

QUALITY ASSURANCE PROJECT PLAN

for the

Virginia River Input Monitoring Program

Prepared by

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for

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for the period July 1, 2003 to June 30, 2004

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I. PROJECT DESCRIPTION

A. Background

Quantification of the loads of nutrient and suspended solids into the Chesapeake Bay, and evaluation of the trends in constituent concentration are necessary in order to determine the effects that these constituents have on the ecosystems of the Chesapeake Bay. The Virginia River Input Monitoring Program (formerly known as the Virginia Fall Line Nutrient Input Program) was developed to quantify and assess the effectiveness of programs aimed at reducing the impact of nutrient and suspended solid inputs. Load estimates can further be used to calibrate and validate the computer-modeling efforts of the Chesapeake Bay Program.

The U.S. Geological Survey (USGS) began monitoring nutrients and suspended-solids in Virginia in 1984 in cooperation with the Virginia Department of Environmental Quality--Chesapeake Bay Office (VDEQ; at that time, the Virginia Water Control Board) to quantify loads entering Chesapeake Bay from its major tributaries in Virginia. The initial monitoring program consisted of collecting water-quality data on a twice-per-month scheduled basis at sites near the Fall Line on four tributaries to the Bay: the James, Rappahannock, Pamunkey, and Mattaponi Rivers. The Fall Line is geographically defined as the point where the Piedmont Physiographic Province meets the Coastal Plain, and in most instances this corresponds to the point farthest downstream that is unaffected by tides. Loads estimated for rivers at the Fall Line can therefore be used as single-point sources of loads to the Chesapeake Bay.

Loads of nutrients and suspended solids are greatest during stormflow conditions because of higher discharge and often higher constituent concentrations. Therefore, the monitoring program was expanded in 1988 to include more frequent water-quality data collection during stormflow conditions at two major Virginia tributaries to the Chesapeake Bay, the James and Rappahannock Rivers. In July of 1989, the Pamunkey, Mattaponi and Appomattox Rivers were added to this storm-monitoring network. A parallel program has been conducted on 4 tributaries in Maryland by the USGS in cooperation with the Maryland Department of the Environment since 1982.

A seven-parameter log-linear-regression model (Cohn, 1989), which includes variables for discharge, seasonality, and time is used to provide estimates of constituent concentration on days when no concentration data are available. The product of estimated concentrations and daily mean discharge provides daily load estimates, which are then summed to provide monthly and annual loads of selected nutrients and suspended solids. To evaluate long-term change in the input of these constituents, flow-adjusted trends in concentration are computed from the regression model (Langland and Others, 1999). Trends in flow-weighted concentration (total monthly load from ESTIMATOR divided by the monthly streamflow), monthly and annual loads, and streamflow are determined through linear-regression models on both transformed and untransformed data (Langland and Others, 1999)

B. Objectives and Scope

The Chesapeake Bay River Input Monitoring Program is being used to define the magnitude, timing, and possible sources of nutrient inputs to the Chesapeake Bay from the non-tidal areas of the larger tributaries in Virginia. This sampling program provides a data base of selected constituents (nutrients and suspended solids) for periods of varying flow and season, which are used to produce estimates of constituent loading to the Chesapeake Bay.

The specific objectives of this program are to:

- (1) describe concentrations of selected nutrients and suspended solids in terms of flow and season for five major tributaries to the Chesapeake Bay in Virginia near the Fall Line,
- (2) compute monthly and annual loads of nutrients and suspended solids,
- (3) compare concentration data and load estimates between rivers,
- (4) compute trends in nutrient and suspended solid loads over time,
- (5) explain possible factors influencing concentration, loads, and trends of nutrients and suspended solids,
- (6) provide data for calibration of the Chesapeake Bay Watershed model and nutrient and sediment loading inputs to the Chesapeake Bay Water-Quality model.
- (7) assess quality-assurance results in order to describe the quality of the analyses provided by the participating laboratories, and
- (8) provide information needed to refine the network design for future monitoring programs for the Chesapeake Bay.

The stations monitored and their station numbers include:

- | | |
|--|--|
| (1) the James River at Cartersville | USGS 02035000, VDEQ TF5.1 (Discontinued 3/2001) |
| (2) the Rappahannock River near Fredericksburg | USGS 01668000, VDEQ TF3.1 (Discontinued 3/2001) |
| (3) the Appomattox River at Matoaca | USGS 02041650, VDEQ TF5.4A (Discontinued 6/1999) |
| (4) the Pamunkey River near Hanover | USGS 01673000, VDEQ TF4.1 (Discontinued 4/2003) |
| (5) the Mattaponi River near Beulahville | USGS 01674500, VDEQ TF4.3 (Discontinued 4/2003) |

Water-quality sample collection began July 1, 1988, for the James and the Rappahannock Rivers, and July 1, 1989, for the Appomattox, Pamunkey, and Mattaponi Rivers. Samples are collected once-per-month scheduled basis, which most often occurs during baseflow conditions. Samples also are collected during stormflow conditions, in order to cover a range in flow conditions. Storm samples and baseflow samples at all stations, are sampled exclusively by USGS personnel. Monthly and annual loads of selected constituents are estimated using a seven-parameter log-linear-regression model (Cohn, 1989).

C. Data Usage

The data collected for the Virginia River Input Monitoring Program are used to help define the magnitude, timing, and sources of nutrient inputs to the Chesapeake Bay from the non-tidal areas of the five major tributaries in Virginia. Additionally, this information can help gauge the success of management practices aimed at reducing these inputs. These data provide a data base of selected nutrients and suspended solids collected during periods of varying flow and season, which are being used to estimate loads to the Chesapeake Bay of the selected constituents.

Concentration data and statistics from the concentration data will be used to describe the water-quality characteristics of each river, including concentration ranges and medians; the relations between concentration and discharge; and concentration and seasonality at each river. The load estimates will be compared to the loads from other rivers in the Chesapeake Bay, in order to see the relative differences between the basins. Differences may be examined using land-use

information, discharge records, and possibly point and nonpoint sources of constituents. Trend estimates will be used to determine the changes in constituent inputs over the period of study, and to assess the impact of management practices implemented during that time.

Historical data may be used as background information for comparison purposes. Quality assurance data are used on an ongoing basis to evaluate field and analytical methods for representativeness, variance, bias, and accuracy.

D. Study Design and Rationale

The contributing basins for this report together comprise about 22 percent of the total Chesapeake Bay drainage area. The James and Rappahannock River basins represent approximately 13 and 4 percent of the Chesapeake Bay drainage area; the Appomattox, part of the lower James River Basin, represents another 2.5 percent; and the Pamunkey and Mattaponi River basins represent about 2 and 1 percent of the total Chesapeake Bay drainage area. The remaining percentage of Virginia within the Chesapeake Bay watershed is comprised of the Potomac River basin and its tributaries including the Shenandoah River, which are monitored by the Virginia and Maryland Districts of the USGS, and are not included in this plan.

Table 1 presents the basin size, the percent land use in the Chesapeake Bay watershed, the percent land use in Virginia and the percent land use within each of the basins monitored for this report. The locations of the five river basins and the River Input monitoring stations are shown in Figure 1. A description of each river basin and each sampling station follows. The rivers are referred to throughout this report in order by decreasing drainage area of each basin.

Table 1. Land use for the Chesapeake Bay, the Chesapeake Bay watershed in Virginia, and selected river basins in Virginia

[mi², square miles;<, less than] (Neumiller and others, 1995; Chesapeake Bay Program, written commun.,1994)

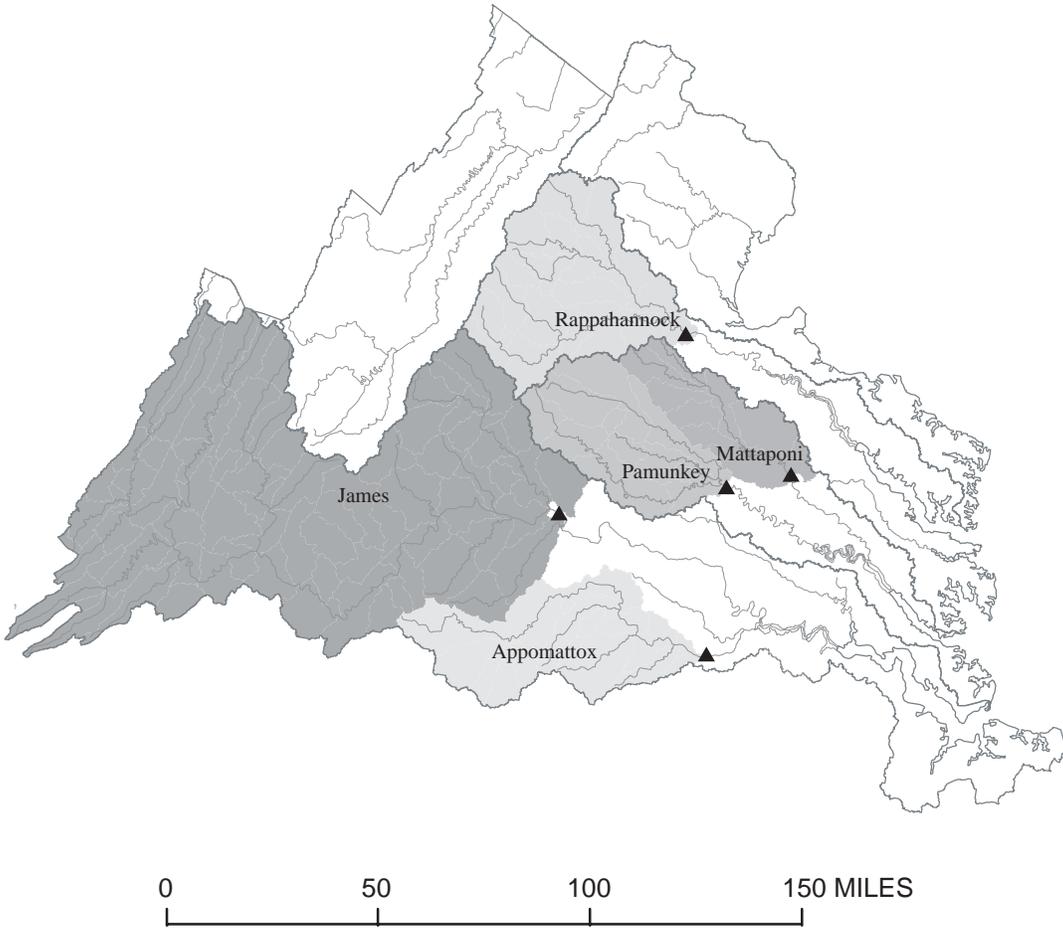
Geographic area	Drainage Area (mi ²)	Urban (percent)	Agricultural (Herbaceous) (percent)	^{a/} Forested (Woody) (percent)	Water (percent)	^{b/} Total (percent)
Chesapeake Bay	64,000	8	33	58	1	100
Virginia	40,815	10	31	58	1	100
James River Basin	10,206	8	25	65	1	99
Rappahannock River Basin	2,848	6	40	54	<1	100
Appomattox River Basin	1,600	3	33	61	<1	98
Pamunkey River Basin	1,474	3	35	59	2	99
Mattaponi River Basin	911	2	27	69	<1	99

^{a/} Includes wetlands.

^{b/} Total percentage below 100 percent is possibly due to rounding and inaccuracies in area estimates.

Figure 1. Location of the five river basins and the River Input Monitoring Stations.

River Input Monitoring Sites



The area of the James River Basin is approximately 10,206 mi², or about one-fourth of the area of Virginia, and is the third largest source of freshwater to the Chesapeake Bay, after the Susquehanna and Potomac Rivers. The James River Basin extends from the eastern part of West Virginia through four physiographic provinces (1) Valley and Ridge, (2) Blue Ridge, (3) Piedmont, and (4) Coastal Plain. The major cities in the James River Basin include Richmond, Lynchburg, Petersburg, Charlottesville, Williamsburg, Hopewell, and parts of Norfolk and Newport News.

The water-quality monitoring station at the James River near Cartersville, Va. (USGS station 02035000 and VDEQ station TF5.1(Discontinued 3/2001)), represents the contributing area (6,257 mi²) to the Chesapeake Bay from Virginia near the Fall Line, or about 60 percent of the James River Basin drainage area. This station is about 40 mi upstream of the Fall Line, but was selected because of the well-documented long-term flow record, and because there are no major streams contributing to the flow between this station and the Fall Line at Richmond. Because of the size of the basin upstream of the sampling station, streamflow varies widely, depending on precipitation patterns which may result in either very localized or widespread stormflow events. The average discharge at this site, computed during a period of 94 years, is 7,077 ft³/s (Prugh and others, 1994). The location of this monitoring site is lat 37°40'16", long 78°05'09" (NAD83), which is at State Highway 45 at the Goochland/Cumberland County line, Va.

The Rappahannock River Basin encompasses a land area of approximately 2,848 mi² which constitutes about 7 percent of the State of Virginia. The river flows from the eastern edge of the Blue Ridge physiographic province through the rolling hills of the Piedmont and Coastal Plain to the Chesapeake Bay, and is the second largest contributor of flow to the Chesapeake Bay from Virginia. The major cities or towns in the basin include Fredericksburg, Warrenton, Winchester, Culpeper, and Orange.

