Peninsula CIMP Appendix C

CIMP Standard Operating Procedures (SOPs)

Appendix C

CIMP: Water Quality Monitoring Standard Operating Procedures

For the Peninsula CIMP Group

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1 INTRODUCTION

This document summarizes the Standard Operation Procedures (SOPs) for water quality and flow sampling and measurement. This document is organized by procedures including an overview of the Permit[1] monitoring requirements, protocols for collecting water quality samples and performing flow monitoring and estimation, dry weather outfall screening requirements, and quality assurance and quality control requirements.

1.1 Definition of SOP Terms

- Aliquot: A discrete sample collected as part of a composite sample.
- Grab Sample: A discrete sample. The sample is typically collected within a short period of time, usually less than 15 minutes. It is analyzed as a single sample and represents an instantaneous point in time. This method is used to collect samples for constituents not amenable to composite sampling due to short holding times and/or specific collection or preservation needs.
- Composite Sample: A sample composed of multiple aliquots. The aliquots are collected at regular intervals based on time or flow rate and composited into one single composite sample for analysis. Composite samples are used to determine an event mean concentration (to the extent that the aliquots are representative of the entire storm hydrograph) or loading of a constituent in water.
- Clean Hands/Dirty Hands: The sampling protocol to be used to handle the sampling equipment and sample bottles (as appropriate) (see Section 4.1.1).

2 PROCEDURES

2.1 Sample Collection Procedures

The Permit requires that samples and measurements taken for the purpose of monitoring shall be representative of the monitored activity. Three types of sampling procedures will be implemented to obtain representative measurements of the monitoring constituents:

- Time-weighted composite samples, which will be used for the majority of constituents for wet weather outfall monitoring. Collection of a time-weighted composite sample will entail collecting one aliquot every 20 minutes during a three (3) hour continuous period of a qualifying storm event, or over the entire storm if the storm duration is predicted to be less than 3 hours (for a total of ten (10) aliquots), weather permitting (Reference: EPA

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[1] This CIMP SOP was developed in accordance with Order No. R4-2012-0175, Monitoring and Reporting Program (MRP) No. CI-6948, dated November 8, 2012.

NPDES Storm Water Sampling Guidance Document EPA 833-B-92-001, 40 CFR 122.21 (g)(7)(ii)). Manual composite sample collection will be performed using a depth integrated sampler and/or a properly cleaned sample container with a pole attachment to collect discrete aliquots that will be combined to form one composite sample per monitoring event. Alternatively a peristaltic pump (such as a Masterflex E/S Portable Sampler with laboratory-cleaned fluoropolymers tubing) or portable autosampler (such as the ISCO 6712 with laboratory-cleaned fluoropolymers tubing) may be used to collect the discrete aliquots that will form the composite sample;

- Grab samples, which will be used for receiving water monitoring and dry weather outfall monitoring. Additionally, grab samples will be collected for wet weather outfall monitoring for bacteria, oil and grease, total petroleum hydrocarbons (TPH), cyanide, total phenols and volatile organic compounds (i.e., MTBE and 2-Chloroethyl vinyl ether only). Grab samples should be collected at the same time field measurements are performed. More details on the sampling procedures are provided in Section 2.4; and
- Field measurements. Field measurements will be gathered for readings that may change in transit between the sampling site and the laboratory. These parameters will include pH, dissolved oxygen, temperature, and specific conductivity. Procedures for measuring these parameters in the field are provided in Section 2.6.3.

In the first year of the monitoring program, outfall monitoring sites will be assessed for the feasibility of installing automated flow monitoring and sampling equipment. Automated monitoring equipment would facilitate the collection of more representative samples that represent a greater portion of flow hydrograph. If automated monitoring equipment is installed at one or more outfall monitoring locations after the first year, this SOP will be updated accordingly.

2.2 Monitoring Program Analytical Requirements

A summary of the monitoring program analytical requirements is provided in Appendix B.[2,3] Appendix B includes the required analytical method, minimum reporting level[4] (i.e., practical

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[2] Appendix B is based on the Permit Attachment E (Monitoring and Reporting Program [MRP] Table E-2 (Storm Water Monitoring Program's Constituents with Associated Minimum Levels) and with requirements added for 303(d)-listed constituents and constituents with Total Maximum Daily Loads (TMDLs), as applicable.

[3] All monitoring, sampling, sample preservation, and analyses must be conducted according to test procedures approved under 40 CFR Part 136 for the analysis of pollutants, unless another test procedure is required under 40 CFR subchapter N or O or is otherwise specified in the Permit for such pollutants. If a particular Minimum Level is not attainable in accordance with procedures set forth in 40 CFR Part 136, the lowest quantifiable concentration of the lowest calibration standard analyzed by a specific analytical procedure may be used instead.

quantitation limit), analysis holding time and container type and preservative. A summary of the sample volume requirements is provided in Table C-1. Note that the sample volume requirements could be reduced after the first significant storm event and the first June dry weather event, if constituents from Permit MRP Table E-2 no longer need to be analyzed because they were either not detected above the analytical method detection limit, or they were detected below the lowest applicable water quality objective.

This SOP is based on information provided by Weck Laboratories in City of Industry, California, Vista Analytical Laboratory in El Dorado Hills California, and Aquatic Bioassay & Consulting laboratories, Inc. (ABC) in Ventura, California (toxicity analyses). Other analytical laboratories may be substituted for monitoring program implementation provided the laboratories meet the following requirements:

1. Certified for such analyses by an appropriate governmental regulatory agency.
2. Participated in "Intercalibration Studies" for stormwater pollutant analysis conducted by the Southern California Municipal Storm Water Monitoring Coalition (SMC)[5].
3. Performs laboratory analyses consistent with the stormwater monitoring guidelines as specified in, the Stormwater Monitoring Coalition Laboratory Guidance Document, 2nd Edition R. Gossett and K. Schiff (2007), and its revisions.

Table C-1. CIMP Sample Volume Requirements

Constituents	**Container Type**	**No. Containers**	**Bottle Volume (mL)**	**Additional Volume Needed for MS/MSD**	
				No. Containers	**Bottle Volume (mL)**
Composite Samples					
Total Hardness, total and dissolved metals	Polyethylene	1	1,000	0	0
Cr6, Total	VOA	1	40	0	0
Cr6, Dissolved	VOA	1	40	0	0
Ammonia, COD, NO3+NO2 as N, TKN	Polyethylene	1	500	0	0

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[4] The Minimum Reporting Level is specified for all constituents listed in MRP Table E-2.

[5] The 'Intercalibration Studies' are conducted periodically by the SMC to establish a consensus based approach for achieving minimal levels of comparability among different testing laboratories for stormwater samples to minimize analytical procedure bias. Stormwater Monitoring Coalition Laboratory Document, Technical Report 420 (2004) and subsequent revisions and augmentations.

Constituents	**Container Type**	**No. Containers**	**Bottle Volume (mL)**	**Additional Volume Needed for MS/MSD**	
				No. Containers	**Bottle Volume (mL)**
BOD, Alkalinity, pH, EC, MBAS, TDS, TSS, Turbidity, VSS	Polyethylene (1 Gallon)	1	3,785	0	0
Chlorinated Herbicides (EPA 515.3)	Amber Glass	1	250	0	0
Organophosphate Pesticides (EPA 525.2)	Amber Glass	2	1,000	2	1,000
Glyphosate (EPA 547)	Amber VOA	1	40	1	40
Chlorinated Pesticides	Amber Glass	2	1,000	2	1,000
Semivolatile Organic Compounds (EPA 625)	Amber Glass	2	1,000	2	1,000
Fluoride (EPA 300.0)	Polyethylene	1	250	0	0
Perchlorate (EPA 314)	Polyethylene	1	250	0	0
Total & Dissolved Phosphorus	Polyethylene	1	500	0	0
Total Organic Carbon	Amber Glass	1	250	0	0
Toxicity (3 test species and TIE for most sensitive species)	Cubitainer (5 Gallon)	1	18,927	N/A	N/A
Composite Sample Subtotal		*18*	*28,832*	*7*	*3,040*
Grab Samples					
Cyanide	Polyethylene	1	500	0	0
Bacteria	Sterile	3	125	0	0
Volatile organic Compounds (EPA 624)	VOA	3	40	3	40
TPH-Diesel, TPH-Motor Oil (EPA 8015)	Amber Glass	2	1,000	2	1,000
Oil & Grease (EPA 1664)	Glass	2	1,000	2	1,000
Phenolics (EPA 420.4)	Amber Glass	1	500	0	0
TOTAL		**30**	**31,997**	**14**	**5,080**

2.3 Aquatic Toxicity Testing and Toxicity Identification Evaluations

The aquatic toxicity testing requirements outlined in the Permit are intended to determine whether water column toxicity is observed in targeted receiving waters and then assess which pollutant categories may potentially be causing the adverse aquatic effects. The results of aquatic toxicity testing are intended to guide future receiving and outfall water quality monitoring and contribute to the identification and control of toxicity causing pollutants in urban runoff through watershed control measures that may include: pollutant source controls, modified minimum control measures (MCMs) and Best Management Practices (BMPs). The following subsections outline the approach for conducting the Peninsula CIMP Group's aquatic toxicity monitoring and evaluation. Control measures and management actions to address confirmed toxicity caused by urban runoff are addressed by the EWMP, either via currently identified management actions or those that are identified via adaptive management of the EWMP.

The approach to conducting aquatic toxicity monitoring is presented in Figure C-1, which describes a general evaluation process for each sample collected as part of routine sampling conducted twice per year in wet weather and once per year in dry weather. Monitoring begins in the receiving water and the information gained is used to identify constituents for monitoring at outfalls to support the identification of pollutants that need to be addressed in the EWMP. The sub-sections below describe the detailed process and its technical and logistical rationale. Although not specified for testing at this time, the freshwater toxicity testing approach is also provided if such testing is initiated at any point during the life of the CIMP.

