggested modifications to ground water sampling procedures based on observations from the colloidal borescope: *Ground Water Monitoring Review*, v. 12, no. 2, p. 155–160.
- Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95–399, 113 p.
- Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1997, Guidelines and standard procedures for studies of ground-water quality—selection and installation of wells, and supporting documentation: U.S. Geological Survey Water-Resources Investigations Report 96–4233, 110 p.
- Maddy, D.V., Lopp, L.E., Jackson, D.L., Coupe, R.H., and Schertz, T.L., 1989, National water information system user's manual—water-quality system: U.S. Geological Survey Open-File Report 89–617, v. 2, chap. 2, 222 p.
- Puls, R.W., and Powell, R.M., 1992, Acquisition of representative ground water quality samples for metals: *Ground Water Monitoring Review*, v. 12, no. 3, p. 167–176.
- Puls, R.W., Powell, R.M., Clark, D.A., and Paul, C.J., 1991, Facilitated transport of inorganic contaminants in ground water, part II, Colloidal transport: Ada, Oklahoma, Robert S. Kerr Laboratory, U.S. Environmental Protection Agency Report EPA/600/m-91/040, 12 p.
- Rantz, S.E., and others, 1982, Measurement and computation of streamflow: Volume 1, Measurement of stage, and Volume 2, Computation of discharge: U.S. Geological Survey Water-Supply Paper 2175, v. 1, p. 1–284, v. 2, p. 285–631.
- Stanley, D.L., Shampine, W.J., and Schroder, L.J., 1992, Summary of U.S. Geological Survey national field quality assurance program from 1979 through 1989: U.S. Geological Survey Open-File Report 92–163, 14 p.
- U.S. Geological Survey, 1978, Sediment, chap. 3 in U.S. Geological Survey, National handbook of recommended methods for water-data acquisition: p. 3–1 to 3–100.
- Ward, J.R., and Harr, C.A., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90–140, 71 p.
- Wells, F.C., Gibbons, W.J., and Dorsey, M.E., 1990, Guidelines for collection and field analysis of water-quality samples from streams in Texas: U.S. Geological Survey Open-File Report 90–127, 79 p.

## SELECTED REFERENCES FOR

### 6.1—TEMPERATURE

- American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, p. 2–59.
- Stevens, H.H. Jr., Ficke, J.F., and Smoot, G.F., 1975, Water temperature—influential factors, field measurement, and data presentation: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D1, 65 p.
- Ween, Sidney, 1968, Care and use of liquid-in-glass laboratory thermometers: *Transactions of Instrument Society of America*, v. 7, no. 2, p. 93–100.
- Wood, W.W., 1976, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, 24 p.

## SELECTED REFERENCES FOR DISSOLVED OXYGEN — 6.2

- American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, p. 4-98 to 4-105.
- American Society for Testing and Materials, 1981, Standard test methods for dissolved oxygen in water, No. D 888: Philadelphia, American Society for Testing and Materials, p. 529-543.
- Brown, Eugene, Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, p. 126-129.
- Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, p. 155-156.
- Skougstad, M.W., Fishman, M.J., Friedman, L.C., Erdmann, D.E., and Duncan, S.S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 626 p.
- Walters, G.L., ed., 1989, Hach water analysis handbook: Loveland, Colo., Hach Company, p. 430-452.
- Weiss, R.F., 1970, The solubility of nitrogen, oxygen and argon in water and seawater: Deep Sea Research, v. 17, p. 721-735.
- Wells, F.C., Gibbons, W.J., and Dorsey, M.E., 1990, Guidelines for collection and field analysis of water-quality samples from streams in Texas: U.S. Geological Survey Open-File Report 90-127, p. 56-65.
- White, A.F., Peterson, M.L., and Solbau, R.D., 1990, Measurement and interpretation of low levels of dissolved oxygen in ground water: Ground Water, v. 28, no. 4, p. 584-590.
- Wood, W.W., 1981, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, p. 22-24.

## SELECTED REFERENCES FOR SPECIFIC ELECTRICAL CONDUCTANCE — 6.3

- American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, p. 2-43 to 2-48.
- American Society for Testing and Materials, 1977, Standard test methods for electrical conductivity and resistivity of water, No. D 1125-77: Philadelphia, American Society for Testing and Materials, p. 138-146.
- Brown, Eugene, Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, p. 148-150.

- Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, p. 461–463.
- Hem, J.D., 1982, Conductance—a collective measure of dissolved ions, *in* Minear, R.A., and Keith, L.H., eds., Water analysis, v. 1, inorganic species, pt. 1: New York, Academic Press, p. 137–161.
- \_\_\_\_\_, 1985, Study and interpretation of chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, p. 66–69.
- Rainwater, F.H., and Thatcher, L.L., 1960, Methods for collection and analysis of water samples: U.S. Geological Survey Water-Supply Paper 1454, p. 275–278.
- Roberson, C.E., Feth, J.H., Seaber, P.R., and Anderson, Peter, 1963, Differences between field and laboratory determinations of pH, alkalinity, and specific conductance of natural water: U.S. Geological Survey Professional Paper 475–C, p. C212–C215.
- Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94–455, 42 p.
- Wells, F.C., Gibbons, W.J., and Dorsey, M.E., 1990, Guidelines for collection and field analysis of water-quality samples from streams in Texas: U.S. Geological Survey Open-File Report 90–127, p. 42–44.
- Wood, W.W., 1981, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, p. 11.

## SELECTED REFERENCES FOR

### 6.4—pH

- American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, p. 4–65 to 4–69.
- Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535–H, 17 p.
- Bates, R.G., 1973, Determination of pH—theory and practice (2d ed.): New York, John Wiley, 479 p.
- Beckman Instruments, Inc., 1986, The Beckman handbook of applied electrochemistry: Fullerton, Calif., 86 p.
- Brown, Eugene, Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, p. 129–130.
- Busenberg, Eurybiades, and Plummer, L.N., 1987, pH measurement of low-conductivity waters: U.S. Geological Survey Water-Resources Investigations Report 87–4060, 21 p.
- Drever, J.I., 1988, The geochemistry of natural waters (2d ed.): Englewood Cliffs, N.J., Prentice-Hall, p. 282–304.
- Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, p. 363–364.
- Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, p. 61–66.

- Orion Research Inc., 1982, Handbook of electrode technology: Cambridge, Mass., p. P2-P4.
- Roberson, C.E., Feth, J.H., Seaber, P.R., and Anderson, Peter, 1963, Differences between field and laboratory determinations of pH, alkalinity, and specific conductance of natural water: U.S. Geological Survey Professional Paper 475-C, p. C212-C215.
- Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 42 p.
- Stumm, Werner, and Morgan, J.J., 1981, Aquatic chemistry—an introduction emphasizing chemical equilibria in natural waters (2d ed.): New York, John Wiley & Sons, p. 131-134 and 483-487.
- Wells, F.C., Gibbons, W.J., and Dorsey, M.E., 1990, Guidelines for collection and field analysis of water-quality samples from streams in Texas: U.S. Geological Survey Open-File Report 90-127, p. 47-50.
- Wood, W.W., 1981, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, p. 12.

---

## SELECTED REFERENCES FOR REDUCTION-OXIDATION POTENTIAL (ELECTRODE METHOD) — 6.5

- Adams, R.N., 1969, Electrochemistry at solid electrodes: New York, Marcel Dekker, 402 p.
- American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, p. 2-60 to 2-63.
- American Society for Testing and Materials, 1990, ASTM Standard Practice D 1498-76, Philadelphia, American Society for Testing and Materials, p. 208-212.
- Back, William, and Barnes, I.L., 1965, Relation of electrochemical potentials and iron content to ground-water flow patterns: U.S. Geological Survey Professional Paper 498-C, 16 p.
- Barcelona, M.J., Holm, T.R., Schock, M.R., and George, G.K., 1989, Spatial and temporal gradients in aquifer oxidation-reduction conditions: Water Resources Research, v. 25, no. 5, p. 991-1,003.
- Baedecker, M.J., and Cozzarelli, I.M., 1992, The determination and fate of unstable constituents of contaminated groundwater, *in* Lesage, Suzanne, and Jackson, R.E., eds., Groundwater contamination and analysis at hazardous waste sites: New York, Marcel Dekker, p. 425-461.
- Bates, R.G., 1973, Determination of pH, theory and practice (2d ed.): New York, John Wiley & Sons, p. 333-336.
- Berner, R.A., 1963, Electrode studies of hydrogen sulfide in marine sediments: *Geochimica et Cosmochimica Acta*, v. 27, p. 563-575.
- \_\_\_\_\_ 1981, A new geochemical classification of sedimentary environments: *Journal of Sedimentary Petrology*, v. 51, 359-365.