The Rappahannock River monitoring station (USGS station 01668000) is located upstream of Fredericksburg, Va. (This USGS station is at a cableway located 4.3 miles upstream of a VDEQ station (TF3.1 (Discontinued 3/2001)) at the Route-1 bridge; data from the VDEQ station is not used in this study). The area of the drainage basin upstream from the sampling station is approximately 1,596 mi², which is about 56 percent of the Rappahannock River basin. Upstream from this station, most of the basin is in the uplands of the Piedmont Province, and because of the high relief, the river produces rapid or "flashy" streamflow peaks as a result of precipitation. The river therefore may carry large loads of suspended solids and other constituents relative to the size of the basin. The agricultural land use in the basin and expansion of the Washington, D.C., suburbs may increasingly affect the water quality of the river by causing elevated sediment concentrations in runoff, and an increase in concentrations of nutrients associated with the sediment, such as total phosphorus. The average discharge at this station is 1,660 ft³/s, computed during a period of 86 years (Prugh and others, 1994). The location of the sites in Spotsylvania County, Va., are: lat 38°18'30", long 77°31'46" (NAD83).

The Appomattox River Basin is within the James River basin, but because the Appomattox River enters the James River below the Fall Line, it is not included as a source to the James River monitoring station at Cartersville, and so is monitored separately. The basin area above the confluence with the James is 1,600 mi², approximately 16 percent of the James River basin and 4 percent of the area of Virginia. The Appomattox River basin begins in the Piedmont physiographic province, and flows through a small portion of the Coastal Plain before it flows into the James River near Hopewell. The Appomattox River basin is primarily rural, although the cities of

Petersburg, Colonial Heights, and Hopewell are within the basin, downstream of the sampling station at Matoaca.

The drainage area of the Appomattox River basin above the sampling station at Matoaca (USGS station 02041650) is approximately 1,344 mi². The monitoring station is unique among the River Input Monitoring stations in that the flow is controlled by a dam at Lake Chesdin, 2.8 miles upstream of the sampling station. This tends to delay water-level rise from storms, so that the water level is very slow to rise and to fall in comparison to the other monitoring stations. Downstream of Lake Chesdin, the steep gradient due to the rapid elevation change, and a streambed of rocks and boulders result in expanses of rapids between the dam and the sampling station. The average discharge at this station is 1,384 ft³/s, computed during a period of 23 years (Prugh and others, 1994). The location of the site in Chesterfield County is lat 37°13' 31", long 77°28' 31" (NAD83).

The total area of the York River Basin is approximately 2,650 mi², about 6.5 percent of Virginia's total land area, consisting of the Pamunkey River, the Mattaponi River, and the coastal area below the sampling stations. Agriculture is an important component of the economy of the York River basin, and the area is primarily rural. Although the Pamunkey and Mattaponi Rivers are often collectively presented as the York and have many similarities, each river has unique basin, flow and water-quality characteristics. The Pamunkey and Mattaponi River basins are monitored above their confluence to form the York, and are reported separately for this study.

The total area of the Pamunkey River Basin is 1,474 mi², or about 4 percent of Virginia. The Pamunkey River basin begins in the lower part of the Piedmont Province where the relief is relatively low and extends into the Coastal Plain. The basin contains expanses of forested wetlands and marshes that are significant sources of wildlife productivity (Virginia Water Control Board, 1988). Ashland and Mechanicsville are the two major towns in the basin.

The Pamunkey River basin monitoring station (USGS station 01673000 and VDEQ station TF4.1 (Discontinued 3/2001)) is located near Hanover, Va. The area of the drainage basin above the sampling station is approximately 1,081 mi², which is about 40 percent of the York River basin. The low relief and relatively wide basin tend to produce stormflow peaks that are slow to peak and to recede. There is some regulation of the Pamunkey River from the dam at Lake Anna, approximately 100 mi upstream of the monitoring station, on the North Anna River. The average discharge at this station is 1,110 ft³/s, computed during a period of 21 years (Prugh and others, 1994). The location of the site in Hanover County, Va., is lat 37°46' 04", long 77°19' 56" (NAD83).

The Mattaponi River basin is 911 mi², or two percent of the area of Virginia, and also is located within both the Piedmont and Coastal Plain physiographic provinces. Like the Pamunkey River, it tends to have expanses of wetland areas (VWCB, 1991). The wetland areas tend to slow flow velocities, and the hydrographs during storms are slower to peak and recede than at the Pamunkey River.

The Mattaponi River monitoring station (USGS station 01674500 and VDEQ station TF4.3 (Discontinued 3/2001)) is located near Beulahville, Va. The area of the drainage basin above the sampling station is approximately 601 mi², which is about 23 percent of the entire York River basin, and two percent of the area of Virginia. Like the Pamunkey, the Mattaponi River basin has expanses of freshwater wetlands (VWCB, 1991). The average discharge at this station is 583 ft³/s, computed during a period of 50 years (Prugh and others, 1994). The location of the site in King

and Queen County is lat 37°53' 16", long 77°09' 47" (NAD83).

All 5 monitoring stations were part of the USGS National Stream Quality Accounting Network (NASQAN) from the mid 1970's through 1992. NASQAN was a nationwide long-term water-quality sampling network, designed for long-term data collection and analysis. The NASQAN data serve as historic background data for these stations, and may be of use in interpretation of the River Input data in the future.

E. Description of Streamflow

Constituent concentrations within a river change as a function of streamflow. In addition, streamflow data is necessary to compute constituent loads. An overview of the streamflow conditions at all five stations is shown in Table 2. Table 2 gives information on the central values of the streamflow (mean and median) as well as the extremes. The monthly mean discharge is computed by averaging the daily mean discharges in each month. The normal range of monthly discharge is the range of flows that could be expected for any individual month and represents flow conditions that are not considered exceptionally high or low. The normal range for a specific month is calculated by ranking all monthly mean discharge values for that month during (over) the period of streamflow record. The 25th percentile, or that flow which is exceeded by 75 percent of the monthly mean discharges, and the 75th percentile, or that flow which is exceeded by 25 percent of the monthly mean discharges, are then determined. The normal range is the range in discharge between these two values. Historically, the monthly mean discharge is in the normal range 50 percent of the time.

Table 2. Drainage area, historic streamflow conditions, and streamflow conditions for the period of study for the River
Input monitoring stations in Virginia

[mi², square miles; ft³/s, cubic feet per second; ft/s, feet per second; --,not applicable]

Time period	Drainage area mi ²	Mean discharge (ft ³ /s)	Median discharge (ft ³ /s)	Maximum Instantaneous discharge (ft ³ /s)	Minimum Instantaneous discharge (ft ³ /s)
<u>James River</u>					
Period of record	6,257	7,059	4,390	362,000	316
October 1987-September 2002	-	6,884	4,060	158,000	424
<u>Rappahannock River</u>					
Period of record	1,596	1,662	974	140,000	5.0
October 1987-September 2002	-	1,810	1,020	74,100	8.8
<u>Appomattox River</u>					
Period of record	1,344	1,314	650	40,800	17
October 1988-September 2002	-	1,137	557	14,100	17
<u>Pamunkey River</u>					
Period of record	1,081	1,074	559	29,900	20
October 1988-September 2002	-	974	441	21,200	20
<u>Mattaponi River</u>					
Period of record	601	569	354	16,900	0.2
October 1988-September 2002	-	491	268	7,910	0.2

F. Monitoring Parameters and Frequency of Collection

Table 3 shows the constituents monitored for this study, the detection limits at each laboratory, and the reference to the method used.

Samples are analyzed for the following constituents:

Nitrogen species --particulate nitrogen, total dissolved nitrogen, dissolved ammonia nitrogen, dissolved nitrite, dissolved nitrate. (Prior to February 1996, total Kjeldahl nitrogen - ammonia plus organic species - was also determined). The concentration of dissolved nitrite-plus-nitrate nitrogen is the sum of dissolved nitrite concentration and dissolved nitrate concentration.

Phosphorus species --particulate phosphorous, total dissolved phosphorous, dissolved orthophosphorus, particulate inorganic phosphorus. (Prior to February 1996, total phosphorus was also determined).

Other species -- dissolved silica, particulate carbon, particulate inorganic carbon, dissolved organic carbon, chlorophyll a, total suspended solids, and suspended sediment (Processed by the USGS sediment lab in Louisville, Kentucky)

Approximately 40 stormflow samples per year were initially needed to accurately estimate loads using the log-linear regression model selected for this study, so that stormflow-sampling criteria were established by determining a gage height that is reached at each river about 40 times per year. At progressively higher gage heights, the water level would be reached on a fewer number of days. Emphasis was placed on sampling throughout the range in storm conditions that existed throughout the sampling period. Currently only 20 storm samples per year are needed to accurately estimate loads using the log-linear regression model selected for this study and utilizing the data previously collected for this project. The current criteria for storm-sampling is to collect a single sample on either the rise, peak, or fall of 20 storm hydrographs. This allows for the identification of the variability associated with each water-quality constituent over a wide range of stormflow events.

Appendix 1 shows an example of the record of field data planned, including quality assurance data. This form is also used by field personnel to document that the sample was collected. This record is kept for each of the 5 stations.

In order to objectively define whether a sample was collected at base flow or stormflow, hydrographs are separated into two components, stormflow and base flow, to determine the contribution of stormflow and base flow to the total annual flow (White and Sloto, 1990.) Hydrograph separations are performed using the local minima technique as described by Pettyjohn and Henning (1979). Samples are determined to be baseflow or stormflow samples based on model output.

Table 3. Virginia River Input Monitoring Program Detection Limits

Table 3.

Analyte	NWIS Code/ Storet Code	VDCLS Analytical Method	Detection Limit ^{1/}	VDCLS Parameter Group	Container
Dissolved Ammonia Nitrogen	00608/ 00608	EPA 350.1	.004 ppm	CNTF	250 mL plastic bottle (HDPE) Filter Immediately and Preserve at 4°C
Dissolved Nitrate	00618/ 00618	EPA 353.2	.004 ppm		
Dissolved Nitrite	00613/ 00613	EPA 353.2	.002 ppm		
Dissolved Orthophosphorus	00671/ 00671	EPA 365.1	.002 ppm		
Dissolved Silica	00955/ 00955	Standard Methods 4500-Si F (17th Ed.)	.1 ppm		
Particulate Nitrogen	00601/ PNWLF	EPA 440.0	.01 ppm	BAYR	1 gallon Cubitainer Preserve at 4°C
Total Dissolved Nitrogen	00602/ TDNLF	Colorimetric, Chesapeake Bay (D'Elia ^{2/})	.004 ppm		
Particulate Phosphorus	00667/ PPWLF	Colorimetric, Chesapeake Bay (Aspila ^{3/})	.0008 ppm		
Particulate Inorganic Phosphorus	/ PIPLF	Colorimetric, Chesapeake Bay (Aspila ^{3/})			
Total Dissolved Phosphorus	00666/ 49572	Colorimetric, Chesapeake Bay (Valderma ^{2/})	.001 ppm		
Particulate Carbon	00694/ PCWLF	EPA 440.0	0.02 ppm		
Particulate Inorganic Carbon	00688/ 00688	EPA 440.0			
Total Suspended Solids	00530/ 00530	Standard Methods 2540 D (17th Ed.)	3 mg/L		
Volatile Suspended Solids	00535/ 00535	Standard Methods 2540 D (17th Ed.)	3 mg/L		
Fixed Suspended Solids	00540/ 00540	Standard Methods 2540 D (17th Ed.)	3 mg/L		
Turbidity	00076/ 82079	EPA 180.1	0.01 NTU		

Table 3.

Analyte	NWIS Code/ Storet Code	VDCLS Analytical Method	Detection Limit ^{1/}	VDCLS Parameter Group	Container
Dissolved Organic Carbon	00681/ 00681		.36 ppm	DOC	Two 40 mL Clear glass vial (baked) Acid preserva- tion
Chlorophyll A	70957/ 32210	EPA 1002-G	.4 ppm	FCHLR	1 - 3 0.7um GF/F glass fiber filter (total volume filtered = 300 mL)

^{1/} Detection limits are determined on a yearly basis by VDCLS, using the procedure found in Appendix B of EPA CFR Part 136

^{2/} D'Elia, C.F., P.A. Steudler and N. Corwin. 1977. Determination of Total Nitrogen in Aqueous Samples Using Persulfate Digestion. *Limnol. Oceanogr.* 22:760-764.

^{3/} Aspila, Agemian and Chau, 1976. A semi-automated method for the determination of inorganic, organic, and total phosphate in sediments. *Analyst* 101:187-197.

^{4/} Valderrama, J.C. 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Mar. Chem.* 10:109-122.

II. PROJECT ORGANIZATION AND RESPONSIBILITY

The organization of the project for the Virginia River Input Monitoring Program is outlined in the diagram below. The duties of the individuals are also described below.