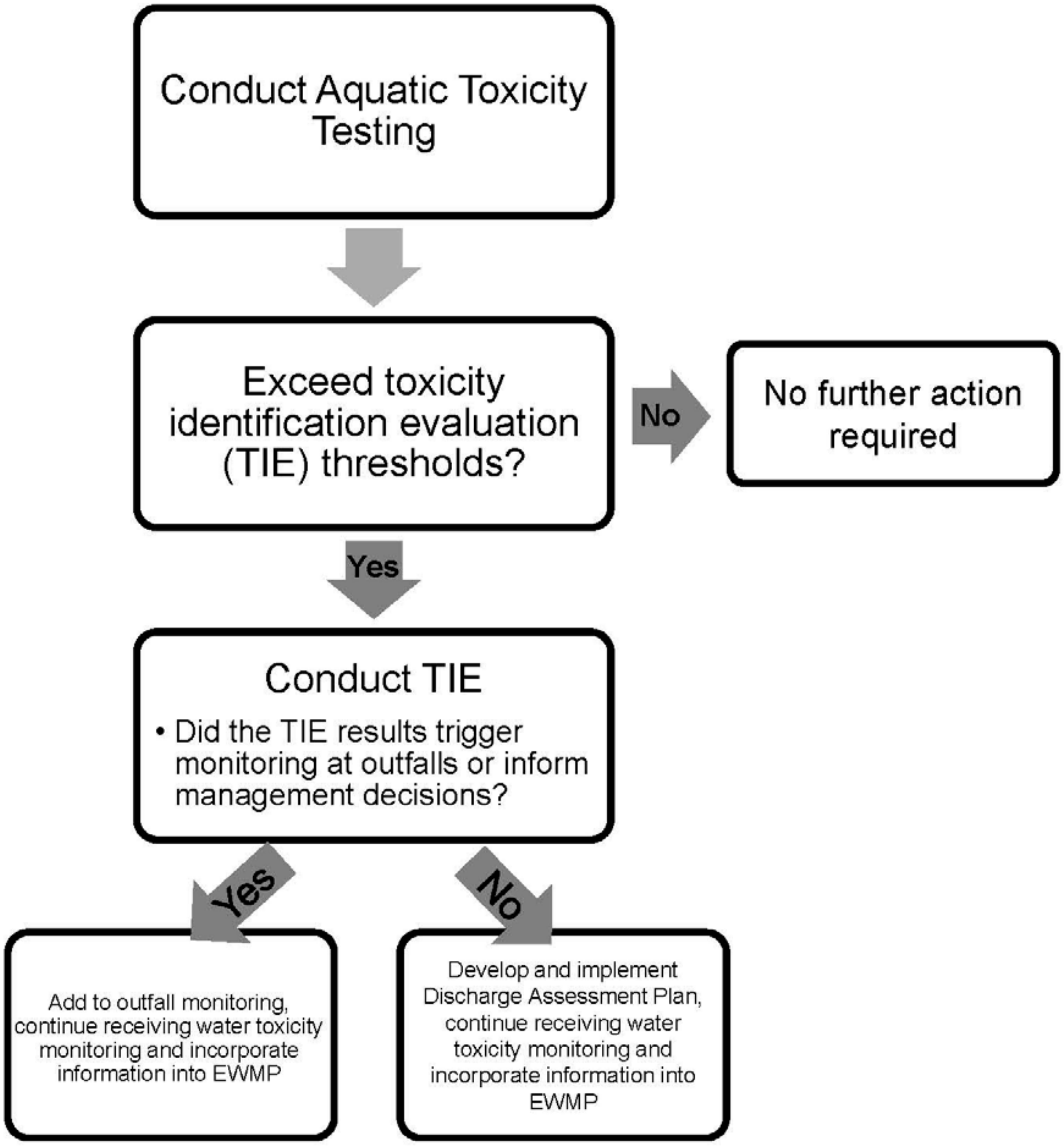


Figure C-1. Generalized Aquatic Toxicity Assessment Process

2.3.1 Sensitive Species Selection

The MRP (page E-32) states that a sensitivity screening to select the most sensitive test species should be conducted unless "a sensitive test species has already been determined, or if there is prior knowledge of potential toxicant(s) and a test species is sensitive to such toxicant(s), then monitoring shall be conducted using only that test species." Previous relevant studies conducted in the watershed should be considered. Such studies may have been completed via previous MS4 sampling, wastewater NPDES sampling, or special studies conducted within the watershed. The following sub-sections discuss the species selection process for assessing aquatic toxicity in receiving waters.

2.3.1.1 Freshwater Sensitive Species Selection

As described in the MRP (page E-31), if samples are collected in receiving waters with salinity less than 1 part per thousand (ppt), or from outfalls discharging to receiving waters with salinity less than 1 ppt, toxicity tests should be conducted on the most sensitive test species in accordance with species and short-term test methods in Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms (EPA/821/R-02/013, 2002; Table IA, 40 CFR Part 136). Static renewal freshwater toxicity test species identified in the MRP are:

- Fathead minnow, *Pimephales promelas* (Larval Survival and Growth Test Method 1000.04).
- Daphnid, *Ceriodaphnia dubia* (Survival and Reproduction Test Method 1002.05).
- Green alga, *Selenastrum capricornutum* (*Raphidocelis subcapitata*) (Growth Test 1003.0).

Low salinity (fresh) receiving water toxicity testing data from within the Peninsula CIMP Area were not identified during CIMP preparation. Toxicity data from the Dominguez Channel and other regional receiving waters, suggest that organophosphate pesticides, pyrethroids, and metals may contribute to aquatic toxicity. Assuming the potential presence of these toxicants in the WMG area, relative sensitivity to these pollutants was a primary consideration in selecting from among the three common test species.

Ceriodaphnia dubia (*C. dubia*) is often used locally and reported upon nationally, as a broad spectrum test species that is sensitive for historical and current use pesticides and metals, and studies indicate that it is more sensitive to the toxicants of concern than *Pimephales promelas* (*P. promelas*) or *Selenastrum capricornutum* (*S. capricornutum*). In *Aquatic Life Ambient Freshwater Quality Criteria - Copper*, the USEPA reports greater sensitivity of *C. dubia* to copper (species mean acute value of 5.93 µg/l) than for *P. promelas* (species mean acute value of 69.93 µg/l; EPA, 2007). *C. dubia*'s relative sensitivity to copper extends to multiple metals. Additionally, researchers at the University of California (UC), Davis reviewed available reported species sensitivity values in developing pesticide criteria for the Central Valley Regional Water Quality Control Board. In developing pesticide criteria for the Central Valley Regional Water Quality Control Board, researchers at University of California at Davis, reported higher sensitivity of *C. dubia* to diazinon and bifenthrin (species mean acute value of 0.34 µg/l and 0.105 µg/l) compared to *P. promelas* (species mean acute value of 7804 µg/l and 0.405 µg/l; Palumbo et al., 2010a,b). Additionally, in a stormwater study for the City of Stockton, urban stormwater runoff found acute and chronic toxicity to *C. dubia*, with no toxicity to *S. capricornutum* or *P. promelas* (Lee and Lee, 2001). The toxicity was attributed to organophosphate pesticides, indicating a higher sensitivity of *C. dubia* compared to *S. capricornutum* or *P. promelas*. While *P. promelas* is generally less sensitive to metals and pesticides, this species can be more sensitive to ammonia than *C. dubia*. However, as ammonia is not typically a constituent of concern for urban runoff and ammonia is not consistently observed above the toxic thresholds in the watershed, *P. promelas* is not considered a particularly sensitive species for evaluating the impacts of urban runoff in receiving waters in the watershed.

S. capricornutum is a species sensitive to herbicides; however, while sometimes present in urban runoff, herbicides are not identified as a potential toxicant in the watershed. Additionally, *S. capricornutum* is not considered the most sensitive species as it is not sensitive to pyrethroids or organophosphate pesticides and is not as sensitive to metals as *C. dubia*. Additionally, the *S. capricornutum* growth test can be affected by high concentrations of suspended and dissolved solids, color, and pH extremes, which can interfere with the determination of sample toxicity. As a result, it is common to manipulate the sample by centrifugation and filtration to remove solids in order to conduct the toxicity test; however, this process may affect the toxicity of the sample. In a study of urban highway stormwater runoff (Kayhanian et. al, 2008), *S. capricornutum* response to the stormwater samples was more variable than the *C. dubia* and the *P. promelas* and in some cases the algal growth was possibly enhanced due to the presence of stimulatory nutrients. Also, in a study on the City of Stockton urban stormwater runoff (Lee and Lee, 2001) the *S. capricornutum* tests rarely detected toxicity where the *C. dubia* and the *P. promelas* regularly detected toxicity.

Based on best professional judgment and local experience with the Permit-identified freshwater species, *C. dubia* is most sensitive to the broadest range of potential toxicant(s) typically found in local fresh receiving waters impacted by urban runoff and will be selected for freshwater toxicity testing by the Peninsula CIMP Group. The species can be maintained in laboratory cultures making them generally available year round. The simplicity of the test, the ease of interpreting results, and relatively small sample volume necessary to run the test, make the test a valuable screening tool. The ease of sample collection and higher sensitivity will support assessing the presence of ambient receiving water toxicity or long term effects of toxic stormwater over time. As such, toxicity testing in the freshwater portions of the watershed will be conducted using *C. dubia*. However, *C. dubia* test organisms are typically cultured in moderately hard waters (80-100 mg/L $CaCO_3$) and can have increased sensitivity to elevated water hardness greater than 400 mg/L $CaCO_3$), which is beyond their typical habitat range. Because of this, in instances where hardness in site waters exceeds 400 mg/L ($CaCO_3$), an alternative test species may be used. Daphnia magna is more tolerant to high hardness levels and is a suitable substitution for *C. dubia* in these instances (Cowgill and Milazzo, 1990).