- Boulegue, Jacques, and Michard, Gil, 1979, Sulfur speciations and redox processes in reducing environments, *in* Jenne, E.A., ed., *Chemical modeling in aqueous systems*: Washington, D.C., American Chemical Society Symposium Series 93, p. 25–50.
- Bricker, O.P., 1965, Some stability relations in the system  $Mn-O_2-H_2O$  at 25°C and 1 atm, total pressure: *American Mineralogist*, v. 50, p. 1,296–1,354.
- \_\_\_\_\_, 1982, Redox potential—its measurement and importance in water systems, *in* Minear, R.A., and Keith, L.H., eds., *Water analysis*, v. 1, pt. 1: Orlando, Fla., Academic Press, p. 55–83.
- Callame, B., 1968, Contribution a l'etude des potentiels d'oxydo-reduction dans les sediments marins: *Cah. Oceanographie*, v. 20, p. 305–319.
- Champ, D.R., Gulens, R.L., and Jackson, R.E., 1979, Oxidation-reduction sequences in ground water flow systems: *Canadian Journal of Earth Science*, v. 16, p. 12–23.
- Chateau, H., 1954, Déterminations précises des potentiels de référence données par les electrodes au calomel entre 5 et 70°C: *Journal de Chimie Physique*, v. 51, p. 590–593.
- Doyle, R.W., 1968, The origin of the ferrous-ion ferric oxide Nernst potential in environments containing dissolved ferrous iron: *American Journal of Science*, v. 266, p. 840–859.
- Edmunds, W.M., 1973, Trace element variations across an oxidation-reduction barrier in a limestone aquifer: *Proceedings of Symposium on Hydrogeochemistry and Biogeochemistry*, Tokyo, 1970, p. 500–527.
- Ficken, J.R., 1988, Recent development of downhole water samplers for trace organics, *in* Collins, A.G., and Johnson, A.I., eds., 1988, *Ground-water contamination—field methods*: American Society for Testing and Materials Special Technical Publication 963, Philadelphia, ASTM, p. 253–257.
- Hem, J.D., 1982, Conductance—a collective measure of dissolved ions, *in* Minear, R.A., and Keith, L.H., eds., *Water analysis*, v. 1, inorganic species, pt. 1: New York, Academic Press, p. 137–161.
- Hostettler, J.D., 1984, Electrode electrons, aqueous electrons, and redox potentials in natural waters: *American Journal of Science*, v. 284, p. 734–759.
- Langmuir, Donald, 1971, Eh-pH determination, *in* Carver, R.E., ed., *Sedimentary petrology*: New York, John Wiley & Sons, p. 597–634.
- Lindberg, R.D., and Runnells, D.D., 1984, Ground water redox reactions—an analysis of equilibrium state applied to Eh measurements and geochemical modeling: *Science*, v. 225, p. 925–927.
- Nordstrom, D.K., 1977, Thermochemical redox equilibria of ZoBell's solution: *Geochimica et Cosmochimica Acta*, v. 41, p. 1,835–1,841.
- Nordstrom, D.K., Jenne, E.A., and Ball, J.W., 1979, Redox equilibria of iron in acid mine waters, *in* Jenne, E.A., ed., *Chemical modeling in aqueous systems*: Washington, D.C., American Chemical Society Symposium Series 93, p. 51–79.
- Pankow, J.F., 1991, *Aquatic chemistry concepts*: Chelsea, Mich., Lewis Publishers, 673 p.
- Sato, Michiaki, 1960, Dissolved oxygen in aqueous systems: *Economic Geology*, v. 55, p. 928–949.
- Stumm, Werner, 1966, Redox potential as an environmental parameter—conceptual significance and operational limitation, *in* *Advances in water pollution research—Proceedings of the Third International Conference*, Munich, Germany, September 1966: p. 283–307.

- Stumm, Werner, and Morgan, J.J., 1981, *Aquatic chemistry—an introduction emphasizing chemical equilibria in natural waters* (2d ed.): New York, John Wiley & Sons, 780 p.
- Thorstenson, D.C., 1984, The concept of electron activity and its relation to redox potentials in aqueous geochemical systems: U.S. Geological Survey Open-File Report 84-072, 45 p.
- Thorstenson, D.C., Fisher, D.W., and Croft, M.G., 1979, The geochemistry of the Fox Hills-Basal Hell Creek aquifer in southwestern North Dakota and northwestern South Dakota: *Water Resources Research*, v. 15, p. 1,479–1,498.
- Truesdell, A.H., 1968, The advantage of using  $p_e$  rather than Eh in redox equilibrium calculations: *Journal of Geological Education*, v. 16, p. 17–20.
- U.S. Geological Survey, 1977, Ground water, chap. 2, in U.S. Geological Survey, *National handbook of recommended methods for water-data acquisition*: p. 2-101 to 2-108.
- Welch, A.H., Lico, M.S., and Hughes, J.L., 1988, Arsenic in ground water of the western United States: *Ground Water*, v. 26, no. 3, p. 333–347.
- Whitfield, M.S., 1974, Thermodynamic limitations on the use of the platinum electrode in Eh measurements: *Limnology and Oceanography*, v. 19, p. 857–865.