Project Officer
 Frederick Hoffman
 Chesapeake Bay Office/ VDEQ
 804-698-4334
 Fax 804-698-4116

Principal Investigator
 Douglas L. Moyer
 U.S. Geological Survey, WRD
 *804-261-2634
 *Fax 804-261-2659

<u>Field Sampling</u>	<u>Laboratory Analysis</u>	<u>Data Management</u>	<u>Data Analysis</u>
USGS *Hydrologic Technicians and Hydrologists as needed	VDCLS Jay Armstrong 804-786-7748 (Nutrients) Bob Potts 804-786-4826 (Solids)	USGS *Hydrologist (2) Hydrologic Technician	USGS *Hydrologist (3)
VDEQ Richmond, VA Lou Seivard 804-527-5065	USGS NWQL 303-467-8000 KY Sediment Lab 502-493-1916	VDEQ Cindy Johnson 804-698-4385	USGS, Baltimore, MD Hydrologist 410-238-4200

*same phone and fax numbers as above

VDEQ, Virginia Department of Environmental Quality, Richmond, VA;
 USGS, U.S. Geological Survey;
 VDCLS, Virginia Division of Consolidated Laboratory Services, Richmond, VA;
 NWQL, USGS National Water Quality Laboratory, Arvada, CO

PROJECT OFFICER

Frederick Hoffman
Virginia Department of Environmental Quality
Box 10009
Richmond, VA

804-698-4335
Fax 804-698-4116

Responsible for overseeing the administrative aspects of the program including fiscal management, coordination among other administrators, and coordination with cooperating agencies and institutions. Approves technical design, conduct, and data analysis of the program.

PRINCIPAL INVESTIGATOR

Douglas L. Moyer
U.S. Geological Survey, WRD
1730 East Parham Road
Richmond, VA 23228

804-261-2634
Fax 804-261-2659

Responsible for the technical design, conduct, and data analysis of the program. Provides guidance to other key personnel and directs the efforts to organize, describe, and interpret the results of the monitoring. Has ultimate responsibility for quality assurance.

FIELD SAMPLING

Supervisory Hydrologic Technician, U.S. Geological Survey, Richmond, VA
Hydrologic Technician(s), U.S. Geological Survey, Richmond, VA
Other Hydrologists and Hydrologic Technicians as needed

Coordinate all field activities of the program, including procuring all necessary equipment, collecting water samples according to the USGS sampling protocol, measuring field parameters, and coordinating all field quality assurance data collection.

LABORATORY ANALYSIS

Virginia Division of Consolidated Laboratories (VDCLS), Richmond, VA

Jay Armstrong - Nutrients

Bob Potts - Solids, Carbon

Complete laboratory analyses on a timely basis and return analytical results to VDEQ-CBO.
Provide assistance with information concerning analytical techniques for constituents.

USGS National Water Quality Laboratory (NWQL), Arvada, CO

John Vasquez, Supervisory Chemist - Nutrients

Harold Ardourel, Supervisory Chemist - Solids

Analyzes laboratory-split samples for quality-assurance purposes. Provides standard-reference samples to VDCLS.

DATA MANAGEMENT

Hydrologist(s), U.S. Geological Survey, Richmond, VA

Hydrologic Technician, U.S. Geological Survey, Richmond, VA

Cindy Johnson, Virginia Department of Environmental Quality, Richmond, VA

Responsible for maintaining the Virginia data base and transferring and checking all data from VDCLS to the USGS. Responsible for facilitating the transfer, collation, and retrieval of the data.
Responsible for quarterly progress reports to VDEQ.

DATA INTERPRETATION

Hydrologist(s), U.S. Geological Survey, Richmond, VA

Hydrologist, U.S. Geological Survey, Baltimore, MD

Responsible for graphing, presentation and interpretation of the data; application of quality assurance data; and all formal report requirements for the program.

III. QA OBJECTIVES AND CRITERIA

Because data collected for the Virginia River Input Monitoring Program are used to (1) help define the magnitude and timing of nutrient inputs to the Chesapeake Bay at the Fall Line and (2) to provide a data base of selected constituents collected during periods of varying flow and season, several general quality assurance objectives are necessary in order for the program to be successful.

For Laboratory precision and accuracy, the Virginia Division of Consolidated Laboratories (DCLS) replicated approximately 10% of the samples and 5% of the samples analyzed are spiked samples. Detailed descriptions of the quality assurance practices for each of the analytical procedures conducted by DCLS, can be found in the following SOPs:

Method 2506 Determination of Carbon and Nitrogen in Particulates of Estuarine/Coastal Water Using Elemental Analysis. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2-510 The Determination of Chlorophylls A, B, & C in Marine and Freshwater Algae by Visible Spectrophotometry. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2523 Determination of Ammonia Nitrogen by Automated Colorimetry. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2524 Total Dissolved Nitrogen and Total Dissolved Phosphorus Automated Colorimetric. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2526 Nitrate Plus Nitrite Nitrogen in Estuarine and Coastal Waters Low level, Automated. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2532 Carbon – Total Organic and Dissolved Organic Carbon. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2538 Phosphorus - Orthophosphate Low Level, Automated. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2539 Determination of Phosphorus in Sediments and Particulates of Estuarine/Coastal Waters. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2543 Molybdate Reactive Silica in Water and Wastewater. Commonwealth

of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

DCLS 2544 Total Suspended Solids. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2590 Determination of Inorganic Carbon in Particulates of Estuarine/Coastal Waters Using Elemental Analysis. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2591 Determination of Inorganic Phosphorus in Sediments and Particulates of Estuarine/Coastal Waters. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

A. Comparability of Results

The data collected for this program must be comparable and reproducible. Therefore, sampling methods and sample analyses must be uniform and consistent among the agencies collecting and analyzing the data. This plan includes (1) a field component to assure that water quality samples are representative of river conditions and (2) a laboratory component to assess the variance, accuracy, and bias of analytical results.

The field component consists of documentation of field conditions, collection procedures, and equipment as follows:

(1) Water quality samples are collected using approved USGS guidelines to ensure the collection of samples that are representative of the river cross-section. These guidelines assure the collection of a representative, composite sample from the horizontal and vertical cross section of the river. To ensure the collection of representative samples, an analysis of historic cross-sectional variability of conductance, water temperature, dissolved oxygen, pH, and suspended sediment was used to determine that the sampling points across each river adequately represented the vertical and horizontal water-quality conditions within the cross section.

(2) Sampling criteria based on flow characteristics are documented for field personnel to ensure that water-quality samples are collected over a range in flow conditions. In addition, detailed recording of field procedures ensures consistency of procedures between field personnel.

(3) Proper use of sampling and monitoring equipment and sample collection techniques by field personnel is verified with in-house testing (field audits) of field procedures through a twice-per-year National Field Quality Assurance Program.

(4) Proper cleaning procedures of sampling equipment is documented through ongoing comparisons of field and equipment blanks, scheduled as in Appendix 1.

The laboratory component of this plan consists of the collection and analysis of duplicate, laboratory-split, and standard-reference samples as follows, and as scheduled in Appendix 1:

(1) Duplicate samples are used to document the variance of the analytical results.

Duplicate samples are prepared by withdrawing two subsamples of the full sample volume collected. Both samples are then analyzed by VDCLS. The second subsample is disguised as an environmental sample by labeling it with a different time from the first subsample.

(2) Laboratory-split samples are used to document bias in the analytical results. Laboratory-split samples are collected in a similar manner to duplicate samples; however, one subsample is analyzed by VDCLS and the other subsample is analyzed by NWQL. The results are used to assess the comparability of results between the two laboratories and to determine any bias.

(3) Standard-reference samples document the ability of a laboratory to accurately analyze samples of known concentrations and to check for bias in analytical results. Standard-reference samples are prepared in the USGS laboratory and submitted to VDCLS and NWQL for analysis.

In addition to the field and laboratory components of the quality assurance plan, there is also in-house checking of data that are received from the laboratory. All data are logged in as they arrive from VDCLS, then later are reviewed for transcription errors and corrected.

Concentrations below the minimum reporting limit (“censored” data) are considered in the regression model to be equal to the minimum reporting limit as long as fewer than 25 percent of the data are censored. The adjusted maximum likelihood estimator (AMLE) is used in the few cases where censoring is greater than 25 percent (Helsel and Cohn, 1988). In summations of total nitrogen and total phosphorus from their respective dissolved and particulate constituents, the sum is taken to be a value less than the combined minimum reporting limits if both the particulate and dissolved values are censored ($<V_1 + <V_2 = <(V_1 + V_2)$). If just one value is censored, the sum is considered to be the uncensored value plus half the minimum reporting limit for the censored value ($<V_1 + V_2 = 0.5V_1 + V_2$).

Calculations for all duplicate data are also performed with the censored data equal to zero in order to define the range of variance for each constituent. Concentrations that appear to be outliers are reexamined, using the field notes to determine the presence of any unusual circumstances or hydrologic conditions. If there is no indication of anything out-of-the-ordinary, the laboratory is asked to review their records for accuracy. If necessary, data are corrected and changes are documented with the rationale and source of changes made.

B. Completeness of Sampling

A complete data set is needed to meet the objectives of the project. In particular, the suites of analyses must be comprehensive, and the sampling coverage must capture the variability of both base-flow and high-flow instantaneous loadings of the constituents. Completeness is documented by:

1. Periodic checks by the project water-quality data base manager which assess the completeness and accuracy of calculations for the analyses.
2. Assessment of the number of samples collected versus the number of samples received. An ongoing list is kept to make sure that all analyses are received from VDCLS. Periodically, this list is sent to VDCLS and VDEQ, for their information and use.
3. Development of as complete and representative a data set as possible, covering all

streamflow conditions.

4. Collection of field and quality-assurance data on a scheduled basis, with documentation of each sample as shown in Appendix 1.

C. Representativeness

The collection of water-quality samples representative of river conditions is essential. Samples therefore are collected using approved USGS protocols for water-quality sampling, ensuring that water-quality conditions are represented as closely as possible.

Water-quality samples are collected by both VDEQ and USGS during baseflow and by the USGS during stormflow using an equal-discharge increment (EDI) method or an equal-width increment (EWI) method, so that a sample representative of stream conditions is obtained. The EDI method, in which samples are obtained at the centroids of equal discharge increments, is normally used in streams with stable channels where discharge ratings change very little during the year. The EWI method, in which samples are collected at centroids of equal-width increments of the stream, is used most often in shallow or sandbed streams where the distribution of water discharge in the cross-section is not stable, or in streams where the distribution of discharge in the cross-section is unknown. Samples are collected using a USGS-designed depth-integrating sampler (designation DH-95 or D-96) when average streamflow velocities exceed 1.5 ft/s, or a weighted sample bottle (WBH-96) at lower velocities when depth-integrating samplers are not effective. A depth-integrating sampler is designed to sample the vertical water column of the river proportionally to the velocity at each depth. These methods are documented by Edwards and Glysson (1988) and Ward and Harr (1990). Sampling equipment specific to each station is documented in Appendix 2.

All samples collected at the James River, Mattaponi River, and Appomattox River stations by USGS personnel are collected by the EDI method. All samples at the Rappahannock River station are collected by USGS personnel using the EWI method. All samples at the Pamunkey River station are collected using an EWI method.

Because, VDEQ personnel did not have access to a depth-integrating sampler, only those historical VDEQ samples collected when stream velocities are less than 1.5 ft/s, when point samplers would be effective according to USGS procedures, are used in this study.

IV. SAMPLING PROCEDURES

Water-quality samples are collected according to established U.S. Geological Survey sampling protocol for nutrients and suspended solids. These methods are documented in the publications *Field methods for measurement of fluvial sediment*, by T.K. Edwards and D.G. Glysson, 1988; U.S. Geological Survey Open-File Report 86-531, in *Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses*, by J.R. Ward and Albert Harr, 1990, U.S. Geological Survey Open-File Report 90-140; and in *U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water*, by A.J. Horowitz and others, 1994, U.S. Geological Survey Open-File Report 94-539.

Samples are collected in a manner ensuring that they are representative of river conditions, which involves collecting horizontally and vertically integrated samples. Sampling equipment is made from non-contaminating materials, which includes epoxy-coated depth integrated samplers for collection of the nutrients and suspended solids samples. Nutrients samples are filtered in the field using an in-line, 0.45 um Gelman capsule filter. All samples are preserved on ice and taken to VDCLS on the same day if possible, or as soon as feasible. (NOTE: Samples prior to January 15, 1994, were filtered in the VDCLS laboratory. After that date, field filtering using the Gelman filter was instituted as part of the procedure.)

Because of variations in flow conditions, width of each streambed, and differences in cross-sectional morphology, sampling procedures between the five rivers differ. Protocols were developed for each site, outlining where samples are to be taken in the cross section, what type and size of sampler to use, how samples are to be labeled, and the number of samples to collect, in order to ensure that all personnel responsible for sampling use the correct procedures. The protocols are attached as Appendix 3.

Field parameters (pH, specific conductance, dissolved oxygen, and water temperature) are collected at five stations along the stream channel cross section. These parameters are collected using a YSI multi-parameter field meter and following standard U.S. Geological Survey protocols (Appendix 6).