2.3.1.2 Saltwater Sensitive Species Selection

Samples collected in receiving waters with salinity equal to or greater than 1 ppt or from outfalls discharging to receiving waters with salinity that is equal to or greater than 1 ppt, should be tested using the most sensitive test species in accordance with *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms (EPA/600/R-95/136, 1995)*. The marine and estuarine test species identified in the MRP are:

- A static renewal toxicity test with the topsmelt, *Atherinops affinis* (Larval Survival and Growth Test Method 1006.015).
- A static non-renewal toxicity test with the purple sea urchin, *Strongylocentrotus purpuratus* (Fertilization Test Method 1008.0).
- A static non-renewal toxicity test with the giant kelp, *Macrocystis pyrifera* (Germination and Growth Test Method 1009.0).

In addition to the three species identified in the MRP, the red abalone, *Haliotis rufescens* (*H. rufescens*), larval development test was also considered given its extensive use in the region.

Although all the species mentioned have been demonstrated as sensitive to a wide variety of toxicants and have been subject to numerous inter- and intra-laboratory testing using standardized toxicants, two species: *Macrocystis pyrifera* (*M. pyrifera*) and *Atherinops affinis* (*A. affinis*); have limitations when used to assess the toxicity of stormwater, as compared to the sea urchin fertilization test and the red abalone larval development test.

The method for *M. pyrifera* is a 48-hour chronic toxicity test that measures the percent zoospore germination and the length of the gametophyte germ tube. Although the test may be sensitive to herbicides, fungicides, and treatment plant effluent, the use of *M. pyrifera* as a test species for stormwater monitoring may not be ideal. Obtaining sporophylls for stormwater testing could also be a limiting factor for selecting this test. Collection of *M. pyrifera sporophylls* from the field is necessary prior to initiating the test and the target holding time for any receiving water or stormwater sample is 36 hours; however, 72 hours is the maximum time a sample may be held prior to test initiation. During the dry season, meeting the 36-72 hour holding time will be achievable; however, field collection during wet weather may be delayed beyond the maximum holding time due to heavy seas and inaccessible collection sites. In addition, collection of *M.*

pyrifera sporophylls during the storm season may include increased safety risks that can be avoided by selection of a different species.

The *A. affinis* test measures the survival and growth test of a larval fish over seven days. At the end of seven days of exposure to a suspected toxicant, the number of surviving fish are recorded, along with their weights, and compared to those exposed to non-contaminated seawater. Positive characteristics of the *A. affiniss* chronic test include the ability to purchase test organisms from commercial suppliers as well as being one of the few indigenous test species that may be used to test undiluted stormwater by the addition of artificial sea salts to within the range of marine receiving waters. Unfortunately, the tolerance of *A. affinis* to chemicals in artificial sea salts may also explain their lack of sensitivity to changes in water quality compared to other test organisms such as the sea urchin or red abalone. There are concerns with the comparability of conducting a seven-day exposure test when most rain events do not occur over a seven-day period.

The *Strongylocentrotus purpuratus* (*S. purpuratus*) fertilization test measures the ability of *S. purpuratus* sperm to fertilize an egg when exposed to a suspected toxicant. The *S. purpuratus* fertilization has been selected as a chronic toxicity test organism in previous MS4 permits and has been used to assess ambient receiving water toxicity, sediment pore water toxicity, as well as stormwater toxicity. The *S. purpuratus* fertilization test is also among the most sensitive test species to metals. The adult test organisms may be purchased and held in the lab prior to fertilization, and the sample volume necessary to conduct the test is small with respect to the other suggested tests. The minimal exposure period (20 min) allows for a large number of tests to be conducted over a short period of time and permits the testing of toxicants that may lose their potency over long periods of time.

The red abalone larval development test measures the percent of abnormal shell development in larvae exposed to toxic samples for 48 hours. The red abalone is commonly used to test treatment plant effluent, but has had limited use in stormwater compared to the *S. purpuratus* fertilization test. The advantages of the red abalone test include a sensitive endpoint, the ability to purchase abalone from commercial suppliers and hold test organisms prior to spawning, and low variability in results compared to other species (e.g., *S. purpuratus* fertilization test). Thus, though not listed as a potential test species for use in stormwater monitoring in the Permit, it was considered as a potentially sensitive species for the purposes of selecting the most sensitive species.

Due to the limitations of the giant kelp germination and growth test and the topsmelt survival and growth test, in addition to not being particularly sensitive to the constituents identified as problematic in stormwater water runoff from the watershed, these tests are not considered particularly helpful in supporting the identification of pollutants of concern. Based on the sensitivity, smaller test volume requirements, their ability to be housed in the lab prior to testing, and shorter exposure times, the *S. purpuratus* fertilization test and the red abalone development test will be considered during sensitive species selection to measure toxicity in marine and estuarine environments. Based on historical data of the sensitivity of the *S. purpuratus* and red abalone tests, and the limiting factors associated with the topsmelt and giant kelp tests, the sensitive species test for marine and estuarine species will be conducted with the *S. purpuratus* and red abalone tests. Species screening was determined to be appropriate for these two species (as opposed to selecting just one) as testing conducted within the region with both species have shown varying sensitivity. Thus, it is appropriate to test both to determine sensitivity at a given site. After the screening testing is completed, monitoring will be conducted with the most-sensitive species.

2.3.2 Testing Period

The following subsections characterize the toxicity testing periods for samples collected during dry and wet weather conditions.

2.3.2.1 Freshwater Testing Periods

Acute toxicity tests would normally be utilized for stormwater toxicity testing to be consistent with the relatively shorter exposure periods of watershed species to potential urban stormwater toxicants and would be conducted in accordance with Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms (EPA, 2002b). Despite the test duration not being typical of stormwater flows, Board staff has recommended that a chronic testing period (typically 7 days) be used for toxicity testing for both survival and reproductive/growth endpoints for *C. dubia* in samples. Chronic testing will be conducted on undiluted samples in accordance with Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms (USEPA, 2002a). Utilization of chronic tests to assess wet weather samples may generate results that are not representative of receiving water conditions.

2.3.2.2 Saltwater Testing Period

Two marine and estuarine toxicity species tests utilize methods that have short durations (20 minutes for the *S. purpuratus* fertilization test and 48 hours for the *H. rufescens* development test), the end points are sub-lethal and can be considered representative of acute or chronic effects. Both test species and test methods are suitable for wet weather and dry weather monitoring.

2.3.3 Toxicity Endpoint Assessment and Toxicity Identification Evaluation Triggers

As directed by the Permit MRP, acute and chronic toxicity test endpoints will be analyzed using the Test of Significant Toxicity (TST) t-test approach specified by the USEPA (USEPA, 2010). The Permit specifies that the chronic in-stream waste concentration (IWC) be set at 100%

receiving water for receiving water samples and 100% discharge for outfall samples. Follow-up triggers are generally based on the Permit specified statistical assessment as described below.

For acute *C. dubia* toxicity testing, follow up toxicity identification evaluation (TIE) testing is warranted if a statistically significant 50% difference in mortality is observed between the sample and laboratory control, a toxicity identification evaluation (TIE) will be performed. TIE procedures are further discussed in detail in the following subsection. Experience conducting TIEs in regional receiving waters supports using a 50% mortality trigger to provide a reasonable opportunity for a successful TIE. During 2003 and 2004 TMDL monitoring in the Calleguas Creek Watershed (CCW), TIEs were initiated for samples exceeding the 50% threshold, the majority of which displayed 100% mortality. In that study, toxicity had degraded in approximately 40% of the samples on which the procedures were initiated making the effort unsuccessful in pinpointing specific toxicants. The Regional Board approved monitoring program for the CCW Toxicity, Chlorpyrifos and Diazinon TMDL utilizes a 50% threshold for TIE initiation. Additionally, a 50% mortality threshold is utilized in the Ventura County MS4 Permit.

For chronic *C. dubia* toxicity testing, if a statistically significant 50% difference in mortality is observed between the sample and laboratory control, a TIE will be performed. If a statistically significant 50% difference in a sub-lethal endpoint is observed between the sample and laboratory control, a confirmatory sample will be collected from the receiving water within two weeks of obtaining the results of the initial sample. If a statistically significant 50% difference in mortality or sub-lethal endpoint is observed between the sample and laboratory control on the confirmatory sample, a TIE will be performed.

For the chronic marine and estuarine tests, the percent effect will be calculated. The percent effect is defined as the difference between the mean control response and the mean IWC response divided by the control response, multiplied by 100. A TIE will be performed if the percent effect value is equal to or greater than 50 percent. The TIE procedures will be initiated as soon as possible after the toxicity trigger threshold is observed to reduce the potential for loss of toxicity during sample storage. If the cause of toxicity is readily apparent or is caused by pathogen related mortality (PRM) or epibiont interference, the result will be rejected. In cases where significant endpoint toxicity effects greater than 50% are observed in the original sample, but the follow-up TIE positive control “signal” is not statistically significant, the cause of toxicity will be considered non-persistent and no sample follow-up testing is required. Future test results should be evaluated to determine if parallel TIE treatments are necessary to provide an opportunity to identify the cause of toxicity.

2.3.4 Toxicity Identification Evaluation Approach

The results of toxicity testing will be used to trigger further investigations to determine the cause of observed laboratory toxicity. The primary purpose of conducting TIEs is to support the identification of management actions that will remove toxicants from the receiving waters. Successful TIEs will guide adaptive outfall monitoring strategies to identify and analyze for suspect pollutant(s) and guide source control efforts.