---

## SELECTED REFERENCES FOR ALKALINITY AND ACID NEUTRALIZING CAPACITY—6.6

- Almgren, Tom, Dryssen, David, and Strandberg, Mats, 1977, Computerized high-precision titrations of some major constituents of seawater on board the R.V. Dmitry Mendeleev: *Deep-Sea Research*, v. 24, p. 345–364.
- American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, *Standard methods for the examination of water and wastewater* (18th ed.): Washington, D.C., American Public Health Association, p. 2-25 to 2-28.
- American Society for Testing and Materials, 1977, *Standard test methods for acidity or alkalinity of water*, No. D 1067: Philadelphia, American Society for Testing and Materials, p. 129–137.
- Baedecker, M.J., and Cozzarelli, I.M., 1992, The determination and fate of unstable constituents of contaminated groundwater, in Lesage, Suzanne, and Jackson, R.E., eds., *Groundwater contamination and analysis at hazardous waste sites*: New York, Marcel Dekker, p. 425–461.
- Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535-H, 17 p.
- Brown, Eugene, Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey *Techniques of Water-Resources Investigations*, book 5, chap. A1, p. 41–44.
- Drever, J.I., 1988, *The geochemistry of natural waters* (2d ed.): Englewood Cliffs, N.J., Prentice-Hall, p. 48–58.
- Edmond, J.M., 1970, High precision determination of titration alkalinity and total carbon dioxide content of sea water by potentiometric titration: *Deep Sea Research*, v. 17, p. 737–750.

- Fishman, M.J., and Friedman, L.C., eds., 1989, *Methods for determination of inorganic substances in water and fluvial sediments*: U.S. Geological Survey Techniques of Water Resources Investigations, book 5, chap. A1, 545 p.
- Hansson, Ingemar, and Jagner, Daniel, 1973, *Evaluation of the accuracy of Gran plots by means of computer calculations—application to the potentiometric titration of the total alkalinity and carbonate content in sea water*: Amsterdam, Elsevier Scientific Publishing Co., 12 p.
- Hem, J.D., 1985, *Study and interpretation of the chemical characteristics of natural water* (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, p. 105–111.
- Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, *U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water*: U.S. Geological Survey Open-File Report 94–539, 57 p.
- Roberson, C.E., Feth, J.H., Seaber, P.R., and Anderson, Peter, 1963, *Differences between field and laboratory determinations of pH, alkalinity, and specific conductance of natural water*: U.S. Geological Survey Professional Paper 475–C, p. C212–C215.
- Stumm, Werner, and Morgan, J.J., 1981, *Aquatic chemistry—an introduction emphasizing chemical equilibria in natural waters* (2d ed.): New York, John Wiley & Sons, p. 171–229.
- Wells, F.C., Gibbons, W.J., and Dorsey, M.E., 1990, *Guidelines for collection and field analysis of water-quality samples from streams in Texas*: U.S. Geological Survey Open-File Report 90–127, 79 p.
- Wood, W.W., 1981, *Guidelines for collection and field analysis of ground-water samples for selected unstable constituents*: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, p. 15–18.
- Yurewicz, M.C., 1981, *Incremental field titration of bicarbonate*: U.S. Geological Survey Water Resources Division Bulletin, October-December 1981, p. 8–13.

## SELECTED REFERENCES FOR

### 6.7—TURBIDITY

- American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, *Standard methods for the examination of water and wastewater* (18th ed.): Washington, D.C., American Public Health Association, p. 2–8 to 2–11.
- American Society for Testing and Materials, 1990, *Annual book of ASTM standards*, v. 11.01, Part 31, "Water," Standard D1889–88a: Philadelphia, American Society for Testing and Materials, p. 309–314.
- Backhus, D.A., Ryan, J.N., Groher, D.M., MacFarlane, J.K., and Gschwend, P.M., 1993, *Sampling colloids and colloid-associated contaminants in ground water*: *Ground Water*, v. 31, no. 3, p. 466–479.
- Edwards, T.K., and Glysson, D.G., 1988, *Field methods for measurement of fluvial sediment*: U.S. Geological Survey Open-File Report 86–531, 118 p.
- Edwards, T.K., and Glysson, D.G., 1998, *Field methods for measurement of fluvial sediment*: *Techniques of Water-Resources Investigations of the United States Geological Survey*, book 3, chap. C2, 80 p.
- Gschwend, P.M., Backhus, D.A., MacFarlane, J.K., and Page, A.L., 1990, *Mobilization of colloids in groundwater due to infiltration of water at a coal ash disposal site*: *Journal of Contaminant Hydrology*, v. 6, p. 307–320.