V. SAMPLE CUSTODY

Samples are collected in 1-liter plastic “cubitainers” provided by VDCLS through the Chesapeake Bay Office of VADEQ, labeled using a VADEQ tag, immediately put on ice and transported to the VDCLS laboratory. No other preservation is necessary. At those times when it is impossible to take samples to the laboratory, samples are refrigerated at 4° C and taken to the laboratory as soon as possible. A Virginia District field form is completed and kept on file in the Virginia District Office as a record of the samples collected, to check for final completeness of the analyses, and to record field measurements, date and time of collection, and any unusual conditions. When laboratory split samples are collected, the NWQL analysis request form is also completed, to be sent with the samples to NWQL. Associated field data are entered into and sample analyses are scheduled using the VADEQ Comprehensive Environmental Data System (CEDS). Suspended-sediment samples are collected in a 1-pint glass bottle, labeled and sent to the USGS sediment laboratory in Louisville, Kentucky. No preservation is necessary for suspended-sediment samples.

Laboratory-split samples for quality assurance are sent to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado and are collected in bottles provided by the NWQL. Quality assurance of materials used in the containment and preservation of water samples for NWQL is performed by NWQL. As soon as possible after field collection, samples are shipped on ice to the laboratory. An NWQL laboratory analytical services request form (Appendix 4) is sent with each sample shipment, which details the analyses to be performed on the samples. Additionally, a field sheet (Appendix 5) which details field conditions and field parameter values is completed for each sampling trip and kept in the office along with a copy of the analytical services request form. (NOTE: Use of sulfuric acid as a preservative for filtered nutrient samples sent to NWQL will begin in January 1999.)

VI. CALIBRATION PROCEDURES AND FREQUENCY

Field parameters (pH, Specific Conductance, and Dissolved Oxygen) are calibrated in the field using a YSI 600XI multiparameter instrument before field data are collected. An equipment calibration log is kept with each multiparameter instrument. This log records the date, results of the calibration, identification of standards, initials of field person, and any corrective actions taken. Both pH and specific conductance standards are supplied by the USGS laboratory in Ocala, Florida; each standard has expiration dates posted on its container.

Calibration of laboratory equipment at VDCLS is documented in the publications entitled *Quality Assurance Plan for the Virginia Division of Consolidated Laboratory Services*, 1982, and *Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments*, by F.C. Friedman and D.E. Erdmann, Washington, U.S. Govt. Print. Off., 1982.

Calibration of the laboratory equipment at the USGS sediment lab in Louisville, KY is documented in the publication entitled *Quality-Assurance Plan for the Analysis of Fluvial Sediment by the Northeastern Region, Kentucky District Sediment Laboratory*, C.J. Sholar and E.A. Shreve: Open-file report 98-384, Louisville, Kentucky 1998.

Calibration of laboratory equipment at NWQL is documented in the publications entitled *Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments*, by F.C. Friedman and D.E. Erdmann, Washington, U.S. Govt. Print. Off., 1982; and in *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments*, M.J. Fishman and L.C. Friedman: Open-file report 85-495, Denver, 1985.

VII. ANALYTICAL PROCEDURES

The majority of samples collected are analyzed by VDCLS. Selected quality-assurance samples are analyzed by either VDCLS or the USGS National Water Quality Laboratory (NWQL) in Arvada, CO. Samples collected prior to January 15, 1994 were filtered and analyzed by VDCLS under criteria established by Clesceri, Greenberg, and Trussell (1989) and the USEPA Environmental Monitoring and Support Laboratory (1983). Beginning January 15, 1994, samples have been filtered in the field using procedures established by Horowitz and others (1994) before being delivered to the laboratory for analysis.

Requirements set by the USEPA for regulatory laboratories state that nutrient samples be filtered within 24 hours and suspended-solids determinations be performed within 7 days. Samples collected on weekends are chilled to 4°C and held until they can be accepted by VDCLS the following week. Approximately one of every ten samples is sent to both VDCLS and NWQL as a quality assurance check of the analytical results. Samples sent to NWQL are filtered and preserved in the field by chilling, then shipped by express mail to the laboratory. The analyses are performed within 7 days after receipt at the laboratory. Analytical methods used at NWQL are documented in Fishman and Friedman (1989).

NWQL performs selected quality assurance analyses of water collected at the five Chesapeake Bay River Input Monitoring stations. The analytical procedures used by the laboratory are standard for use in water quality studies, and are documented in the publication entitled, *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments*, Book 5, Chapter A1, M.J. Fishman and L.C. Friedman, Open-file report 85-495, Denver, 1985.

In some instances, the analytical method for certain constituents differs for the total constituent and the dissolved constituent. For each analytical method there is a range within which the actual concentration is expected, so that it is possible for the analytical result of the total concentration of a particular constituent to be less than that of the dissolved concentration for that constituent. Minimum reported concentrations may differ according to the detection limit, depending on the specific technique done by the laboratory. VDCLS has Standard Operating Procedures (SOP) for each laboratory analyte. The reference for each laboratory analyte SOP can be found in Section III (QA Objectives and Criteria).

The concentration of total nitrogen for this project is computed as the sum of particulate nitrogen and dissolved nitrogen for VDCLS samples and as the sum of dissolved nitrite-plus-nitrate nitrogen concentration and total ammonia-plus-organic (Kjeldahl) nitrogen concentration for NWQL samples. Prior to February 1996, total nitrogen was computed as the sum of dissolved nitrite-plus-nitrate nitrogen concentration and total Kjeldahl nitrogen concentration for VDCLS samples. Total phosphorous is computed as the sum of particulate phosphorous and dissolved phosphorous.

VIII. DATA REDUCTION, VALIDATION, AND REPORTING

Samples are collected, preserved and transported according to accepted SOP methods to DCLS Central Receiving by a DCLS selected courier. Central Receiving (DCLS) personnel log in samples and distribute them to the appropriate laboratory for analysis. After analysis, the data results are transformed into the correct concentration units, keyed into the LIMS system (Laboratory Information Management System) by the chemist completing the analysis and reviewed by the appropriate laboratory personnel. Upon approval the results are shipped back to VADEQ via FDT transfer and entered into the CEDS2000 database. In the event data sheets are utilized to submit the samples to DCLS (e.g. due to a CEDS/WQM system failure) the results are printed out onto laboratory sheets and given to the VADEQ Laboratory Liaison. Results returned on paper are keyed into the CEDS2000 system by personnel in the Office of Water Programs Division and forwarded to the appropriate region or the Central office project manager. When laboratory-split samples are collected, the NWQL analysis request form is also completed and sent with the samples to NWQL.

Data go through a series of screens and reviews to identify invalid, qualified or QA supported data by both DEQ and USGS personnel. The qualified and QA supported data are then entered into the QWDATA water-quality data base. Additionally, the water-quality data are posted on the River Input Monitoring web site (<http://va.water.usgs.gov/chesbay/RIMP/index.html>)

The USGS Virginia District field sheet that details field conditions and field parameter values is completed for each sampling trip and kept in the USGS Office along with a copy of the analytical services request forms. The field parameter values are entered into the Virginia District QWDATA water-quality data base at the office.

Selected quality-assurance analyses will be performed by the USGS laboratory in Denver, Colorado. The laboratory maintains its own rigorous quality control program and incorporates this information into a user-friendly quality-assurance data base. All laboratory data are reviewed by project personnel. The data are verified by comparing values with the ranges of values from prior samplings and by the review of data plots. If an error is found with the analysis, a re-run is requested, if within one month of sampling.

Water-quality analyses performed are stored on the Virginia District QWDATA water-quality data base. Raw data are published in the USGS Annual Report for Virginia. The appropriate data originator is notified of errors so that the source data bases can be corrected and thus remain consistent with all others.

IX. INTERNAL QC CHECKS

A. Field

The quality assurance practices of field procedures include documentation of cross-section, depth-integrated variability; quality assurance of field personnel; documentation of field sampling status; and collection of field, equipment, and laboratory blanks. These practices are described in greater detail in Section III.

B. Laboratory

VDCLS--The quality assurance practices of VDCLS including quality control, quality assurance of analytical results, quality assurance of all materials used in the preservation and containment of water-quality samples, and the blind- reference sample quality assurance program, are documented in *Quality Assurance Plan for the Virginia Division of Consolidated Laboratory Services*. In each laboratory analyte SOP (see section III QA Objectives and Criteria), there is a quality control section that addresses a) assessing laboratory performance, and b) assessing analyte recovery and data quality. Most analytical procedures used are referenced in *Chemical Analysis for Water and Wastes: USEPA-600/4-79-020*, Environmental Protection Agency, 1979, and *Standard Methods for the Examination of Water and Wastewater* (17th ed) edited by Cleceri et al., 1989.

NWQL-- The quality assurance practices of NWQL are documented in the Techniques of Water Resources Investigations (TWRI) report entitled *Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments*, Book 5, Chapter A6, by F.C. Friedman and D.E. Erdmann, Washington, U.S. Govt. Print. Off., 1982. Included in this publication are: analytical methods development procedures; standard quantitative analysis techniques; instrumental techniques; laboratory quality control; quality assurance monitoring; documentation, summary, and evaluation of data; and material evaluation. Additional references are: USGS National Water-Quality Laboratory (NWQL) Quality Control Manual (Pritt and Raese, 1995) and Quality Control at the USGS National Water-Quality Laboratory, USGS Fact Sheet 026-98, at http://nwql.usgs.gov/Public/pubs/QC_Fact/text.html.

Analytical procedures and quality control of NWQL, including accuracy and precision statements, are documented in the TWRI report entitled *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments*, Book 5, Chapter A1, M.J. Fishman and L.C. Friedman, Open-file report 85-495, Denver, 1985.

USGS Sediment Laboratory in Kentucky -- The quality assurance practices of the USGS sediment lab are documented in the Open-File report entitled *Quality-Assurance Plan for the Analysis of Fluvial Sediment by the Northeastern Region, Kentucky District Sediment Laboratory*, OFR 98-384, by C.J. Sholar and E.A. Shreve, 1998. Included in this publication are: analytical methods development procedures; standard quantitative analysis techniques; instrumental techniques; laboratory quality control; quality assurance monitoring; documentation, summary, and evaluation of data; and material evaluation.

Quality assurance of analytical results received from the participating laboratories incorporate both quality control and quality assurance monitoring. Quality-control monitoring is accomplished through the use of a personal and a computerized data review. Several computer

checks are made which “flag” a possible error in analysis. These flags are documented on the analytical report specific to each sample. The completed analytical report is then reviewed by NWQL quality-assurance personnel prior to its release from the laboratory. The reviewers judge whether there is a reason for the data to have “failed” a check. If analytical error is suspected, a re-run of the sample is requested. Quality-assurance monitoring is also performed by the requestor of the analysis, whose familiarity with the site may allow them to identify an error that was not apparent to the laboratory personnel. If an error is found with the analysis, a re-run is requested.

Quality assurance of all materials used in the preservation and containment of water samples is performed by the USGS laboratory. Preservation materials, such as sulfuric acid, and sample bottles are randomly sampled by lot or batch number for any elevated trace metals and major cations and anions that may be present. If elevated levels are indeed found in either of these, the laboratory conducts additional sampling of the preservation materials and bottles, and if necessary, recalls them.

VDCLS and NWQL both participate in a nation-wide Standard-Reference Sample (SRS) quality-assurance program. This program was designed to evaluate the performance of each participating laboratory as well as monitor long-term trends in the bias and accuracy of analytical methodologies. Samples are prepared at the NWQL, Arvada, CO. Samples are prepared by the USGS Branch of Quality Assurance from which they are subsequently distributed to laboratories across the country. Results are published twice yearly and distributed to each participating laboratory and USGS Offices in each state.

X. PERFORMANCE AND SYSTEM AUDITS

Project reviews are conducted quarterly by USGS staff, and periodically by the USGS Area Water-Quality Specialist. USGS technical reviews are conducted periodically at the request of the principal investigator.

A District Water-Quality Review is held every three years by the USGS Regional Water-Quality Specialist and Regional Staff. Field methods are observed for consistency with national USGS procedures, and the District water-quality data base is examined for agreement between laboratory and field data. Checks are also done to ensure that the local water-quality data base, QWDATA, and the National data base, STORET, are in agreement.

The project officer and other staff from VaDEQ are kept informed of the status of the project on a quarterly basis by the development of a quarterly report detailing the number of samples collected per site and any problems associated with sampling or analysis.

Both VDCLS and NWQL participate in a Standard-Reference Sample quality-assurance program that analyzes the laboratory's performance as described previously.

XI. PREVENTIVE MAINTENANCE

Preventive maintenance of field instruments is done on a routine basis to ensure that the instruments remain in good working order. All potentially fragile electrodes and cells are stored in such a manner as to prevent breakage. Additionally, they are kept clean and free from any build-up that may affect their performance; rejuvenation of electrodes is performed periodically. All field meters and calibration standards are removed from vehicles and brought indoors after use to avoid mechanical or electronic problems caused by extremes in temperature. Batteries are changed and/or units recharged regularly.

All field instruments are calibrated prior to use, as described in Section VI, Calibration Procedures and Frequency. If an instrument is not in good working order, spare instruments are readily available so that there is no interference with field operations. Instruments in need of repair are repaired in a timely manner.