The TIE approach is divided into three phases as described in USEPA's 1991 Methods for Aquatic Toxicity Identification Evaluations – Phase I Toxicity Characterization Procedures – Second Edition (EPA/600/6-9/003) and briefly summarized as follows:

- Phase I utilizes methods to characterize the physical/chemical nature of the constituents which cause toxicity. Such characteristics as solubility, volatility and filterability are determined without specifically identifying the toxicants. Phase I results are intended as a first step in specifically identifying the toxicants but the data generated can also be used to develop treatment methods that remove the toxicity without specifically identifying the toxicants.
- Phase II utilizes methods to specifically identify toxicants, or toxicant pollutant class.
- Phase III utilizes methods to confirm the identity of suspected toxicant(s).

TIE methods will generally adhere to USEPA procedures documented in conducting TIEs (USEPA, 1991, 1992, 1993a-b). A Phase I TIE will be conducted on samples that exceed the TIE. Water quality data will be reviewed to support future evaluation of potential toxicants. TIEs will perform the manipulations described in Table C-2.

Toxicity causation will be tentatively identified based on the treatments in Table C-2 and, when possible, the results verified based on water column chemistry analyses. After an initial determination of the cause of toxicity, the information may be used during future TIEs to target the expected toxicant(s) or provide new treatments to narrowly identify the toxicant cause(s). Moreover, if the toxicant or toxicant class is not initially identified, toxicity monitoring during subsequent events will confirm if the toxicant is persistent or a short-term episodic occurrence.

Table C-2 Aquatic Toxicity Identification Evaluation (TIE) Sample Manipulations

TIE Sample Manipulation	Expected Response
Adjust to between pH 7 and 8.5	Alters toxicity in pH sensitive compounds (i.e., ammonia and some trace metals)
Filtration or centrifugation	Removes particulates and associated toxicants
Ethylene Diamine Tetra Acetic Acid (EDTA)	Chelates trace metals, particularly divalent cationic metals
Sodium thiosulfate (STS) addition	Reduces toxicants attributable to oxidants (i.e., chlorine) and some trace metals
Piperonyl Butoxide (PBO)	Reduces toxicity from organophosphate pesticides such as diazinon, chlorpyrifos and malathion, and enhances pyrethroid toxicity
Carboxylesterase addition(1)	Hydrolyzes pyrethroids
Solid Phase Extraction (SPE) with C18 column	Removes non-polar organics (including pesticides) and some relatively non-polar metal chelates
Sequential Solvent Extraction of C18 column	Further resolution of SPE-extracted compounds for chemical analyses
No Manipulation	Baseline test for comparing the relative effectiveness of other manipulations

Carboxylesterase addition has been used in recent studies to help identify pyrethroid-associated toxicity (Wheelock et al., 2004; Weston and Amweg, 2007). However, this treatment is experimental in nature and should be used along with other pyrethroid-targeted TIE treatments (e.g., PBO addition).

As the primary goals of conducting TIEs is to identify pollutants for incorporation into outfall monitoring, narrowing the list of toxicants following Phase I TIEs via Phase II or III TIEs is not necessary if the toxicant class determined during the Phase I TIE is sufficient for: (1) identifying additional pollutants for outfall monitoring; and/or (2) identifying control measures. Thus, if the specific pollutant(s) or the analytical class of pollutant (e.g., metals that are analyzed via USEPA Method 200.8) are identified then sufficient information is available to inform the addition of pollutants to outfall monitoring.

Phase II TIEs may be utilized to identify specific toxicants in a sample if information beyond that gained via the Phase I TIE and review of chemistry data is needed to identify monitoring or management actions. Phase III TIEs will be conducted following any Phase II TIEs.

TIEs will be considered inconclusive if:

- The toxicity is persistent (i.e., observed in the positive control), and
- The cause of toxicity cannot be attributed to a class of constituents (e.g., insecticides, metals, etc.) that can be targeted for monitoring or additional source controls.

If (1) a combination of causes act in a synergistic or additive manner are identified; (2) the toxicity can be removed with a treatment or combination of the TIE treatments; or (3) the analysis of water quality data collected during the same event identifies the pollutant or analytical class of pollutants, the result of a TIE is considered conclusive.

Note that the MRP (page E-33) allows a TIE Prioritization Metric to be used in ranking sites for TIEs. As the extent to which TIEs will be conducted is unknown, prioritization cannot be assessed at this time, but may be utilized in the future based on the results of toxicity monitoring and the CIMP adaptive management.

2.3.5 Discharge Assessment

The Peninsula CIMP Group will prepare a Discharge Assessment Plan (DAP), if TIEs, from consecutive sampling events, are inconclusive. The Discharge Assessment will only be initiated after consecutive inconclusive TIEs, because of the inherent variability associated with the toxicity and TIE testing methods. The DAP will consider observed receiving and outfall toxicants above known species effect levels and the relevant exposure periods compared to the duration of the observed toxicity. The DAP will identify:

- Additional potential receiving water toxicity monitoring to evaluate the spatial extent of toxicity.
- The toxicity test species to be utilized. If a different species is proposed, justification for the substitution will be provided.
- The number and location of monitoring sites and their spatial relation to the observed receiving water toxicity.
- The number of monitoring events that will be conducted, a schedule for conducting the monitoring, and a process for evaluating the completion of the assessment monitoring.

The DAP will be submitted to Regional Board staff for comment within 60 days of receipt of notification of the second consecutive inconclusive result. If no comments are received within 30 days, it will be assumed that the approach is appropriate for the given situation and the DAP will be implemented within 90-days of submittal. If comments are received within 30 days, the Plan will be resubmitted to Regional Board staff and the DAP will be implemented within 90-days of submittal of a version of the Plan that does not receive comments from Regional Board staff.

2.3.6 Follow Up on Toxicity Testing Results

The MRP (page E-33) indicates the following actions should be taken when a toxicant or class of toxicants is identified through a TIE:

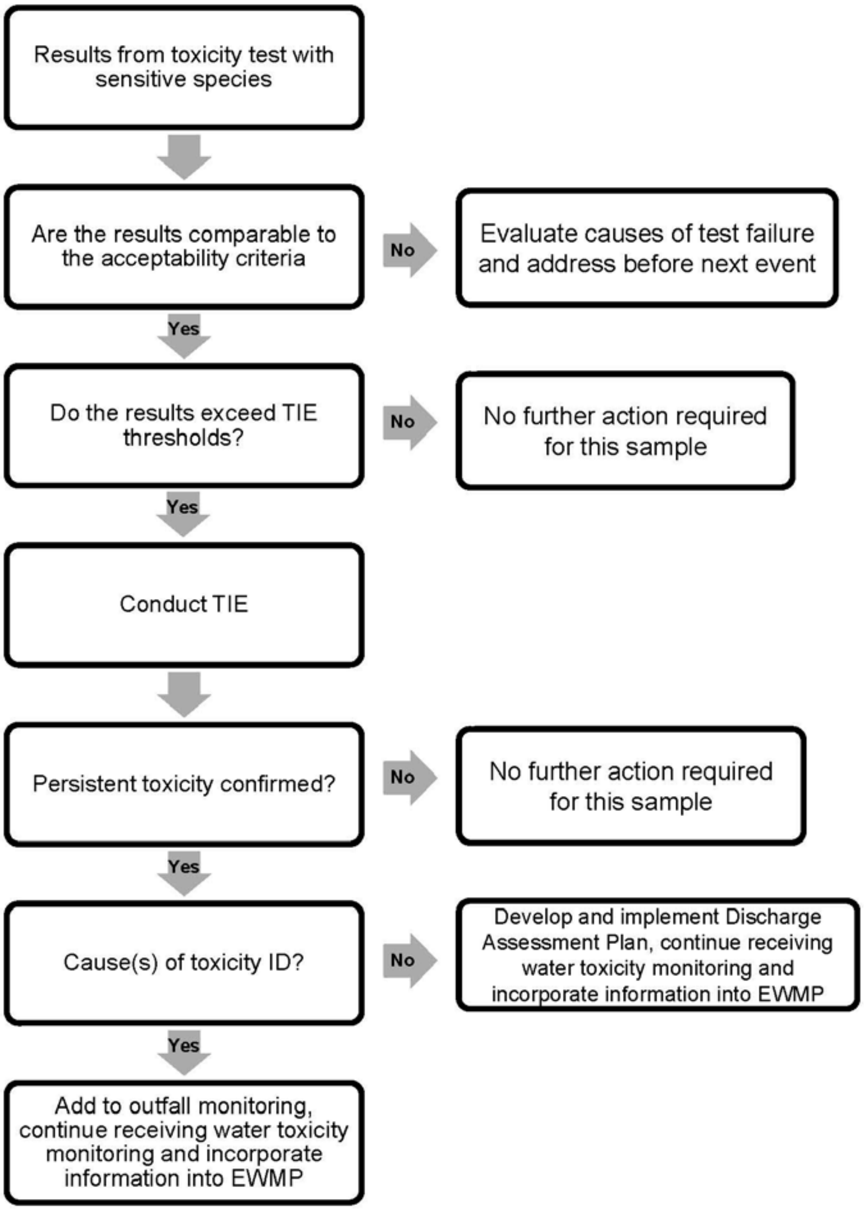
- The Peninsula CIMP Group shall analyze for the toxicant(s) during the next scheduled sampling event in the discharge from the outfall(s) upstream of the receiving water location.
- If the toxicant is present in the discharge from the outfall at levels above the applicable receiving water limitation, a toxicity reduction evaluation (TRE) will be performed for that toxicant.
- The list of constituents monitored at outfalls identified in the CIMP will be modified based on the results of the TIEs.

Monitoring for constituents identified based on the results of a TIE will occur as soon as feasible following the completion of a successful TIE (i.e., the next monitoring event that is at least 45 days following the toxicity laboratory's report transmitting the results of a successful TIE).