- Hach, C.C., Vanous, R.D., and Heer, J.M., 1990, Understanding turbidity measurement, technical information series—Booklet No. 11, first ed: Loveland, Colorado, Hach Company, 11 p.
- Hydrologic Instrumentation Facility, 1994, Turbidity meter tests, *in* Instrument News: Stennis Space Center, Miss., U.S. Geological Survey, Hydrologic Instrumentation Facility, June 1994, p. 11–12.
- Kearl, P.M., Korte, N.E., and Cronk, T.A., 1992, Suggested modifications to ground water sampling procedures based on observations from the colloidal borescope: *Ground Water Monitoring Review*, v. 12, no. 2, p. 155–160.
- King, Karl, 1991, Four-beam turbidimeter for low NTU waters, *in* Water, October 1991, *Journal of the Australian Water and Wastewater Association*.
- McCluney, W.R., 1975, Radiometry of water turbidity measurements: *Water Pollution Control Federation*, v. 47, no. 2, p. 252–266.
- McCoy, W.F., and Olson, B.H., 1986, Relationship among turbidity, particle counts and bacteriological quality within water distribution lines: *Water Research*, v. 20, no. 8, p. 1023–1029.
- Nightingale, H.I., and Bianchi, W.C., 1977, Ground-water turbidity resulting from artificial recharge: *Ground Water*, v. 15, no. 2, p. 146–152.
- Pickering, R.J., 1976, Measurement of turbidity and related characteristics of natural waters: U.S. Geological Survey Open-File Report 76–153, 13 p.
- Puls, R.W., and Powell, R.M., 1992, Acquisition of representative ground water quality samples for metals: *Ground Water Monitoring Review*, v. 12, no. 3, p. 167–176.
- Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94–455, 42 p.
- Shelton, L.R., and Capel, P.D., 1994, Guidelines for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94–458, 20 p.
- Strausberg, S.I., 1983, Turbidity interferes with accuracy in heavy metal concentrations: *Industrial Wastes*, v. 29, no. 2, p. 16–21.
- U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: EPA/600/4/79/020, p. 180.1–1 to 180.1–3.
- U.S. Environmental Protection Agency, 1994, Technical notes on drinking water methods: EPA/600/R-94/173, October 1994, p. 28.
- U.S. Geological Survey, 1984, Chemical and physical quality of water and sediment, chap. 5, *in* U.S. Geological Survey, National handbook of recommended methods for water-data acquisition: p. 5–1 to 5–194.
- Ward, J.R., and Harr, C.A., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90–140, 71 p.
- Wells, M.C., Magaritz, Mordeckai, Ameil, A.J., Rophe, Benjamin, and Ronen, Daniel, 1989, Determination of in situ metal partitioning between particulate matter and ground water: *Naturwissenschaften*, v. 76, no. 12, p. 568–570.

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## INTERNAL DOCUMENTS

The following training documents and memorandums are available in U.S. Geological Survey, Water Resources Division (WRD) offices nationwide. The technical memorandums listed are available electronically on the World Wide Web. The URL is: <http://water.usgs.gov/public/admin/memo>.

Sylvester, M.A., Kister, L.R., and Garrett, W.B., eds., 1990, Guidelines for collection, treatment, and analyses of water samples—U.S. Geological Survey Western Region Field Manual: U.S. Geological Survey, Western Region, Internal Document, 144 p.

U.S. Geological Survey, 1990, Water-Quality Field Techniques Training Manual: Quality of Water Service Unit, Ocala, Fla., Internal Document, 164 p.

## Technical Memorandums

### Water Quality

- 76.25-t. WATER QUALITY—Analytical methods: microbiological. September 1, 1976.
- 79.10. ANALYTICAL METHODS—Recommended procedures for calibrating dissolved oxygen meters. March 14, 1979.
- 81.11. WATER QUALITY—New tables of dissolved oxygen saturation values. May 8, 1981.
- 81.15. WATER QUALITY—New tables of dissolved oxygen saturation values: amendment of quality of water technical memorandum no. 81. May 27, 1981.
- 93.10. PROGRAMS AND PLANS—(1) Disposal of petri dishes containing bacteria media, and (2) Aspergillus. April 19, 1993.

### WRD

- 91.09. PUBLICATIONS—Quality systems terminology. November 28, 1990.

## PUBLICATIONS ON TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS

The U.S. Geological Survey publishes a series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The material is grouped under major subject headings called books and is further divided into sections and chapters. For example, Section A of Book 9 (Handbooks for Water-Resources Investigations) pertains to collection of water-quality data. The chapter, which is the unit of publication, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises.

The reports listed below are for sale by the U.S. Geological Survey, Branch of Information Services, Box 25286, Federal Center, Denver, Colorado 80225 (authorized agent of the Superintendent of Documents, Government Printing Office). Prepayment is required. Remittance should be sent by check or money order payable to the U.S. Geological Survey. Prices are not included because they are subject to change. Current prices can be obtained by writing to the above address. When ordering or inquiring about prices for any of these publications, please give the title, book number, chapter number, and "U.S. Geological Survey Techniques of Water-Resources Investigations."