XII. ASSESSMENT OF DATA VARIABILITY, BIAS, ACCURACY, REPRESENTATIVENESS, AND COMPLETENESS

Assessment of data variability and bias for the Virginia River Input Monitoring Program consists of collecting and analyzing duplicate and laboratory-split samples. The purpose of these quality assurance practices is to quantify the variability of results from VDCLS, the major laboratory that provides analyses for this study, and to check for bias at VDCLS and NWQL. In addition, a Wilcoxon signed-rank test is used to evaluate differences in data results between laboratories.

Between 5 and 10 percent of the samples collected at each monitoring site are collected as duplicate samples. For each duplicate sampling, two unmarked duplicate samples labeled five minutes apart will be collected from the same churnsplitter and sent to VDCLS for the purpose of checking the analytical precision of the laboratory. Between 5 and 10 percent of the samples collected at each monitoring site are collected as laboratory-split samples. From a churnsplitter, one sample will be sent to the VDCLS for analysis and the other to NWQL for the purpose of verifying that these two laboratories are producing comparable results. Any statistical difference ($p < 0.1$) between the two laboratories is examined for possible sources of differences or analytical problems.

Field blanks analyzed by VDCLS are used to verify that clean sampling techniques are used by field personnel. Field blanks are collected by processing an analyte-free water through sampling equipment at the field site.

In order to verify that proper cleaning techniques are being used by field personnel, equipment blanks are obtained four times a year, on random occasions. Equipment blanks are subjected to all aspects of sample collection and field processing, but are generated in the relatively controlled environment of the Virginia District Laboratory. These blanks are collected by processing analyte-free water through sampling vessels, churn splitters, tubing, and filters. If contamination is observed in the equipment blanks, additional sequential equipment blanks will be obtained by collecting individual blank samples after each sequential step in the generation of an equipment blank. If contamination is observed in the field blanks, equipment blanks may be collected more than the scheduled four times a year in order to determine if the source of the contamination is field equipment.

Periodically, standard-reference samples are submitted to VDCLS and the NWQL in order to check analytical results against a known standard. This allows for determination of the accuracy of each laboratory and the presence of any bias. Sources of reference samples may be either the Environmental Protection Agency or a commercial laboratory.

Completeness is assessed by comparing the number of base flow and stormflow samples completed with those scheduled. The reasons for any discrepancies are well documented.

XIII. CORRECTIVE ACTION FOR OUT-OF-CONTROL SITUATIONS

Out-of-control situations may occur in the field or in the laboratory as a result of equipment breakdown, despite careful planning and attention to procedures.

The primary methods for correcting out-of-control situations in the field are (1) repairing, recalibrating, or adjusting the malfunctioning instruments; or (2) substituting an alternative piece of equipment. Notes are made in the field log books and on the sampling field sheet when out-of-control situations occur. In most instances, no data are lost due to malfunctioning field equipment.

Potential out-of-control situations occurring in the laboratory may be identified by determining constituent concentrations that do not follow established concentration/discharge patterns or that seem out of range. The primary method of correcting out-of-control situations at VDCLS is to first re-examine the paperwork for clerical or translation errors, such as an incorrect date or station. The next step would be to examine the field paperwork to look for any written observations of problems at the site. Finally, if the source of the questionable value could not be discerned, the next step is to contact the laboratory to ask for confirmation of that concentration and to ask for any bench observations that might influence the sample concentrations. Based on the result of any of these steps, any mismatched site information and data would be corrected if possible. No data are ever changed unless there is a logical, fact-based reason for doing so. Any changes and the rationale for the changes are clearly documented on the District Field Sheet and initialed by the Project Chief or a senior project person.

XIV. QA REPORTING PROCEDURES

All samples collected at the five rivers will be analyzed at VDCLS in Richmond, VA. VDCLS performance will be evaluated through the use of duplicate and standard-reference samples. Results of the laboratory's performance will be documented with the quarterly reports, pending the receipt of analyses from the laboratory.

Interlaboratory performance is also evaluated using laboratory-split samples to compare analytical results from VDCLS and NWQL. These results are included in the quarterly report. Current evaluation of the quality-assurance data includes performing a Wilcoxon signed-rank test to determine statistical differences between laboratories. Findings are documented in the formal reports, and new procedures or quality-assurance tests are suggested when there is cause for question.

Additionally, interlaboratory performance is evaluated through a round-robin split sample program for several laboratories participating in the Chesapeake Bay monitoring program. This program is being conducted through the USGS Baltimore Office.

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APPENDIX 1 -- EXAMPLE OF FIELD DATA RECORD

Base Flow sampling schedule for station 01674500 -- **MATTAPONI RIVER**, 7-1-03--6-30-04

	B F 0 1	B F 0 2	B F 0 3	F B L K a	B F 0 4	B F 0 5	B F 0 6	D U P L b	B F 0 7	B F 0 8	B F 0 9	S P L T c	B F 1 0	B F 1 1	B F 1 2
Gage Height															
Scheduled Date															
Sample Date															
Personnel															
Lab Sheet to Doug															
Data back from State															
Entered in QWDATA															
Cursory Check															
QA check															
Problems															
Problems solved															
Qtr Rpt															

a FBLK--field blank

b.DUPL--duplicate

c. SPLT--lab split

High Flow sampling schedule for station 01674500 -- **MATTAPONI RIVER**, 7-1-03--6-30-04

	H F 0 1	H F 0 2	F B L K a	H F 0 3	H F 0 4	H F 0 5	D U P L b	H F 0 6	H F 0 7	H F 0 8	S P L T c	H F 0 9	H F 1 0	H F 1 1	H F 1 2	F B L K a	H F 1 3	H F 1 4	H F 1 5	D U P L b	H F 1 6	H F 1 7	H F 1 8	S P L T c	H F 1 9	H F 2 0	H F 2 1	
Gage Height																												
Sampled Date																												
Personnel																												
Lab Sheet to Doug																												
Data back from State																												
Entered into QWDATA																												
Cursory Check																												
QA check																												
Problems																												
Problems solved																												
Qtr Rpt																												

a FBLK--field blank

b.DUPL--duplicate

c. SPLT--lab split

APPENDIX 2 -- CRITERIA FOR EQUIPMENT USE

Table 1. Criteria for equipment use during stormflow and base-flow sampling at James River near Cartersville (02035000)

[NA, not applicable]

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<2.5	Weighted bottle	NA	1
2.5-12	DH-95	3/16	1
12 -15	DH-95	1/8	1
>16	D-96	1/8	3 (bag)

Table 2. Criteria for equipment use during stormflow and base-flow sampling at Rappahannock River near Fredericksburg (01668000)

[NA, not applicable]

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<3	Weighted bottle	NA	1
3- 9	DH-95	1/4	1
9-12	DH-95	3/16	1
>12	DH-95	1/8	1

Table 3. Criteria for equipment use during stormflow and base-flow sampling at Appomattox River at Matoaca (02041650)

[NA, not applicable]

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<3.5	Weighted bottle	NA	1
3.5 - 7.5	DH-95	3/16	1
7.5 - 15	DH-95	1/8	1
>16	D-96	1/8	3 (bag)

Table 4. Criteria for equipment use during stormflow and base-flow sampling at Pamunkey River near Hanover (01673000)

[NA, not applicable]

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<9	Weighted bottle	NA	1
9 - 15	DH-95	3/16	1
>16	D-96	3/16	3 (bag)

Table 5. Criteria for equipment use during stormflow and base-flow sampling at Mattaponi River near Beulahville (01674500)

[NA, not applicable]

APPENDIX 3 -- FIELD SAMPLING PROCEDURES

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<11	Weighted bottle	NA	1
11- 15	DH-95	3/16	1
>16	D-96	1/8	3 (bag)

**RIVER INPUT MONITORING PROCEDURES AT
JAMES RIVER NEAR CARTERSVILLE (02035000)**

Please complete the following tasks in the order they are listed.

1. Look at the sampling schedule in the QW Area and determine if a quality assurance sample is scheduled. If no extra samples are to be taken, the following items are required:

EQUIPMENT: Cooler with approx. 5" of ice; cleaned and bagged churnsplitter; cleaned and bagged glass sampling bottle for sampler; YSI 600XL field meter and standards (dissolved oxygen, conductance, pH); 4 cubitainers, plus at least 1 extra; VDCLS labels; tubing, filters and pump.

PAPERWORK: Virginia District Field Sheet

If quality assurance samples are to be taken, take extra cubitainers, filter, and tubing, VDCLS lab sheets and USGS lab sheets. All necessary forms are in the River Input folders in the lab.

2. Upon arrival at the site, read the gage height and note if the level is rising or falling. Note time, dial reading, and inside gage reading. Set out safety cones and put on safety vest.

3. Set up sampling equipment. Refer to sampler protocol sheet to determine which sampler should be used. If using the DH-95 or D-96 (use only the nylon nozzles), have wire cutters with you at each station on the bridge. Allow the YSI meter to stabilize prior to calibration.

4. Calibrate dissolved oxygen, pH, and specific conductance, recording calibrations on the field sheets and noting any problems. Once dissolved oxygen, pH, and specific conductance are calibrated, lower the YSI multiparameter probes into the mid-point of the water column and allow to equilibrate.

5. Collect five depth-integrated subsamples from the Cartersville Bridge and composite in the churnsplitter.

Subsamples will be collected from the centroids of five equal-discharge river increments. The table below details the sampling locations at the foot markings on the bridge at various stages.

Gage height (ft)	Sampling locations (ft)
All gage heights	260, 380, 500, 620, 740

Depth-integrating sampling equipment is used to collect samples when the mean stream velocity exceeds 1.5 f/s, which corresponds to a gage height of about 2.5 feet. When the gage height is below 2.5 feet, samples are collected using a weighted bottle. The depth-integrating sampler is not effective at low velocities. The table below summarizes the equipment needs for sampling at various river stages.

Gage height (ft)	Sampler	Nozzle (inch)
<2.5	Weighted bottle	NA
2.5 - 12	DH-95	3/16
12 - 16	DH-95	1/8
16 - 32	D-96	1/8

Minimum amount of water to collect during routine sampling:

Sampler	Amount of water
Weighted bottle	2 bottles at each station
DH-95	2 bottles at each station

Minimum amount of water to collect when doing duplicates or lab splits:

Sampler	Amount of water
Weighted bottle	2 bottles at each station
DH-95	2 bottles at each station

The time of sample will be the temporal mid-point of sampling. If collecting a sample for VDCLS only, label the sample on quarter hours.

Duplicates should be labeled 15 minutes after the regular samples (i.e., 1200 for the first set of samples and 1215 for the second set of samples). Circle “Duplicate” on Virginia District field sheet, and enter the respective times.

Lab splits should be labeled 5 minutes after the regular samples. (i.e. VDCLS 1200 and USGS 1205). Circle “Labsplit” on Virginia District field sheet, and enter the respective times.

6. To process the unfiltered samples, sample-rinse cubitainers thoroughly, then fill. Churn continuously without breaking the water surface while filling. If collecting lab split to be sent to NWQL, preserve with 1 mL 4.5N sulfuric acid. Wear latex gloves when working with sulfuric acid. Similarly, to process suspended-sediment samples, fill unrinsed 1-pint glass container with approximately 400 mL of raw water

while churning continuously.

7. To process the filtered samples, first connect the tubing to the pump, and then connect the filter (Gelman Sciences® 0.45 µm polysulfone filter) to the end of the tubing. Run approximately 500 mL of sample through the tubing and filter to sample-rinse. Next, sample-rinse the cubitainers thoroughly with filtered water, then fill.

8. Fill out labels with appropriate times as described above, and place samples in ice. All shaded boxes on laboratory forms are REQUIRED and MUST match the information on the label for each sample.

9. Collect the field parameters insitu (water temperature, specific conductance, pH, and dissolved oxygen) at the five water-quality stations along the channel crosssection. Record all field parameter values from each station on the field sheet. Report the median field parameter value. At the field vehicle, determine and record the barometric pressure and air temperature. Please note on the field sheet the water quality instruments used and the serial numbers.

10. Clean and store instruments and equipment. Pick up any safety cones.

11. Return to gage house and record gage height reading. Note on the field sheet if the level was rising or falling by reading the CR10 interface. If the level changed significantly during sample, record the gage height that was taken closest to the time put on the sample labels.

12. Take samples to Virginia Division of Consolidated Labs (VDCLS). If samples were taken on the weekend or late in the afternoon, put samples in USGS District lab refrigerator. Write down any sampling problems or observations on the USGS field sheet (i.e., river especially muddy, meter calibration problems and how fixed, other equipment problems. ANY information can sometimes help.). Enter field data and schedule sample analyses using VADEQ CEDS.

**RIVER INPUT MONITORING PROCEDURES AT
RAPPAHANNOCK RIVER NEAR FREDERICKSBURG (01668000)**

Please complete the following tasks in the order they are listed.