The requirements of the TREs will be met as part of the adaptive management process in the Peninsula EWMP rather than conducted via the CIMP. The identification and implementation of control measures to address the causes of toxicity are tied to management of the stormwater program, not the CIMP. It is expected that the requirements of TREs will only be conducted for toxicants that are not already addressed by an existing Permit requirement (i.e., TMDLs) or existing or planned management actions.

2.3.7 Summary of Aquatic Toxicity Monitoring

The approach to conducting aquatic toxicity monitoring as described in the previous sections is summarized in detail in Figure C-2. The intent of the approach is to identify the cause of toxicity observed in receiving water to the extent possible with the toxicity testing tools available, thereby directing outfall monitoring for the pollutants causing toxicity with the ultimate goal of supporting the development and implementation of management actions.



Test failure includes pathogen or epibont interference, which should be addressed prior to the next toxicity sampling event.

For freshwater, the TIE threshold is equal to or greater than 50% (≥50%) mortality in an acute (wet weather) or chronic (dry weather) test. If a ≥50% effect in a sub-lethal endpoint for chronic test is observed during dry weather, a follow up sample will be collected within two weeks of the completion of the initial sample collection. If the follow up sample exhibits a ≥50% effect, a TIE will be initiated.

For marine waters and estuarine waters, the TIE threshold is the percent effect value ≥50%. If a ≥50% or greater effect is observed during dry weather a follow up sample will be collected within two weeks of the initial sample collection and if the follow up sample exhibits a ≥50% effect, a TIE will be initiated.

The goal of conducting Phase I TIEs is to identify the cause of toxicity so that outfall monitoring can incorporate the toxicant(s) into the list of constituents monitored during outfall monitoring. Thus, if specific toxicant(s) or the analytical class of toxicants (i.e., metals that are analyzed via EPA Method 200.8) are identified, sufficient information is available to inform the addition of pollutants to the list of pollutants monitored during outfall monitoring.

Figure C-2. Detailed Aquatic Toxicity Assessment Process

2.3.8 List of Laboratories Conducting Analysis

The chosen laboratories will be able to meet the measurement quality objectives set forth in the CIMP. Laboratories will meet California Environmental Laboratory Accreditation Program (ELAP) and/or National Environmental Laboratory Accreditation Program (NELAP) certifications and any data quality requirements specified in this document. Due to contracting procedures and solicitation requirements, qualified laboratories have not yet been selected to carry out the analytical responsibilities described in this CIMP. Selected laboratories will be listed, per the example shown in Table C-3, along with lab certification information. Following the completion of the first monitoring year, the pertinent laboratory specific information will be included in the Integrated Monitoring Compliance Report Section of the Annual Report. At the end of each subsequent monitoring year, the Peninsula CIMP Group will assess the laboratories performance and at that time a new laboratory may be chosen.

Table C-3 Summary of Laboratories Conducting Analysis for the Peninsula CIMP

Laboratory(1)	**General Category of Analysis**	**Lab Certification No. & Expiration Date(2)**

Information for all laboratories will be added to this table following their selection and upon CIMP update.
Lab certifications are renewed on an annual basis.

2.3.8.1 Alternate Laboratories

In the event that the laboratories selected to perform analyses for the CIMP are unable to fulfill data quality requirements outlined herein (e.g., due to instrument malfunction), alternate laboratories will be selected to meet the same requirements that the primary labs have met. The original laboratory selected may recommend a qualified laboratory to act as a substitute. However, the final decision regarding alternate laboratory selection rests with the Peninsula CIMP Group.

2.4 Safety Considerations

Stormwater monitoring activities create hazardous conditions and safety is a primary concern. Prior to the commencement of field monitoring activities, a project Health and Safety Plan should be developed. The information in this SOP should be used as general guidance for developing a Health and Safety Plan for field activities.

General hazardous conditions associated with sampling include:

- Hazardous weather conditions (e.g., wind, lightning, flooding, etc.)
- Hazards associated with chemicals
- Biological hazards (e.g., rodents and snakes)
- Physical hazards (e.g., traffic, falling objects, sharp edges, slippery footing, and the potential for lifting injuries from opening or removing access panels and manhole covers, etc.)
- The CIMP monitoring program does not require sampling in confined spaces (e.g., manholes). If this were the case, the sampling team would need to be trained in and follow confined spaced entry procedures.

Preparation and training of all sampling personnel will be completed before beginning any sampling task. Extreme care will be taken to allow for safety precautions including proper equipment and appropriate operational techniques, sufficient time to accomplish the task, training on potential hazards, and emergency procedures. Sampling crews will consist of a minimum of three people.

If for any reason manual sample collection appears to be unsafe, samples will not be collected. If possible, samples will be collected at a later time when conditions are safe. A throw rope will be easily accessible in each truck cab and at the ready during manual sample collection if conditions warrant.

Basic emergency precautions include having access to both local emergency phone numbers and communication equipment (i.e., smart phones/cellular phones) and ensuring that personnel are trained in first aid and carry first aid equipment.

2.4.1 Hazardous Weather Conditions

Common sense should dictate whether sampling should be conducted during adverse weather conditions. No sampling personnel should place themselves in danger during high winds, lightning storms, or flooding conditions which might be unsafe. Under extreme conditions, a less hazardous storm event should be sampled.

2.4.2 Chemical Hazards

Sampling personnel can also be at risk of exposure to hazardous chemicals-either chemicals in the actual stormwater discharge or the preservatives in some of the sample containers. Therefore, direct contact with the bottle preservatives and the stormwater (if hazardous chemicals are suspected to be present; pathogens which are biological hazards are also likely present in stormwater) should be avoided. Sampling personnel should wear gloves and safety glasses to avoid skin and eye exposure to harmful chemicals. Sampling personnel should be trained to avoid exposure and instructed as to what to do if exposure occurs (e.g., flush the eyes, rinse the skin, ventilate the area, etc.).

Sampling personnel should keep Safety Data Sheets (SDS) (formerly Material Safety data Sheets) readily available for all solutions used for field measurements and refer to them to ensure that pH buffers or other chemicals are handled safely.

2.4.3 Biological Hazards

Stormwater sampling personnel may also encounter biological hazards such as rodents, snakes, and insects. The sampling crew should remain alert to these hazards. Monitoring supplies for certain locations should include insect repellant and a first aid kit.

2.4.4 Physical Hazards

The sampling crew should be aware of a number of physical hazards that could cause accidents at the sampling site. These hazards include traffic hazards, sharp edges, falling objects, slippery footing, and lifting injuries from removing manhole covers. Sampling personnel should pay close attention in order to prevent these safety hazards at all times.

If the monitoring activity encroaches on the public right of way, traffic cones, warning signs, and barricades should be placed in appropriate places around the monitoring activities. Sampling personnel should wear a reflective safety vest in high-traffic areas.

Working in and around water bodies carries the inherent risk of drowning. Life jackets should be worn when sampling in more than a few feet of water, or when sampling in swift currents.

2.5 Water Quality Sampling Procedures

The methods summarized below are for the collection and recording of samples needed to assess water quality parameters. This includes manual composite and grab sampling techniques that include using a depth integrated sampler or an intermediate sample container attached to a pole. Alternatively, composite sample aliquots may be collected manually using a peristaltic pump or portable autosampler.

Field measurements will be made for parameters that have the potential to change in transit between the monitoring location and analytical laboratory. Detailed notes of all activities conducted in the field will be kept in a site specific field logbook for eventual electronic database entry and reporting purposes. All records made in the field and reported by the analytical laboratory will follow the proper sample identification protocol and will be consistent with the chain of custody form.

2.5.1 Outfall Composite Sample Aliquots

Wet weather outfall samples, when feasible, will be collected before the associated receiving water sample is collected, at locations where paired outfall and receiving water locations exist.

For inaccessible sample locations, a Nasco swing sampler equipped with a borosilicate glass or Teflon bottle (or similar equipment) will be used to collect 10 time-weighted aliquots. Refer to Section 2.1 for a discussion of time-weighted composite sample aliquot collection times. Sample aliquots will be collected from the middle of the outfall flow, to the extent feasible. The same procedures for grab sample collection as stated in Section 2.5.2 for receiving water sampling will be conducted for the outfall sampling. Aliquots may be composited in the field by the sample personnel, or may be delivered individually to the laboratory for lab compositing.

2.5.2 Receiving Water and Outfall Grab Samples

Receiving water sampling will be conducted after the outfall sampling is performed, where paired outfall and receiving water locations exist, as feasible. At Peninsula-RW1 and Peninsula-RW2, grab samples will be collected from a boat in accordance with City of Los Angeles Environmental Monitoring Division (EMD) standard operating procedures.

Outfall grab samples will be collected upon arrival at approximately the same time as when the field measurements are performed, as feasible. Outfall grab samples will be collected directly into sample bottles, where feasible, or using equipment equivalent to that used for stormwater outfall monitoring (see Section 2.5.1).

All dry weather outfall sampling will be conducted using grab samples due to the unknown frequency and duration of flows. For stormwater outfall sampling, grab samples will be collected for the following parameters:

- Oil and grease
- TPH
- Total phenols
- Bacteria
- Other VOCs

These samples should be collected directly in the sample bottles that will be provided to the analytical lab (i.e., a transfer bottle should not be used). Where practical, samples collected by direct submersion will be collected mid-channel/outfall. The bottles should therefore not contain preservatives that could be lost when immersing the bottle in the receiving water; therefore the sample bottles will be preserved immediately upon arrival at the laboratory.

Grab sample containers designated for volatile organic compound analysis will have zero headspace.

2.5.3 Receiving Water and Outfall Field Measurements

Field measurements are to be performed for pH, dissolved oxygen, temperature, and specific conductivity. If the field instrumentation malfunctions these parameters should be analyzed at the analytical laboratory; however there will be holding time issue that could affect data quality. For example, the holding time for pH analysis is 15 minutes, which is why pH should be measured in the field. Field measurements will be performed upon arrival, as feasible.