### **Book 1. Collection of Water Data by Direct Measurement**

#### ***Section D. Water Quality***

- 1-D1. Water temperature—influential factors, field measurement, and data presentation, by H. H. Stevens, Jr., J. F. Ficke, and G. F. Smoot: USGS—TWRI Book 1, Chapter D1. 1975. 65 pages.
- 1-D2. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents, by W. W. Wood: USGS—TWRI Book 1, Chapter D2. 1976. 24 pages. [Reprinted 1981]

### **Book 2. Collection of Environmental Data**

#### ***Section D. Surface Geophysical Methods***

- 2-D1. Application of surface geophysics to ground-water investigations, by A. A. R. Zohdy, G. P. Eaton, and D. R. Mabey: USGS—TWRI Book 2, Chapter D1. 1974. 116 pages.
- 2-D2. Application of seismic-refraction techniques to hydrologic studies, by F. P. Haeni: USGS—TWRI Book 2, Chapter D2. 1988. 86 pages.

#### ***Section E. Subsurface Geophysical Methods***

- 2-E1. Application of borehole geophysics to water-resources investigations, by W. S. Keys and L.M. MacCary: USGS—TWRI Book 2, Chapter E1. 1971. 126 pages.
- 2-E2. Borehole geophysics applied to ground-water investigations, by W. S. Keys: USGS—TWRI Book 2, Chapter E2. 1990. 150 pages.

### *Section F. Drilling and Sampling Methods*

2-F1. Application of drilling, coring, and sampling techniques to test holes and wells, by Eugene Shuter and W. E. Teasdale: USGS—TWRI Book 2, Chapter F1. 1989. 97 pages.

## **Book 3. Applications of Hydraulics**

### *Section A. Surface-Water Techniques*

3-A1. General field and office procedures for indirect discharge measurements, by M. A. Benson and Tate Dalrymple: USGS—TWRI Book 3, Chapter A1. 1967. 30 pages.

3-A2. Measurement of peak discharge by the slope-area method, by Tate Dalrymple and M. A. Benson: USGS—TWRI Book 3, Chapter A2. 1967. 12 pages.

3-A3. Measurement of peak discharge at culverts by indirect methods, by G. L. Bodhaine: USGS—TWRI Book 3, Chapter A3. 1968. 60 pages.

3-A4. Measurement of peak discharge at width contractions by indirect methods, by H. F. Matthai: USGS—TWRI Book 3, Chapter A4. 1967. 44 pages.

3-A5. Measurement of peak discharge at dams by indirect methods, by Harry Hulsing: USGS—TWRI Book 3, Chapter A5. 1967. 29 pages.

3-A6. General procedure for gaging streams, by R. W. Carter and Jacob Davidian: USGS—TWRI Book 3, Chapter A6. 1968. 13 pages.

3-A7. Stage measurement at gaging stations, by T. J. Buchanan and W. P. Somers: USGS—TWRI Book 3, Chapter A7. 1968. 28 pages.

3-A8. Discharge measurements at gaging stations, by T. J. Buchanan and W. P. Somers: USGS—TWRI Book 3, Chapter A8. 1969. 65 pages.

3-A9. Measurement of time of travel in streams by dye tracing, by F. A. Kilpatrick and J. F. Wilson, Jr.: USGS—TWRI Book 3, Chapter A9. 1989. 27 pages.

3-A10. Discharge ratings at gaging stations, by E. J. Kennedy: USGS—TWRI Book 3, Chapter A10. 1984. 59 pages.

3-A11. Measurement of discharge by the moving-boat method, by G. F. Smoot and C. E. Novak: USGS—TWRI Book 3, Chapter A11. 1969. 22 pages.

3-A12. Fluorometric procedures for dye tracing, Revised, by J. F. Wilson, Jr., E. D. Cobb, and F. A. Kilpatrick: USGS—TWRI Book 3, Chapter A12. 1986. 34 pages.

3-A13. Computation of continuous records of streamflow, by E. J. Kennedy: USGS—TWRI Book 3, Chapter A13. 1983. 53 pages.

3-A14. Use of flumes in measuring discharge, by F. A. Kilpatrick and V. R. Schneider: USGS—TWRI Book 3, Chapter A14. 1983. 46 pages.

3-A15. Computation of water-surface profiles in open channels, by Jacob Davidian: USGS—TWRI Book 3, Chapter A15. 1984. 48 pages.

3-A16. Measurement of discharge using tracers, by F. A. Kilpatrick and E. D. Cobb: USGS—TWRI Book 3, Chapter A16. 1985. 52 pages.