1. Look at the sampling schedule in the QW Area and determine if a quality assurance sample is scheduled. If no extra samples are to be taken, the following items are required:

EQUIPMENT: Cooler with approx. 5" of ice; cleaned and bagged churnsplitter; cleaned and bagged glass sampling bottle for sampler; YSI 600XL field meter and standards (dissolved oxygen, conductance, pH); 4 cubitainers, plus at least 1 extra; VDCLS labels; tubing, filters and pump.

PAPERWORK: Virginia District Field Sheet

If quality assurance samples are to be taken, take extra cubitainers, filter, and tubing, VDCLS lab sheets and USGS lab sheets. All necessary forms are in the River Input folders in the lab.

2. Upon arrival at the site, read the gage height and note if the level is rising or falling. Note time, dial reading, and inside gage reading. Set out safety cones and put on safety vest.

3. Calibrate dissolved oxygen, pH, and specific conductance, recording calibrations on the field sheets and noting any problems. Once dissolved oxygen, pH, and specific conductance are calibrated, lower the YSI multiparameter probes into the mid-point of the water column and allow to equilibrate.

4. Set up sampling equipment. Refer to sampler protocol sheet to determine which sampler should be used. If using the DH-95 or D-96 (use only the nylon nozzles), the following equipment is required: wire cutters, gloves (leather and nitrile), cable pullers, life vest, spare nylon nozzles, flat-head screwdriver, sampler pin, cleaned and bagged churnsplitter, and cleaned and bagged glass bottle. If using the weighted bottle sampler, you will need: rope, cleaned and bagged churnsplitter, cleaned and bagged sample bottle, and cable pullers. Put on life vest. Inspect the cableway and surrounding area for damage before climbing the tower and entering the cart.

5. Make sure the brake is on before unlocking the locks. Take the brake off, continue to hold the brake rod, and ride to the left bank. Use the cable pullers to slow the cart until reaching the first sampling point. Be alert for submerged logs. If the sampler cable becomes snagged, let all the line out and quickly cut the line.

6. Collect water ten depth-integrated subsamples from the cableway and composite in the churnsplitter. Subsamples will be collected from the centroids of ten equal-width river increments. Depth-integrating sampling equipment will be used to collect samples when the mean stream velocity exceeds 1.5 f/s, which corresponds to a gage height of about 3 feet. When the gage height is below 3 feet, samples are collected using a weighted bottle. The depth-integrating sampler is not effective at low velocities. Ten equally-spaced depth integrated samples will be collected. The table below summarizes the equipment needs for sampling at various river stages

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
< 3	Weighted bottle	NA	1
3 - 9	DH-95	1/4	1
9 - 12	DH-95	3/16	1
> 12	DH-95	1/8	1

Minimum amount of water to collect during routine sampling.:

Sampler	Amount of water
Weighted bottle	1 bottle at each station
DH-95	1 bottles at each station

Minimum amount of water to collect when doing duplicates or lab splits:

Sampler	Amount of water
Weighted bottle	1 bottle at each station
DH-95	1 bottle at each station

The time of sample will be the temporal mid-point of sampling. If collecting a sample for VDCLS only, label the sample on quarter hours.

Duplicates should be labeled 15 minutes after the regular samples (i.e., 1200 for the first set of samples and 1215 for the second set of samples). Circle “Duplicate” on Virginia District field sheet, and enter the respective times.

Lab splits should be labeled 5 minutes after the regular samples. (i.e. VDCLS 1200 and USGS 1205). Circle “Labsplit” on Virginia District field sheet, and enter the respective times.

7. To process the unfiltered samples, sample-rinse cubitainers thoroughly, then fill. Churn continuously without breaking the water surface while filling. If collecting lab split to be sent to NWQL, preserve with 1 mL 4.5N sulfuric acid. Wear latex gloves when working with sulfuric acid. Similarly, to process suspended-sediment samples, fill unrinsed 1-pint glass container with approximately 400 mL of raw water while churning continuously.

8. To process the filtered samples, first connect the tubing to the pump, and then connect the filter (Gelman Sciences® 0.45 µm polysulfone filter) to the end of the tubing. Run approximately 500 mL of sample through the tubing and filter to sample-rinse. Next, sample-rinse the cubitainers thoroughly with filtered water, then fill.

9. Fill out labels with appropriate times as described above, and place samples in ice. All shaded boxes on laboratory forms are REQUIRED and MUST match the information on the label for each sample.

10. Collect the field parameters insitu (water temperature, specific conductance, pH, and dissolved oxygen) at the right edge of water. Collect a total of five readings for each field parameter. Record all field parameter values on the field sheet. Report the median field parameter value. At the field vehicle, determine and record the barometric pressure and air temperature. Please note on the field sheet the water quality instruments used and the serial numbers.

11. Clean and store instruments and equipment. Pick up any safety cones.

12. Return to gage house and record gage height reading. Note on the field sheet if the level was rising or falling by reading the CR10 interface. If the level changed significantly during sample, record the gage height that was taken closest to the time put on the sample labels.

13. Take samples to Virginia Division of Consolidated Labs (VDCLS). If samples were taken on the weekend or late in the afternoon, put samples in USGS District lab refrigerator. Write down any sampling problems or observations on the USGS field sheet (i.e., river especially muddy, meter calibration problems and how fixed, other equipment problems. ANY information can sometimes help.). Enter field data and schedule sample analyses using VADEQ CEDS.

**RIVER INPUT MONITORING PROCEDURES AT
APPOMATTOX RIVER AT MATOACA (02041650)**

Please complete the following tasks in the order they are listed.

1. Look at the sampling schedule in the QW Area and determine if a quality assurance sample is scheduled. If no extra samples are to be taken, the following items are required:

EQUIPMENT: Cooler with approx. 5" of ice; cleaned and bagged churnsplitter; cleaned and bagged glass sampling bottle for sampler; YSI 600XL field meter and standards (dissolved oxygen, conductance, pH); 4 cubitainers, plus at least 1 extra; VDCLS labels; tubing, filters and pump.

PAPERWORK: Virginia District Field Sheet

If quality assurance samples are to be taken, take extra cubitainers, filter, and tubing, VDCLS lab sheets and USGS lab sheets. All necessary forms are in the River Input folders in the lab.

2. Upon arrival at the site, read the gage height and note if the level is rising or falling. Note time, dial reading, and inside gage reading. Set out safety cones and put on safety vest.
3. Set up sampling equipment. Refer to sampler protocol sheet to determine which sampler should be used. If using the DH-95 or D-96 (use only the nylon nozzles), have wire cutters with you at each station on the bridge. Allow the YSI meter to stabilize prior to calibration.
4. Calibrate dissolved oxygen, pH, and specific conductance, recording calibrations on the field sheets and noting any problems. Once dissolved oxygen, pH, and specific conductance are calibrated, lower the YSI multiparameter probes into the mid-point of the water column and allow to equilibrate.
5. Collect four depth-integrated subsamples from the Matoaca Bridge and composite in the churnsplitter.

Subsamples will be collected from the centroids of four equal-discharge river increments corresponding to 12.5%, 37.5%, 62.5% and 87.5% of the cumulative flow. The table below details the sampling locations at the foot markings on the bridge at various stages.

Gage height (ft)	Sampling locations (ft)
<12	140, 195, 240, 295
>12	120, 180, 240, 295

Depth-integrating sampling equipment will be used to collect samples when the mean stream velocity exceeds 1.5 ft/s, which corresponds to a gage height of about 3.5 feet. When the gage height is below 3.5 feet, samples are collected using a weighted bottle. The depth-integrating sampler is not effective at low velocities. The table below summarizes the equipment needs for

sampling at various river stages .

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
< 3.5	Weighted bottle	NA	2
3.5 - 7.5	DH-95	3/16	1
7.5 - 15	DH-95	1/8	1
> 16	D-96	1/8	3 (Bag)

Minimum amount of water to collect during routine sampling:

Sampler	Amount of water
Weighted bottle	2 bottle at each station
DH-95	2 bottles at each station

Minimum amount of water to collect when doing duplicates or lab splits:

Sampler	Amount of water
Weighted bottle	2 bottle at each station
DH-95	2 bottle at each station

The time of sample will be the temporal mid-point of sampling. If collecting a sample for VDCLS only, label the sample on quarter hours.

Duplicates should be labeled 15 minutes after the regular samples (i.e., 1200 for the first set of samples and 1215 for the second set of samples). Circle “Duplicate” on Virginia District field sheet, and enter the respective times.

Lab splits should be labeled 5 minutes after the regular samples. (i.e. VDCLS 1200 and USGS 1205). Circle “Labsplit” on Virginia District field sheet, and enter the respective times.

6. To process the unfiltered samples, sample-rinse cubitainers thoroughly, then fill. Churn continuously without breaking the water surface while filling. If collecting lab split to be sent to NWQL, preserve with 1 mL 4.5N sulfuric acid. Wear latex gloves when working with sulfuric acid. Similarly, to process suspended-sediment samples, fill unrinsed 1-pint glass container with approximately 400 mL of raw water while churning continuously.

7. To process the filtered samples, first connect the tubing to the pump, and then connect the filter (Gelman Sciences® 0.45 µm polysulfone filter) to the end of the tubing. Run approximately 500 mL of sample through the tubing and filter to sample-rinse. Next, sample-rinse the cubitainers thoroughly with filtered water, then fill.

8. Fill out labels with appropriate times as described above, and place samples in ice. All shaded boxes on laboratory forms are REQUIRED and MUST match the information on the label for each sample.

9. Collect the field parameters insitu (water temperature, specific conductance, pH, and dissolved oxygen) at five water-quality stations along the channel crosssection. Record all field parameter values from each station on the field sheet. Report the median field parameter value. At the field vehicle, determine and record the barometric pressure and air temperature. Please note on the field sheet the water quality instruments used and the serial numbers.
10. Clean and store instruments and equipment. Pick up any safety cones.
11. Return to gage house and record gage height reading. Note on the field sheet if the level was rising or falling by reading the CR10 interface. If the level changed significantly during sample, record the gage height that was taken closest to the time put on the sample labels.
12. Take samples to Virginia Division of Consolidated Labs (VDCLS). If samples were taken on the weekend or late in the afternoon, put samples in USGS District lab refrigerator. Write down any sampling problems or observations on the USGS field sheet (i.e., river especially muddy, meter calibration problems and how fixed, other equipment problems. ANY information can sometimes help.). Enter field data and schedule sample analyses using VADEQ CEDS.

**RIVER INPUT MONITORING PROCEDURES AT
PAMUNKEY RIVER NEAR HANOVER (01673000)**

Please complete the following tasks in the order they are listed.

1. Look at the sampling schedule in the QW Area and determine if a quality assurance sample is scheduled. If no extra samples are to be taken, the following items are required:

EQUIPMENT: Cooler with approx. 5" of ice; cleaned and bagged churnsplitter; cleaned and bagged glass sampling bottle for sampler; YSI 600XL field meter and standards (dissolved oxygen, conductance, pH); 4 cubitainers, plus at least 1 extra; VDCLS labels; tubing, filters and pump.

PAPERWORK: Virginia District Field Sheet

If quality assurance samples are to be taken, take extra cubitainers, filter, and tubing, VDCLS lab sheets and USGS lab sheets. All necessary forms are in the River Input folders in the lab.

2. Upon arrival at the site, read the gage height and note if the level is rising or falling. Note time, dial reading, and inside gage reading. Set out safety cones and put on safety vest.

3. Set up sampling equipment. Refer to sampler protocol sheet to determine which sampler should be used. If using the DH-95 or D-96 (use only the nylon nozzles), have wire cutters with you at each station on the bridge. Allow the YSI meter to stabilize prior to calibration.

4. Calibrate dissolved oxygen, pH, and specific conductance, recording calibrations on the field sheets and noting any problems. Once dissolved oxygen, pH, and specific conductance are calibrated, lower the YSI multiparameter probes into the mid-point of the water column and allow to equilibrate.

5. Collect five depth-integrated subsamples from the Hanover Bridge and composite in the churnsplitter.

Subsamples will be collected at the center of five equal-width-increment sections. The width of the increments to be sampled is determined by dividing the stream width by 5 (number of verticals). The equal-width-increment method is used at this site because the streambed, and therefore distribution of water discharge in the cross section, is not stable.

Depth-integrating sampling equipment will be used to collect samples when the mean stream velocity exceeds 1.5 ft/s, which corresponds to a gage height of 9.0 feet. When the gage height is below 9.0 feet, grab samples will be collected with a weighted bottle sampler from the five determined locations. The table below summarizes the equipment needs for sampling at various river stages.

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<9	Weighted bottle	NA	1
9 - 15	DH-95	3/16	1
>16	D-96	3/16	3 (Bag)

Minimum amount of water to collect during routine sampling:

Sampler	Amount of water
Weighted bottle	2 bottles at each station
DH-95	2 bottles at each station

Minimum amount of water to collect when doing duplicates or lab splits:

Sampler	Amount of water
Weighted bottle	2 bottles at each station
DH-95	2 bottles at each station

The time of sample will be the temporal mid-point of sampling. If collecting a sample for VDCLS only, label the sample on quarter hours.

Duplicates should be labeled 15 minutes after the regular samples (i.e., 1200 for the first set of samples and 1215 for the second set of samples). Circle “Duplicate” on Virginia District field sheet, and enter the respective times.