Field measurements will be performed as follows:

- Perform field measurements at the same time the grab samples are collected.
- Water temperature and dissolved oxygen must be measured directly within the water body (in situ). pH and conductivity often are measured in situ but may also be measured in a subsample of a composite or grab sample.
- Make field measurements only with properly calibrated instruments**.** Calibration is required at the field site for many, but not all, instruments and depends on the technology employed by the instrument. Follow the manufacturer's instructions about instrument calibration.
- Review the instrument log book(s) before leaving for the field site to ensure that problems previously encountered have been resolved and that the appropriate instrument and site maintenance were performed.
- Backup instruments and batteries should be readily available and in good working condition.
- Allow at least 60 seconds (or follow the manufacturer's guidelines) for sensors to equilibrate with sample water. Record the median of the final three or more readings as the value to be reported for that measurement point.
- Check instrument precision and accuracy (variability and bias) periodically while at a field site; precision and accuracy may vary, depending on the instrument used, sampling conditions, and the expertise of personnel.

Detailed information about field instruments including required supplies, maintenance, calibration, measurement, and troubleshooting is available from the USGS National Field Manual for the Collection of Water-Quality. This information is included as Attachment C.1 of this SOP.

2.5.4 Field Logbook

All visits to the sampling stations should be recorded in the site-specific logbook (such as a Rite-in-the-Rain bound journal No. 390F). Logbook entries should include: names of personnel performing the sample collection and field measurements; date and time for all measurements recorded and sample aliquots/grabs collected, receiving water flow measurements; and tasks performed while on site. Field measurement information will be recorded in the field logbook including the date

The logbooks will be filled out with a blue or black indelible ballpoint pen. If recording in a Rite-in-the-Rain logbook or on other water-resistant surface, an all-weather or bullet pen should be used. Using a pencil is not acceptable. In addition, felt-tipped pens (for example, Sharpie®) should not be used as their use could compromise the quality of data for samples for analysis of volatile organic compounds.

2.5.5 Sample Identification Protocol

The sample identification naming convention for each wet and dry weather event will be as follows:

Table C-4. CIMP Monitoring Locations and Descriptions

Station ID	Sample Type	Location[6]	Location Coordinates		Sample Event ID
			Latitude	Longitude	
Peninsula-RW1	Receiving Water/Ocean	Malaga Cove	33.80339	-118.39919	Peninsula-RW1-DATE (MM-DD-YY)
Peninsula-SD1	Storm Drain	Malaga Creek	33.80092	-118.39100	Peninsula-SD1-DATE (MM-DD-YY)
Peninsula-RW2	Receiving Water/Ocean	Abalone Cove	33.73965	-118.38152	Peninsula-RW2-DATE (MM-DD-YY)
Peninsula-SD2	Storm Drain	McCarrell Canyon Creek	33.74123	-118.38799	Peninsula-SD2-DATE (MM-DD-YY)
RHE City Hall	Storm Drain	Adjacent to parking lot behind Rolling Hills Estates City Hall	34.03141	-118.84124	RHECH-DATE (MM-DD-YY)

In addition, field QA/QC samples including duplicate samples and field blank will be submitted to the laboratory "blind", which means these samples will be given fictitious IDs. For example, the field duplicate collected at Peninsula-RW1 could be named on the chain of custody form as "Peninsula-RW3-DATE".

2.5.6 Chain of Custody Procedures

All samples will be submitted to the analytical laboratories under proper chain of custody (COC) procedures. Sample custody must be traceable from the time of sample collection until results are reported. A sample is considered under custody if the sample is:

- In actual possession.

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[6] The receiving water and outfall monitoring locations are shown on Figure 3 of the CIMP, and descriptions of the monitoring locations are provided in Appendix B of the CIMP.

- In view after in physical possession.
- Placed in a secure area (accessible by or under the scrutiny of authorized personnel only after in possession).

The following special notes should be added to COC forms when applicable:

- Filter for all dissolved constituents immediately upon arrival at the laboratory (and properly preserve the sample).
- Identify the sample for MS/MSD analysis.
- Preserve samples for oil and grease and TPH immediately upon arrival at the laboratory (these bottles should not contain preservative which could be lost during the sampling process).

Example COCs provided by Weck and ABC laboratories are included in Attachment C.2.

2.6 Flow Estimation and Monitoring Methods

The Permit requires flow monitoring for receiving waters and monitoring or estimation for outfalls. Flow monitoring activities will be performed after the water quality samples are collected, to minimize the potential for sample contamination from wading and other water disturbance activities.

2.6.1 Outfalls

Depending on site conditions and safety, the appropriate field methodology for monitoring flow will be selected. The following list includes the recommended flow monitoring methods (in order of prioritization):

1. Continuous automated flow monitoring devices;
2. Portable area velocity flow meter; or
3. Recording the time required to fill a container of known volume.

If none of the aforementioned methodologies are suitable due to safety hazards or site conditions, the flow will be estimated for stormwater outfall monitoring events using drainage area, impervious cover, and precipitation data. Discharge from monitored outfalls will be characterized in accordance with EPA flow estimation procedures in the NPDES Storm Water Sampling Guidance Document (US EPA, 1992). The EWMP Group is responsible for developing accurate drainage area and runoff coefficient information for each monitored outfall.

The US EPA provides an example in which rain gauge data are used to approximate flow rate using a variation of the rational method to incorporate measured rainfall data (US EPA, 1992). The general form of this equation gives flow rate (Q) in terms of hourly rainfall intensity (i), drainage area (A), and runoff coefficient (C).

Classic Rational Method: $Q = C \times i \times A$

A simple example calculation is shown below for a drainage area less than 40 acres.

Site Characteristics:

Drainage Area (A): 31.5 Acres

Runoff Coefficient (C): 0.21 for low-density single family residential (per LA Hydrology Manual)

Rainfall Characteristics:

Total Rainfall Depth for Storm Event:	0.4 inches
Measured 15-minute Rainfall Intensity:	0.12 inches/15 minutes

$$Incremental\ Flow\ Rate\ (Q) = 0.21 \times \frac{0.12\ in}{15\ min} \times \frac{60\ min}{1\ \text{hr}} \times 31.5\ ac = 3.2\ cfs$$

The incremental flow rate will be calculated for each collected sample, based on the hourly rainfall intensity for the hour preceding the sample collection (e.g., a sample collected at 8:30 will rely on the hourly rainfall total recorded between 7:30 and 8:30).

Similarly, the runoff volume can be estimated using rainfall data. The following example uses the catchment and rainfall data to approximate discharge volume:

$$Total\ Runoff\ Volume = 0.21 \times 0.4\ in \times \frac{1\ ft}{12\ in} \times 31.5\ ac = 0.221\ ac\ ft$$

2.6.2 Receiving Waters

Flow monitoring of the receiving waters is not applicable for the ocean monitoring locations proposed herein.

3 NON-STORMWATER OUTFALL SCREENING

The non-stormwater outfall screening process and schedule is described in Section 4 of the CIMP. The field data sheet included in Attachment C.3 will be used to record data collected during non-stormwater outfall screening activities. These data will be entered into the CIMP Group's electronic inventory as described in the CIMP.

4 QUALITY ASSURANCE/QUALITY CONTROL

4.1 Clean Sampling Techniques

Due to the analytical practical quantitation limits required for certain parameters (e.g., trace metals, organics, and bacteria), and the potential for improper sampling techniques (including exposure from the ambient environment) to result in sample contamination at levels detectable by the analytical accuracy of the method, Clean Sampling Techniques will be used during the collection of samples. Moreover, because a sampling apparatus (e.g., swing sampler) may be used to collect composite sample aliquots for some of the monitoring program parameters, the sampling equipment will be properly cleaned by the laboratory (see Sections 4.5.3 and 4.5.4). Therefore, dedicated sampling equipment is required for each site. The sampling equipment will also be properly stored in between sample aliquot collection in accordance with Clean Sampling Techniques. In terms of handling sample containers, bottles will be handled following the "Clean Hands/Dirty Hands" procedure outlined below.

There are numerous routes by which samples may become contaminated. For example, potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs (dirt and dust from automobile exhaust, cigarette smoke, nearby roads, corroded or rusted bridges, wires, and poles). Even human contact can be a source of trace metals contamination (e.g., mercury amalgam fillings). The following materials have been found to contain trace metals and therefore should not be used to hold liquids that come in contact with the sample or must not contact the sample, unless these materials have been shown to be free of the metals of interest at the desired level:

- Pyrex
- Kimax,
- Methacrylate
- Polyvinylchloride
- Nylon,
- Vycor
- In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided.

All sampling equipment and sample containers used for metals determinations will be nonmetallic and free from any material that may contain metals. Sampling personnel are required to wear clean, non-talc gloves at all times when handling sampling equipment and sample containers. Personnel should avoid hand contact with contaminating surfaces (such as equipment, coins, food).

4.1.1 Clean Hands/Dirty Hands Procedures

Due to the logistics of manual composite sample collection, field procedures require a minimum of two field people assuming the “Dirty Hands” (DH1 and DH2) role. The second DH person can also assist with completing the necessary sample documentation (e.g., filling out the logbook and sample bottle labels).

Upon arrival at the sampling site, two members of the sampling team are designated as “Dirty Hands” (DH1) and “Clean Hands” (CH); if available, a third member is designated as DH2. All operations involving contact with the sample bottle are handled by CH. DH1 (and DH2, if available) is responsible for unsealing outer plastic bags and operating the sampling equipment (avoiding contact with the cleaned parts and the sample bottle for the DH-81 and the Swing Sampler bottle), and for all other activities that do not involve direct contact with the sample (e.g., opening coolers, calibrating field instruments).