3-A17. Acoustic velocity meter systems, by Antonius Laenen: USGS—TWRI Book 3, Chapter A17. 1985. 38 pages.

3-A18. Determination of stream reaeration coefficients by use of tracers, by F. A. Kilpatrick, R. E. Rathbun, Nobuhiro Yotsukura, G. W. Parker, and L. L. DeLong: USGS—TWRI Book 3, Chapter A18. 1989. 52 pages.

3-A19. Levels at streamflow gaging stations, by E. J. Kennedy: USGS—TWRI Book 3, Chapter A19. 1990. 31 pages.

3-A20. Simulation of soluble waste transport and buildup in surface waters using tracers, by F.A. Kilpatrick: USGS—TWRI Book 3, Chapter A20. 1993. 38 pages.

3-A21. Stream-gaging cableways, by C. Russell Wagner: USGS—TWRI Book 3, Chapter A21. 1995. 56 pages.

#### **Section B. Ground-Water Techniques**

3-B1. Aquifer-test design, observation, and data analysis, by R. W. Stallman: USGS—TWRI Book 3, Chapter B1. 1971. 26 pages.

3-B2. Introduction to ground-water hydraulics, a programmed text for self-instruction, by G. D. Bennett: USGS—TWRI Book 3, Chapter B2. 1976. 172 pages.

3-B3. Type curves for selected problems of flow to wells in confined aquifers, by J. E. Reed: USGS—TWRI Book 3, Chapter B3. 1980. 106 pages.

3-B4. Regression modeling of ground-water flow, by R. L. Cooley and R. L. Naff: USGS—TWRI Book 3, Chapter B4. 1990. 232 pages.

3-B4. Supplement 1. Regression modeling of ground-water flow—Modifications to the computer code for nonlinear regression solution of steady-state ground-water flow problems, by R.L. Cooley: USGS—TWRI Book 3, Chapter B4. 1993. 8 pages.

3-B5. Definition of boundary and initial conditions in the analysis of saturated ground-water flow systems—An introduction, by O. L. Franke, T. E. Reilly, and G. D. Bennett: USGS—TWRI Book 3, Chapter B5. 1987. 15 pages.

3-B6. The principle of superposition and its application in ground-water hydraulics, by T. E. Reilly, O. L. Franke, and G. D. Bennett: USGS—TWRI Book 3, Chapter B6. 1987. 28 pages.

3-B7. Analytical solutions for one-, two-, and three-dimensional solute transport in ground-water systems with uniform flow, by E. J. Wexler: USGS—TWRI Book 3, Chapter B7. 1992. 190 pages.

#### **Section C. Sedimentation and Erosion Techniques**

3-C1. Fluvial sediment concepts, by H. P. Guy: USGS—TWRI Book 3, Chapter C1. 1970. 55 pages.

3-C2. Field methods for measurement of fluvial sediment, by T.K. Edwards and G.D. Glysson: USGS—TWRI Book 3, Chapter C2. 1998. 80 p.

3-C3. Computation of fluvial-sediment discharge, by George Porterfield: USGS—TWRI Book 3, Chapter C3. 1972. 66 pages.

### **Book 4. Hydrologic Analysis and Interpretation**

#### **Section A. Statistical Analysis**

4-A1. Some statistical tools in hydrology, by H. C. Riggs: USGS—TWRI Book 4, Chapter A1. 1968. 39 pages.

4-A2. Frequency curves, by H.C. Riggs: USGS—TWRI Book 4, Chapter A2. 1968. 15 pages.

#### **Section B. Surface Water**

4-B1. Low-flow investigations, by H.C. Riggs: USGS—TWRI Book 4, Chapter B1. 1972. 18 pages.

4-B2. Storage analyses for water supply, by H.C. Riggs and C.H. Hardison: USGS—TWRI Book 4, Chapter B2. 1973. 20 pages.

4-B3. Regional analyses of streamflow characteristics, by H.C. Riggs: USGS—TWRI Book 4, Chapter B3. 1973. 15 pages.

### *Section D. Interrelated Phases of the Hydrologic Cycle*

- 4–D1. Computation of rate and volume of stream depletion by wells, by C. T. Jenkins: USGS—TWRI Book 4, Chapter D1. 1970. 17 pages.