Lab splits should be labeled 5 minutes after the regular samples. (i.e. VDCLS 1200 and USGS 1205). Circle “Labsplit” on Virginia District field sheet, and enter the respective times.

6. To process the unfiltered samples, sample-rinse cubitainers thoroughly, then fill. Churn continuously without breaking the water surface while filling. If collecting lab split to be sent to NWQL, preserve with 1 mL 4.5N sulfuric acid. Wear latex gloves when working with sulfuric acid. Similarly, to process suspended-sediment samples, fill unrinsed 1-pint glass container with approximately 400 mL of raw water while churning continuously.
7. To process the filtered samples, first connect the tubing to the pump, and then connect the filter (Gelman Sciences® 0.45 µm polysulfone filter) to the end of the tubing. Run approximately 500 mL of sample through the tubing and filter to sample-rinse. Next, sample-rinse the cubitainers thoroughly with filtered water, then fill.
8. Fill out labels with appropriate times as described above, and place samples in ice. All shaded boxes on laboratory forms are REQUIRED and MUST match the information on the label for each sample.
9. Collect the field parameters insitu (water temperature, specific conductance, pH, and dissolved oxygen) at five water-quality stations along the channel crosssection. Record all field parameter values from each station on the field sheet. Report the median field parameter value. At the field vehicle, determine and record the barometric pressure and air temperature. Please note on the field sheet the water quality instruments used and the serial numbers.
10. Clean and store instruments and equipment. Pick up any safety cones.
11. Return to gage house and record gage height reading. Note on the field sheet if the level was rising or

falling by reading the CR10 interface. If the level changed significantly during sample, record the gage height that was taken closest to the time put on the sample labels.

12. Take samples to Virginia Division of Consolidated Labs (VDCLS). If samples were taken on the weekend or late in the afternoon, put samples in USGS District lab refrigerator. Write down any sampling problems or observations on the USGS field sheet (i.e., river especially muddy, meter calibration problems and how fixed, other equipment problems. ANY information can sometimes help.). Enter field data and schedule sample analyses using VADEQ CEDS.

**RIVER INPUT MONITORING PROCEDURES AT
MATTAPONI RIVER NEAR BEULAHVILLE (01674500)**

Please complete the following tasks in the order they are listed.

1. Look at the sampling schedule in the QW Area and determine if a quality assurance sample is scheduled. If no extra samples are to be taken, the following items are required:

EQUIPMENT: Cooler with approx. 5" of ice; cleaned and bagged churnsplitter; cleaned and bagged glass sampling bottle for sampler; YSI 600XL field meter and standards (dissolved oxygen, conductance, pH); 4 cubitainers, plus at least 1 extra; VDCLS labels; tubing, filters and pump.

PAPERWORK: Virginia District Field Sheet

If quality assurance samples are to be taken, take extra cubitainers, filter, and tubing, VDCLS lab sheets and USGS lab sheets. All necessary forms are in the River Input folders in the lab.

2. Upon arrival at the site, read the gage height and note if the level is rising or falling. Note time, dial reading, and inside gage reading. Set out safety cones and put on safety vest.
3. Set up sampling equipment. Refer to sampler protocol sheet to determine which sampler should be used. If using the DH-95 or D-96 (use only the nylon nozzles), have wire cutters with you at each station on the bridge. Allow the YSI meter to stabilize prior to calibration.
4. Calibrate dissolved oxygen, pH, and specific conductance, recording calibrations on the field sheets and noting any problems. Once dissolved oxygen, pH, and specific conductance are calibrated, lower the YSI multiparameter probes into the mid-point of the water column and allow to equilibrate.
5. Collect four depth-integrated subsamples from the Beulahville bridge and composite in the churnsplitter.

Subsamples will be collected from the centroids of four equal-discharge river increments. The table below details the sampling locations at the foot markings on the bridge at various stages.

Gage height (ft)	Sampling locations (ft)
<6	85, 73, 65, 53
6 - 12	91, 77, 65, 53
>12	100, 72, 58, 40

Depth-integrating sampling equipment will be used to collect samples when the mean stream velocity exceeds 1.5 ft/s, which corresponds to a gage height of about 11 feet. When the gage height is below 11 feet, samples are collected using a weighted bottle. The depth-integrating sampler is not effective at low velocities. The table below summarizes the equipment needs for sampling at various river stages.:

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<11	Weighted bottle	NA	1
11 - 15	DH-95	3/16	1
>16	D-96	1/8	3 (Bag)

Minimum amount of water to collect during routine sampling

Sampler	Amount of water
Weighted bottle	2 bottles at each station
DH-95	2 bottles at each station

Minimum amount of water to collect when doing duplicates or lab splits:

Sampler	Amount of water
Weighted bottle	2 bottles at each station
DH-95	2 bottles at each station

The time of sample will be the temporal mid-point of sampling. If collecting a sample for VDCLS only, label the sample on quarter hours.

Duplicates should be labeled 15 minutes after the regular samples (i.e., 1200 for the first set of samples and 1215 for the second set of samples). Circle "Duplicate" on Virginia District field sheet, and enter the respective times.

Lab splits should be labeled 5 minutes after the regular samples. (i.e. VDCLS 1200 and USGS 1205). Circle "Labsplit" on Virginia District field sheet, and enter the respective times.

6. To process the unfiltered samples, sample-rinse cubitainers thoroughly, then fill. Churn continuously without breaking the water surface while filling. If collecting lab split to be sent to NWQL, preserve with 1 mL 4.5N sulfuric acid. Wear latex gloves when working with sulfuric acid. Similarly, to process suspended-sediment samples, fill unrinsed 1-pint glass container with approximately 400 mL of raw water while churning continuously.

7. To process the filtered samples, first connect the tubing to the pump, and then connect the filter (Gelman Sciences[®] 0.45 µm polysulfone filter) to the end of the tubing. Run approximately 500 mL of sample through the tubing and filter to sample-rinse. Next, sample-rinse the cubitainers thoroughly with filtered water, then fill.
8. Fill out labels with appropriate times as described above, and place samples in ice. All shaded boxes on laboratory forms are REQUIRED and MUST match the information on the label for each sample.
9. Collect the field parameters insitu (water temperature, specific conductance, pH, and dissolved oxygen) at five water-quality stations along the channel crosssection. Record all field parameter values from each station on the field sheet. Report the median field parameter value. At the field vehicle, determine and record the barometric pressure and air temperature. Please note on the field sheet the water quality instruments used and the serial numbers.
10. Clean and store instruments and equipment. Pick up any safety cones.
11. Return to gage house and record gage height reading. Note on the field sheet if the level was rising or falling by reading the CR10 interface. If the level changed significantly during sample, record the gage height that was taken closest to the time put on the sample labels.
12. Take samples to Virginia Division of Consolidated Labs (VDCLS). If samples were taken on the weekend or late in the afternoon, put samples in USGS District lab refrigerator. Write down any sampling problems or observations on the USGS field sheet (i.e., river especially muddy, meter calibration problems and how fixed, other equipment problems. ANY information can sometimes help.). Enter field data and schedule sample analyses using VADEQ CEDS.

**APPENDIX 4 --NATIONAL WATER QUALITY LABORATORY
ANALYTICAL REQUEST FORM**

**APPENDIX 5 -- VIRGINIA DISTRICT OFFICE RIVER INPUT MONITORING
FIELD SHEET**



U. S. GEOLOGICAL SURVEY SURFACE-WATER QUALITY NOTES



NWIS RECORD NO _____

STATION NO. _____ SAMPLE DATE ____/____/____ MEAN SAMPLE TIME(CLOCK) _____
 STATION NAME _____ SAMPLE MEDIUM ____ SAMPLE TYPE ____ TIME DATUM ____ (eg. EST, EDT, UTC)
 PROJECT NO. _____ - _____ PROJ NAME _____ SAMPLE PURPOSE (71999) ____ PURPOSE OF SITE VISIT (50280) ____
 SAMPLING TEAM _____ TEAM LEAD SIGNATURE _____ DATE ____/____/____
 START TIME _____ GAGE HT _____ TIME _____ GHT _____ TIME _____ GHT _____ TIME _____ GHT _____ END TIME _____ GHT _____

QC SAMPLE COLLECTED? EQUIP BLANK ____ FIELD BLANK ____ SPLIT ____ CONCURRENT ____ SEQUENTIAL ____ SPIKE ____ TRIP BLANK ____ OTHER ____
 NWIS RECORD NOS. _____

LABORATORY INFORMATION

SAMPLES COLLECTED: NUTRIENTS ____ MAJOR IONS ____ TRACE ELEMENTS: FILTERED ____ UNFILTERED ____ MERCURY ____ VOC ____ RADON ____
 TPC ____ (VOL FILTERED ____ mL) TPC ____ (VOL FILTERED ____ mL) PIC ____ (VOL FILTERED ____ mL) DOC ____ ORGANICS: FILTERED ____ UNFILTERED ____
 ISOTOPES ____ MICROBIOLOGY ____ CHLOROPHYLL ____ BOD ____ COD ____ ALGAE ____ INVERTEBRATES ____ FISH ____ BED SED. ____
 SUSP. SED. ____ CONC. SIF SIZE RADIOCHEMICALS: FILTERED ____ UNFILTERED ____ OTHER _____ OTHER _____
 LABORATORY SCHEDULES: _____
 LAB CODES: _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE
 COMMENTS: _____ DATE SHIPPED ____/____/____

FIELD MEASUREMENTS

GAGE HT (00065) _____ ft	COND (00095) _____ μ S/cm@25 °C	CARBONATE (00452) _____ mg/L
Q, INST. (00061) _____ cfs MEAS. RATING EST.	TEMP, AIR (00020) _____ °C	HYDROXIDE (71834) _____ mg/L
DIS. OXYGEN (00300) _____ mg/L	TEMP, WATER (00010) _____ °C	E. COLI () _____ col/100mL
BAROMETRIC PRES. (00025) _____ mm Hg	TURBIDITY (61028) _____ ntu	FECAL COLIFORM (31625) _____ col/100mL
DO SAT. (00301) _____ %	ALKALINITY () _____ mg/L	TOTAL COLIFORM (31501) _____ col/100 mL
eH (00090) _____ mvolts	ANC () _____ mg/L	OTHER: _____
pH (00400) _____ UNITS	BICARBONATE (00453) _____ mg/L	OTHER: _____

SAMPLING INFORMATION

Sampler Type (84164) _____ Sampler ID _____ Sample Compositor/Splitter: PLASTIC TEFLON CHURN CONE OTHER _____
 Sampler Bottle/Bag Material: PLASTIC TEFLON OTHER _____ Nozzle Material: PLASTIC TEFLON OTHER _____ Nozzle Size: 3/16" 1/4" 5/16"
 Stream Width: _____ ft mi Left Bank _____ Right Bank _____ Mean Depth: _____ ft Ice Cover _____ % Ave. Ice Thickness _____ in.
 Sampling Points: _____
 Sampling Location: WADING CABLEWAY BOAT BRIDGE UPSTREAM DOWNSTREAM SIDE OF BRIDGE _____ ft mi above below gage _____
 Sampling Site: POOL RIFFLE OPEN CHANNEL BRAIDED BACKWATER Bottom: BEDROCK ROCK COBBLE GRAVEL SAND SILT CONCRETE OTHER _____
 Stream Color: BROWN GREEN BLUE GRAY CLEAR OTHER _____ Stream Mixing: WELL-MIXED STRATIFIED POORLY-MIXED UNKNOWN OTHER _____
 Weather: **SKY**- CLEAR PARTLY CLOUDY CLOUDY **PRECIP**- LIGHT MEDIUM HEAVY SNOW RAIN MIST **WIND**- CALM LIGHT BREEZE GUSTY WINDY EST. WIND SPEED _____
TEMP- VERY COLD WARM HOT **COMMENTS** _____
 Sampling Method (82398): EWI [10] EDI [20] SINGLE VERTICAL [30] MULT VERTICAL [40] OTHER _____ Stage: STABLE, NORMAL STABLE, HIGH RISING FALLING PEAK
 OBSERVATIONS: _____

COMPILED BY: _____ CHECKED BY: _____ DATE: _____

STN NO _____

METER CALIBRATIONS

TEMPERATURE Meter MAKE/MODEL _____ S/N _____ Thermister S/N _____ Thermometer ID _____

Lab Tested against NIST Thermometer/Thermister? N Y Date: ___/___/___ ± _____ °C

Measurement Location: CONE SPLITTER CHURN SPLITTER SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **MEDIAN:** _____ °C **REMARK** _____ **QUALIFIER** _____

pH Meter MAKE/MODEL _____ S/N _____ Electrode No. _____ Type: GEL LIQUID OTHER _____

Sample: FILTERED UNFILTERED CONE SPLITTER CHURN SPLITTER SINGLE POINT AT _____ FT DEEP VERTICAL AVG. OF _____ POINTS

pH BUFFER	BUFFER TEMP	THEO-RETICAL pH FROM TABLE	pH BEFORE ADJ.	pH AFTER ADJ.	SLOPE	MILLI-VOLTS	BUFFER LOT NO.	BUFFER EXPIRATION DATE	COMMENTS
pH 7									
pH 7									
pH 7									
pH ____									
pH ____									
pH ____									
CHECK pH ____									

TEMPERATURE CORRECTION FACTORS FOR BUFFERS APPLIED?