The sampling team should ideally approach the site from down current and downwind to prevent contamination of the sample by particles sloughing off the equipment. If it is not possible to approach from both, the site should be approached from downwind.

Sampling personnel are to implement the following procedures “Clean Hands/Dirty Hands” procedures:

1. At the site, all sampling personnel must put on clean gloves before commencing sample collection activity.
2. “Dirty Hands" must open the cooler or storage container, remove the double-bagged sampling equipment from storage, and unzip the outer bag.
3. Next, "Clean Hands" opens the inside bag containing the portion of the DH-81 sampler in contract with the sample bottle, or the sample bottle for the Swing Sampler, removes the DH-81/bottles, and reseals the inside bag. "Dirty Hands" then reseals the outer bag.
4. "Clean Hands" unscrews the bottle cap and, while holding the cap upside down, discards the dilute acid solution from the bottle into a carboy for wastes.
5. “Dirty Hands” operates the DH-81 and Swing Sampler making sure to not come into contact with the laboratory-cleaned portions of the DH-81 or the sample bottles. Discard the first sample aliquot that is collected for each sampling round to generate the composite sample; begin filling the sample bottles with the second sample collected.
6. Collection of Non-Metallic Constituents: Dirty Hands unscrews the bottle caps for all containers except for the metals containers. Dirty Hands pours an aliquot from the DH-81 or Swing Sampler bottle into each sample container. Dirty Hands should not touch the DH-81 or Swing Sampler bottle (Clean Hands to provide assistance as needed).

7. Collection of Samples for Metals Analysis: Sample bottles designated for metals analysis are double-bagged at the analytical laboratory. Dirty Hands opens the outer bag. Clean Hands opens the inside bag and removes the sample bottle and uncaps the lid. Dirty Hands pours the sample aliquot into the metals bottle. Clean Hands screws the cap on the bottle and places the bottle back in the inner bag and seals the inner bad. Dirty Hands seals the outer bag. (Note that the sample label cannot contact the sample bottle and should be placed on the outer bag).
8. All parties should change gloves for the collection of each sample aliquot. Wearing multiple layers of gloves allows rapid glove changes.
9. If additional sample aliquots are required, rinse DH-81 bottle and Swing Sample bottle with the laboratory-provided deionized water and place back in the plastic double bag following CH/DH procedures.
10. If the sampler will not be reused during a field trip, rinse sampler components with laboratory-provided deionized water before they dry and place them into a plastic bag for transporting to the office laboratory to be cleaned for the next sampling event.

4.2 Quality Control Requirements for Field Measurements

Quality control requirements for field measurements are summarized below in Table C-5; these requirements are adapted from the State Water Boards' Surface Water Ambient Monitoring Program Requirements.

Table C-5. Field Measurement Quality Control Requirements

Parameter	Dissolved Oxygen	pH	Specific Conductance	Temperature
Analytical Method	Field measurement using approved method (i.e., membrane electrode method [SM 4500 O G] or equivalent)	Field measurement using approved method (i.e., electrometric [EPA 150.2], potentiometric [SM 4500 H B], or equivalent)	Field measurement using approved method (i.e., conductivity meter [EPA 120.1] or equivalent)	Field measurement using approved method (i.e., thermometer [SM 2550 B] or equivalent)
Units	mg/L	pH	µS/cm	°C
Resolution	0.01	0.01	1	0.1
Instrument Accuracy	±0.2	±0.2	±0.5%	±0.15
Points per Calibration	1	2	Per manufacturer	Per manufacturer
Pre-Sampling Calibration Check Frequency	Before every monitoring day on-site (re-calibrate if change of elevation is >500 m or barometric pressure > 2 mm Hg)	Per manufacturer	Per manufacturer	Per manufacturer

Parameter	Dissolved Oxygen	pH	Specific Conductance	Temperature
Post-Sampling Calibration Check Frequency	After every monitoring day (within 24 hours)	Per manufacturer	Per manufacturer	Per manufacturer
Allowable Drift	±0.5 or 10%	±0.2 units	±10%	±0.5

4.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

The monitoring program goal is to collect one MS/MSD per sampling event (the MS/MSD can be either an outfall or receiving water sample). Whether the MS/MSD analysis is feasible using a project sample depends on the feasibility of obtaining the additional sample volume required for the MS/MSD analysis (see Table 2-1).

If sufficient sample cannot be collected for the MS/MSD, the laboratory will use a non-project sample that is analyzed part of the analysis batch as the MS/MSD sample; MS/MSD results for a non-project sample will not be used in the QA/QC evaluation of project samples.

4.4 Field Duplicate

Field duplicates will be collected at a frequency of one duplicate per year for wet weather events and one duplicate per year for dry weather events (for a total of two field duplicates per year). For each time-weighted aliquot, the field duplicate will be collected immediately after all the original sample is collected. The field duplicate will be analyzed for all monitoring parameters required at the specific site selected. Field duplicates will be submitted to the laboratory as “blind” samples.

4.5 Field Equipment Blanks

Field equipment blanks will be collected at a frequency of once per year for the purposes of evaluating sample contamination from the monitoring equipment and procedures. One blank will be collected for the DH-81 assembly and one blank will be collected for the Swing Sampler. The field blank will consist of by filling a large carboy or other appropriate container with reagent water in the laboratory, transporting the filled container to the sampling site, processing the water through the normal sampling steps (e.g., immersing the DH-81 or Swing Sampler bottle in the carboy) including implementing CH/DH sampling protocols.

Field equipment blanks will only be analyzed for trace metals, PCBs and DDTs, and any other constituents detected at less than one order of magnitude above the analytical practical quantitation limit. Therefore, the field equipment blanks should be collected after the data from the first storm event sampled have been evaluated.

4.5.1 Trip Blank

Trip blanks are provided by the laboratory and should be placed in coolers containing samples designated for volatile organic compound analysis, which for the monitoring program are only MTBE and EPA 624 constituents.

4.5.2 Bottle Blanks

Bottle blanks will be performed at the analytical laboratory by analyzing reagent water poured into any cleaned transfer bottles (e.g., the swing sampler bottle). Bottle blanks will be performed by the laboratory once per year and analyzed for trace metals and PCBs/DDTs.

4.5.3 Sampling Equipment Cleaning Procedures

Whenever possible, sampling devices should be cleaned and prepared for field use in a class 100 clean room. The laboratory will implement the following steps for cleaning the US DH-81 sampler prior to each use:

1. Disassemble the DH-81 (making sure that the nozzle is unscrewed from the cap) and soak components in detergent solution for 30 minutes. Put on appropriate disposable, powderless gloves. Scrub components with a soft brush or sponge and rinse thoroughly. Change gloves.
2. Soak each nonmetallic component in a 5-percent trace-metal-grade HCl solution for 30 minutes, followed by copious rinsing with deionized water. Acid rinse only nonmetal parts **(**acid must not contact the metal collar on the DH-81 sampler). Change gloves.
3. That the DH-81 should not be rinsed with methanol because samples will be analyzed for total organic carbon (TOC) and use of methanol could result in false positive detections.
4. Reassemble the sampler. Place the sampler into double plastic bags and seal for storage and transport.

4.5.4 Laboratory Sample Bottle Cleaning Procedures

US DH-81 and Swing Sampler bottle cleaning will be performed following US EPA cleaning procedures for trace elements (USEPA, 1996a):

1. Fill a precleaned basin with a sufficient quantity of a 0.5% solution of liquid detergent (alkaline Detergent such as Liquinox, Alconox, or equivalent.), and completely immerse the bottle. Allow to soak in the detergent for at least 30 minutes.
2. Using a pair of clean gloves and clean nonmetallic brushes, thoroughly scrub down all materials with the detergent.

3. Place the scrubbed materials in a precleaned basin. Change gloves.
4. Thoroughly rinse the inside and outside of each piece with reagent water until there is no sign of detergent residue (e.g., until all soap bubbles disappear).
5. After soaking, use clean gloves and tongs to remove the bottle and thoroughly rinse with distilled, deionized water.
6. Change gloves and immerse the bottle in a hot (50-60°C) bath of 1 N trace metal grade HCl, and allow to soak for at least 48 hours. Then thoroughly rinse the bottle with reagent water.
7. Fill the bottle with a weak acid solution (0.1% (v/v) ultrapure HCl).
8. Double-bag the bottle in a polyethylene bag to prevent contamination of the surfaces with dust and dirt. Store at room temperature until sample collection.
9. Perform a bottle blank after the first bottle cleaning procedure of the year.

5 REFERENCES

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Attachment C.1: USGS protocols for Field Measurements (from National Field Manual for the Collection of Water-Quality)

Reference-Selected Chapters from:
National Field Manual for the Collection of Water-Quality Data
Techniques of Water-Resources Investigations
Book 9
Handbooks for Water-Resources Investigations
http://water.usgs.gov/owq/FieldManual/

TEMPERATURE 6.1

Revised by **Franceska D. Wilde**

Tables

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TEMPERATURE 6.1

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

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

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

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

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

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

6.1.1 EQUIPMENT AND SUPPLIES

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

Table 6.1–1. Equipment and supplies used for measuring temperature[1]
[–, minus; +, plus; °C, degrees Celsius; L, liter; µS/cm, microsiemens per centimeter at 25°C]

✓ Calibration thermometer, liquid-in-glass or electronic-thermistor thermometer, either National Institute of Standards and Technology (NIST) certified or manufacturer-certified as NIST traceable. Must carry certificate of NIST traceability; its use not allowed after expiration of certification.
  - Temperature range, at least –5 to +45°C
  - 0.1°C graduations (liquid-in-glass) or less

✓ Thermometer, liquid-in-glass sensor, nonmercury-filled for field use
  - Temperature range, at least –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 office-laboratory certified against a properly certified calibration thermometer (see above)

✓ Thermistor Thermometer
  - Calibrated accuracy within 0.1°C to 0.2°C
  - Digital readout to at least 0.1°C
  - Office-laboratory certified against a calibration thermometer (see above)

✓ Dewar flask and (or) plastic beakers (assorted sizes)

✓ Water bath, refrigerated (if available—see section 6.1.2)

✓ Soap solution (1 L), nonphosphate laboratory detergent

✓ Deionized water (1 L), maximum conductivity of 1 µS/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

[1] Modify this list to meet specific needs of the field effort.