## **Book 5. Laboratory Analysis**

### *Section A. Water Analysis*

- 5–A1. Methods for determination of inorganic substances in water and fluvial sediments, by M.J. Fishman and L. C. Friedman, editors: USGS—TWRI Book 5, Chapter A1. 1989. 545 pages.
- 5–A2. Determination of minor elements in water by emission spectroscopy, by P. R. Barnett and E.C. Mallory, Jr.: USGS—TWRI Book 5, Chapter A2. 1971. 31 pages.
- 5–A3. Methods for the determination of organic substances in water and fluvial sediments, edited by R.L. Wershaw, M.J. Fishman, R.R. Grabbe, and L.E. Lowe: USGS—TWRI Book 5, Chapter A3. 1987. 80 pages.
- 5–A4. Methods for collection and analysis of aquatic biological and microbiological samples, by L.J. Britton and P.E. Greenson, editors: USGS—TWRI Book 5, Chapter A4. 1989. 363 pages.
- 5–A5. Methods for determination of radioactive substances in water and fluvial sediments, by L.L. Thatcher, V.J. Janzer, and K.W. Edwards: USGS—TWRI Book 5, Chapter A5. 1977. 95 pages.
- 5–A6. Quality assurance practices for the chemical and biological analyses of water and fluvial sediments, by L.C. Friedman and D.E. Erdmann: USGS—TWRI Book 5, Chapter A6. 1982. 181 pages.

### *Section C. Sediment Analysis*

- 5–C1. Laboratory theory and methods for sediment analysis, by H. P. Guy: USGS—TWRI Book 5, Chapter C1. 1969. 58 pages.

## **Book 6. Modeling Techniques**

### *Section A. Ground Water*

- 6–A1. A modular three-dimensional finite-difference ground-water flow model, by M. G. McDonald and A. W. Harbaugh: USGS—TWRI Book 6, Chapter A1. 1988. 586 pages.
- 6–A2. Documentation of a computer program to simulate aquifer-system compaction using the modular finite-difference ground-water flow model, by S. A. Leake and D. E. Prudic: USGS—TWRI Book 6, Chapter A2. 1991. 68 pages.
- 6–A3. A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 1: Model Description and User's Manual, by L. J. Torak: USGS—TWRI Book 6, Chapter A3. 1993. 136 pages.
- 6–A4. A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 2: Derivation of finite-element equations and comparisons with analytical solutions, by R. L. Cooley: USGS—TWRI Book 6, Chapter A4. 1992. 108 pages.
- 6–A5. A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 3: Design philosophy and programming details, by L. J. Torak: USGS—TWRI Book 6, Chapter A5, 1993. 243 pages.
- 6–A6. A coupled surface-water and ground-water flow model (MODBRANCH) for simulation of stream-aquifer interaction by E.D. Swain and Eliezer J. Wexler: USGS—TWRI Book 6, Chapter A6, 1996. 125 pages.

## Book 7. Automated Data Processing and Computations

### *Section C. Computer Programs*

- 7-C1. Finite difference model for aquifer simulation in two dimensions with results of numerical experiments, by P.C. Trescott, G. F. Pinder, and S. P. Larson: USGS—TWRI Book 7, Chapter C1. 1976. 116 pages.
- 7-C2. Computer model of two-dimensional solute transport and dispersion in ground water, by L.F. Konikow and J.D. Bredehoeft: USGS—TWRI Book 7, Chapter C2. 1978. 90 pages.
- 7-C3. A model for simulation of flow in singular and interconnected channels, by R.W. Schaffranek, R. A. Baltzer, and D. E. Goldberg: USGS—TWRI Book 7, Chapter C3. 1981. 110 pages.

## Book 8. Instrumentation

### *Section A. Instruments for Measurement of Water Level*

- 8-A1. Methods of measuring water levels in deep wells, by M.S. Garber and F.C. Koopman: USGS—TWRI Book 8, Chapter A1. 1968. 23 pages.
- 8-A2. Installation and service manual for U.S. Geological Survey manometers, by J. D. Craig: USGS—TWRI Book 8, Chapter A2. 1983. 57 pages.

### *Section B. Instruments for Measurement of Discharge*

- 8-B2. Calibration and maintenance of vertical-axis type current meters, by G. F. Smoot and C.E. Novak: USGS—TWRI Book 8, Chapter B2. 1968. 15 pages.

## Book 9. Handbooks for Water-Resources Investigations

### *Section A. National Field Manual for the Collection of Water-Quality Data*

- 9-A6. Field measurements, by F.D. Wilde and D.B. Radtke, editors: USGS—TWRI Book 9, Chapter A6. 1998 [variously paged].
- 9-A7. Biological indicators, by D.N. Myers and F.D. Wilde, editors: USGS—TWRI Book 9, Chapter A7. 1997 [variously paged].
- 9-A8. Bottom-material samples, by D.B. Radtke: USGS—TWRI Book 9, Chapter A8, 1998 [variously paged].
- 9-A9. Safety in field activities, by S.L. Lane and R.G. Fay: USGS—TWRI Book 9, Chapter A9. 1998 [variously paged].