CALIBRATION COMMENTS:

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **USE:** _____ **UNITS** **REMARK** _____ **QUALIFIER** _____

SPECIFIC CONDUCTANCE Meter MAKE/MODEL _____ S/N _____ Sensor Type: DIP CUP FLOW-THRU OTHER _____

Sample: CONE SPLITTER CHURN SPLITTER SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS

Temperature compensation:

STD VALUE	STD TEMP	SC BEFORE ADJ.	SC AFTER ADJ.	STD LOT NO	STD EXPIRATION DATE	COMMENTS

AUTO
MANUAL CORR. FACTOR= _____

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **MEDIAN:** _____ **μS/cm** **REMARK** _____ **QUALIFIER** _____

DISSOLVED OXYGEN Meter MAKE/MODEL _____ S/N _____ Probe No. _____

Sample: SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS BOD BOTTLE OTHER _____ Stirrer Used? Y N

Air Calibration Chamber in Water _____ Air-Saturated Water _____ Air Calibration Chamber in Air _____ Winkler Titration _____ Other _____

Battery Check: REDLINE _____ RANGE _____ THERMISTER Check? Y N Zero DO Check: Y N Solution Date _____

WATER TEMP °C	BAROMETRIC PRESSURE mm Hg	DO TABLE READING mg/L	SALINITY CORR. FACTOR	DO BEFORE ADJ.	DO AFTER ADJ.

Zero Meter Reading _____ mg/L Adj. to _____ mg/L
Membrane Changed? N Y Date: ___/___/___ Time: _____
Barometer Calibrated? N Y Date: ___/___/___ Time: _____

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **MEDIAN:** _____ **mg/L** **REMARK** _____ **QUALIFIER** _____

STN NO _____

OXYGEN DEMAND (BOD) (CBOD)

BLANKS

BOTTLE NO.	INITIAL BOD	DO OR CBOD	5-DAY BOD	DO OR CBOD	BOD	CBOD	AVERAGE	
							BOD	CBOD

RESIDUAL CHLORINE			
	positive/negative	sodium sulfite added	sodium sulfite normality
field test	+ / -		
lab test	+ / -		
After 5-day bod/cbod	+ / -		

SAMPLE

BOTTLE NO.	SAMPLE SIZE DILUTION	INITIAL BOD	DO OR CBOD	5-DAY BOD	DO OR CBOD	BOD	CBOD

CALCULATIONS

$$BOD_5 \text{ (mg/L)} = \frac{D_1 - D_2}{P}$$

where D_1 = initial DO of sample
 D_2 = final DO of sample after 5 days, and
 P = decimal volumetric fraction of sample used.

COMMENTS _____

DISSOLVED OXYGEN USING WINKLER METHOD

TITRANT: PAO SODIUM THIOSULFATE OTHER _____ TITRANT NORMALITY _____ N D.O. = _____ mg/L

FINAL BURETTE READING						
INITIAL BURETTE READING						
mL TITRANT USED						
mL WATER TITRATED						

COMMENTS _____

DISSOLVED OXYGEN (mg/L) = $\left(\frac{200}{\text{mL water titrated}} \right) \times \text{mL TITRANT} \times \text{CF}^*$ *APPLY CORRECTION FACTOR (CF) IF TITRANT HAS A NON-STANDARD NORMALITY (STANDARD NORMALITY = 0.025N) CF = NORMALITY OF TITRANT/0.025

TURBIDITY CALIBRATION

Meter: MAKE/MODEL _____ S/N _____ Type: TURBIDIMETER SUBMERSIBLE SPECTROPHOTOMETER

Sample: SAMPLE STORED? Y N HOW LONG? _____

SAMPLE DILUTED? Y N VOL. OF DILUTION WATER _____ mL SAMPLE VOLUME _____ mL

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

A= NTU IN DILUTED SAMPLE
 B= VOLUME OF DILUTION WATER, mL
 C= SAMPLE VOLUME, mL

	Date Prepared	Concentration NTU	Temperature °C	Initial instrument reading	Reading after adjustment
Stock Turbidity Standard					
Zero NTU Standard (DIW)					
Standard 1					
Standard 2					
Standard 3					

COMMENTS _____

FIELD READING #1 _____ #2 _____ #3 _____ #4 _____ #5 _____ MEDIAN _____ NTU REMARK _____ QUALIFIER _____

APPENDIX 6 -- STANDARD OPERATING PROCEDURES FOR THE COLLECTION OF FIELD PARAMETERS (pH, Specific Conductance, Dissolved Oxygen, and Temperature) AND CHLOROPHYLL a



6.4 pH

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

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2 — pH

pH

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 $25^\circ C$); a solution is considered basic, or alkaline, when OH^- activity is greater than H^+ activity.
- ▶ Carbon dioxide (CO_2)-free water at $25^\circ C$ is considered neutral because activities of H^+ and OH^- are equal.

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

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 pH¹

[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 ± 0.1 units
 - Temperature range of at least 0 to $+45^\circ\text{C}$
 - Millivolt readout with accuracy of ± 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

¹Modify 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 CO₂ 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:

$$E = E^0 - S(\text{pH})$$

where

S = slope, and

E = electrode pair potential in mV.

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

$$E_1 = E^0 - S(\text{pH}_1)$$

and

$$E_2 = E^0 - S(\text{pH}_2)$$

or

$$S = \frac{E_2 - E_1}{\text{pH}_1 - \text{pH}_2}$$

and

$$E^0 = E_2 + S(\text{pH}_2).$$

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 ± 2 mV; the slope remains fairly constant to within ± 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 replugin 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.

10 — pH

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 ± 0.1 pH units.
 - Meters reading to three or more places to the right of the decimal may not provide better accuracy than ± 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.

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 ± 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 CO₂) 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 ± 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 ± 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"> • Buffers may be contaminated or old—use fresh buffers. • Faulty electrode—recondition electrode (see discussion in section 6.4.1 on electrode maintenance, cleaning, and storage). • Weak batteries—replace.
Slow response time	<p>For liquid-filled electrodes:</p> <ul style="list-style-type: none"> • Weak filling solution—change filling solution (section 6.4.1). • No filling solution—add fresh solution (section 6.4.1). • Dirty tip—clean with soap solution. Do not scratch electrode tip. • Chemical deposits—place electrode in a 0.1 M HCl solution for about 30 minutes. • Clogged or partially clogged junction—unclog by placing electrode tip in 0.1 M KCl solution at 90°C for about 15 minutes. Do not boil calomel electrodes (section 6.4.1). • Water is cold or of low ionic strength—longer equilibration time is needed (be patient). • Weak batteries—replace with new batteries. <p>For gel-filled electrodes:</p> <ul style="list-style-type: none"> • Dirty bulb—rinse with deionized water. • Clogged junction—liquify gel by placing electrode into warm (~60°C) water for one minute or less.
Erratic readings	<ul style="list-style-type: none"> • Loose or defective connections—tighten, clean, or replace connections. • Broken or defective cable—repair or replace cable. • Static charge—polish face of meter with antistatic solution. • Loose battery connection—tighten. • Air bubbles in the electrode bulb—shake gently. • Too much pressure in flowthrough chamber—reduce pressure. • Weak batteries—replace with new batteries.

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.



6.3 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°C). The method described in this section for measuring conductivity is applicable to surface water and ground water, from fresh to saline.

Specific electrical conductance (conductivity): a measure of the electrical conductance of a substance normalized to unit length and unit cross section at a specified temperature.

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 conductivity¹
[°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°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, or backup instrument
- ✓ Conductivity probes that approximate and bracket field values
- ✓ Composite or surface-water samples
- ✓ Flowthrough 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

¹Modify 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°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.

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 ≤ 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 ± 5 percent for conductivity $\leq 100 \mu\text{S}/\text{cm}$, or ± 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 CO₂ 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"> • Standards may be old or contaminated—use fresh standards. • 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. • Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air. • Weak batteries—replace. • Temperature compensation incorrect—ensure that thermometer is operating properly and is calibrated. • Sensor constant incorrect—replace sensor.
Erratic instrument readings	<ul style="list-style-type: none"> • Loose or defective connections—tighten or replace. • Broken cables—repair or replace. • Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air. • Rapid changes in water temperature—measure in situ. • Outgassing of ground-water sample—use a downhole instrument; if unavailable, use a flowthrough chamber. • Broken sensor—replace.
Instrument requires frequent recalibration	<ul style="list-style-type: none"> • 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.

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.



6.2 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^{TM,1} 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.

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.

¹Rhodazine-DTM, 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 determination¹

[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°C to $+45^{\circ}\text{C}$
 - Measure concentrations ≥ 1 to 20 mg/L
 - Minimum scale readability, preferably 0.05 mg/L DO
 - Calibrated accuracy within 5 percent or ± 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 solution²: 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

¹Modify 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.

²Prepare 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

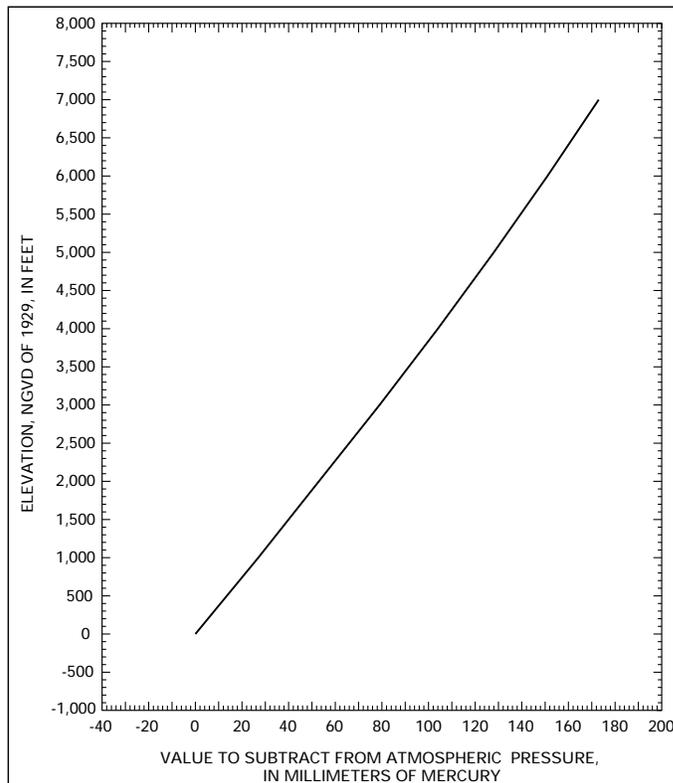


Figure 6.2-1. Factors used to correct atmospheric pressures adjusted to sea level.

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.

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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 ± 0.05 mg/L.**

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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.

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 ± 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.

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

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 μmoles/L) or 0 to 40 mg/L (0 to 13 μmoles/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.

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™ 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™ 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™ 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	12.0	11.9	11.8	11.7	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	11.1	11.0	11.0	10.9	10.8	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	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.3	10.2	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	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	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	9.5	9.4	9.4	9.3	9.2	9.2	9.1	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
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
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
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	6.7
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
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	6.6
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
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	6.5
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	6.6	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
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	6.3
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	6.3	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	6.2
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
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	6.1
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
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	6.0
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
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
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	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

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	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	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	7.5	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	0.942	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



6.1 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.

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

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 temperature¹
[°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°C
0.1°C graduated
- ✓ Thermometer, liquid-in-glass sensor
Temperature range –5 to +45°C
Minimum 0.5°C graduated
Calibrated accuracy within 1 percent of full scale or 0.5°C, whichever is less
Calibrated and District certified against calibration (NIST) thermometer
- ✓ Thermistor thermometer
Calibrated accuracy within 0.1°C to 0.2°C
Digital readout to at least 0.1°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

¹Modify 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.

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

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.

Chlorophyll Collection and Processing for Fall Line Stations

- Standard collection procedures are followed, ensuring ample volume for sediment, nutrient, and chlorophyll samples. (approx. 5 liters sample needed)
- After drawing sediment sample, draw 500mL sample into amber bottle for chlorophyll filtration and set aside.
- Complete nutrient samples, raw and filtered.
- Assemble filter apparatus
 - Filter flask
 - Magnetic base and cup
 - Hand vacuum pump
- Apply filter to base, attach cup, moisten filter with DI
- Gently agitate sample
- Measure 100mL sample in graduated cylinder and pour into cup
- Add 10 drops (1mL) Magnesium Carbonate solution to sample cup
- Apply vacuum and filter sample (vacuum not to exceed 15 cm/Hg, 6 in/Hg)
- When sample is filtered, remove cup. Using forceps remove filter and fold in half with particulate material inside
- Place inside foil sheet
- Repeat filtration three times, placing all filters in same foil sheet and ensuring they are separated within
- Wrap in larger foil sheet and place label on foil ensuring the number of filters and volume filtered through each is noted on the label
- Place in whirl-pac or Ziploc and put on ice until delivery
- Clean all equipment with liquinox and rinse well with tap and DI