Temperature-measuring instruments for field and laboratory (calibration) use can be either a liquid-in-glass or thermistor thermometer. Field personnel should be familiar with the instructions for use of the thermometer that are provided by the manufacturer.

- **Liquid-in-glass field thermometer**—Total immersion thermometers that are filled with a stable liquid, such as alcohol, are recommended for water measurements in the field. (Partial immersion thermometers are not recommended: these have a ring or other mark to indicate the required immersion depth.) Thermometers for field use must not be mercury filled. Before making temperature measurements, check the type of liquid-filled thermometer being used.
- **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 are incorporated into digital thermometers, individual-parameter instruments (such as conductivity and pH meters), and multiparameter instruments used for surface-water and ground-water measurements.

CAUTION:

Do not use mercury-filled thermometers in the field.

MAINTENANCE, CLEANING, AND STORAGE

Liquid-in-glass and thermistor thermometers can become damaged or out of calibration, especially as a consequence of thermal shock or extended exposure to direct sunlight. It is important to be familiar with and to follow the manufacturer's instructions for use and care.

- Keep a log book for each thermometer in which the date, time, and location of every calibration are recorded.
  - — Avoid direct exposure of the thermometer to sunlight.
  - — Avoid submerging the thermometer sensor in corrosive solutions.
  - — Follow the calibration guidelines and protocols described in section 6.1.2.

  - — Digital thermometer casings should not be submerged in water unless the manufacturer affirms that they are waterproof. Do not allow any liquid to enter open jacks that are part of some digital thermometers.

- ▶ Keep thermometers clean.
  - — Clean thermometer sensors with a soft cloth dipped in a mild solution of lukewarm water and nonphosphate detergent.
  - — If the digital thermometer case needs to be disinfected, use a weak (0.005 percent) bleach solution.
  - — **Do not autoclave the thermometer** (unless autoclaving is sanctioned by the manufacturer).
  - — If your digital thermometer has a detachable sensor with a plug termination, periodically wipe off or clean the sensor contacts. **Dirty contacts can affect temperature readings.**
  - — Blot the thermometer sensor dry after use.
  - — To clean an LCD lens, use only plastic-approved lens cleaners; do not use alcohol, acetone, or other harsh chemicals, as these will fog the lens.

- ▶ Store thermometers securely when not in use.
  - — Keep thermometers in a clean protective case when not in use. Each thermometer sensor and the case must be free of sand and debris.
  - — Keep thermometers dry and in a protective case during transit.
  - — Store liquid-filled thermometers with the bulb down.
  - — Store thermometers in a cool place and inside a building when not in use; do not leave a thermometer in a vehicle that could change in temperature to very hot or very cold, resulting in thermal shock to the thermometer.
  - — Check the batteries of thermistor-type thermometers for proper voltage before using.
  - — Record the calibration data in the log book for each thermometer—liquid-in-glass, thermistor thermometer, or thermistor-containing field-measurement instrument. Note if a thermometer has been serviced or replaced.

CALIBRATION 6.1.2

Thermometer calibration differs from the process by which a pH or conductivity sensor is adjusted until the accuracy of its performance conforms to that of an accepted calibration standard. For temperature measurements, calibration[2] refers to a comparison or accuracy check at specified temperatures against a thermometer that is certified by the National Institute of Standards and Technology (NIST), or is manufacturer-certified as NIST traceable. Calibration should be performed in a laboratory environment every 6 to 12 months, depending on the manufacturer's recommendation.

- **Field thermometers:** Only calibration thermometers having current NIST certification or traceability can be used for checking the accuracy of (calibrating) field thermometers.
  - **In the case of continuous monitors,** a nonmercury calibration thermometer can be used in the field to check or monitor temperature readings whenever other field-measurement sensors are calibrated. See Wagner and others (2006) for specific guidelines for continuous monitors.
- **Calibration thermometers** are calibrated during their manufacture and certified as NIST-certified or NIST-traceable at the manufacturing laboratory. The USGS requires that calibration thermometers be recertified by a professional calibration service at least every 2 years, or be replaced with a calibration thermometer having current certification.
  - Calibration thermometers should be reserved for calibration and should not be used routinely as field thermometers (see **TECHNICAL NOTE**). **Mercury-filled thermometers must never be used outside of the laboratory.**
  - The thermistors included in other field-measurement instruments must be calibrated (checked) routinely, as specified below for thermistor thermometers, since accurate determination of other field measurements depends on the accuracy of temperature measurements. Thermistors that are incorporated into instruments designed to measure, for example, specific electrical conductance, dissolved oxygen, and pH commonly provide automatic temperature compensation.

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[2] Calibrate: "To check, adjust, or systematically standardize the graduations of a quantitative measuring instrument" (American Heritage Dictionary, 1976).

  - **All thermometers must be tagged with their most recent date and source of certification** (NIST-certified or -traceable source for calibration thermometers and office-laboratory source for field thermometers).

- **A log book is required** in which the calibration and certification history of each calibration and field thermometer is recorded.

> **TECHNICAL NOTE:** The accuracy of a thermometer may vary over time, depending on factors such as the quality of its manufacture, the frequency of its use, and the conditions to which it is exposed. Shock, contamination, rapid heating and cooling, and mechanical stress are some factors that can affect the stability of a liquid-in-glass or thermistor thermometer (ICL Calibration Laboratories, 2003, 2005; ASTM International, 2005).

6.1.2.A CALIBRATION THERMOMETERS

Calibration thermometers (table 6.1-1) can be either a liquid-in-glass (mercury or spirit) or thermistor (digital) type thermometer, but must carry a current NIST certification or NIST-traceable certification that is no more than 2 years old. The actual duration of the calibration depends on the date of thermometer certification (not the date of purchase), how frequently the thermometer is used, and the conditions (thermal, chemical, and physical) to which it has been subjected during field operations and storage (see “Maintenance, cleaning, and storage” in section 6.1.1).

- **Check that the calibration thermometer has an NIST certification or traceable certificate that is within a 2-year period of original certification or recertification.**

- **Liquid-in-glass calibration thermometer:**
  - Before each use, inspect the thermometer for cracks, internal condensation, and liquid separation; if any of these conditions are observed, the thermometer must be replaced.
  - If the thermometer has been stored or used improperly, exposed at some length to sunlight or heat, or if its accuracy is otherwise in question, **check its readings at temperatures of approximately 0°, 25°, and 40°C, against those of another calibration thermometer that has been certified within the past 2 years.** If the environmental air or water temperatures to be measured fall below or exceed this range, add calibration points to bracket the anticipated temperature range.

- **Thermistor calibration thermometer:**
  - — Before each use, inspect the instrument (temperature sensor, digital display, wires or leads, and plugs) for signs of wear or damage; check that batteries are at full voltage.
  - — If the thermometer has been improperly stored or used, exposed at some length to sunlight or heat or extreme cold, or if its accuracy is otherwise in question, check its readings at five temperatures within the range of 0° to 40°C, against those of another currently certified calibration thermometer. If the environmental air or water temperatures to be measured fall below or exceed this range, add calibration points to bracket the anticipated temperature range.
- **Once NIST certification has expired** (exceeded the 2-year USGS limit):
  - — The thermometer either must be replaced with a currently certified thermometer or be recertified through a professional calibration service.[3] An office-laboratory calibration check does not constitute recertification of NIST traceability of a calibration thermometer.
  - — It is advisable to replace all mercury thermometers with a spirit or thermistor thermometer in order to avoid potential mercury contamination. The mercury thermometer must be disposed of in strict accordance with safety regulations.

Do not use calibration thermometers as routine field thermometers. Reserve their use for calibrating field thermometers.

FIELD THERMOMETERS 6.1.2.B

Field thermometers, whether of the liquid-in-glass or thermistor (digital) type, and whether or not they are themselves NIST-traceable,

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[3] The cost of commercial calibration services can vary widely. Examples of laboratories that are accredited to perform thermometer calibrations and certification include: National Institute of Standards and Technology (http://ts.nist.gov/ts/htdocs/230/233/calibrations/); ICL Calibration Laboratories (www.icllabs.com); Lab Safety Supply, Inc. (https://www.labsafety.com/calibration). (URLs cited were accessed 11/28/2005).

require regular accuracy checks against a calibration thermometer. Carry an extra thermometer in the event that the accuracy of a field thermometer is in question. **Note, however, that field checking of a thermometer's accuracy does not substitute for the required annual laboratory calibration.**

- ▶ At a minimum, calibrate each field thermometer every 12 months—the time interval depends on the amount of use and abuse to which the thermometer has been subjected and on its manufacture. According to thermometer manufacturers, some models of thermistor thermometers require calibration every 6 months (YSI, 2005). Quarterly or possibly monthly calibration can be required if the thermometer is in heavy use; was exposed to thermal shock, an extended period of direct sunlight, or extreme shifts in temperature; or was exposed to aggressive chemical solutions. The calibration history from the log book can indicate the expected life of the thermometer.
- ▶ **Each thermometer that passes the accuracy check must be tagged with the date of calibration.** Thermometers that do not pass the accuracy check must be repaired, if possible, or else discarded or otherwise retired from use.
- ▶ The annual calibration of field thermometers can be performed in the office laboratory or by an NIST-accredited commercial laboratory. To calibrate a thermometer, check its readings across a range of temperatures as described below in the instructions for water-bath calibration procedures. Temperature checks must bracket and include points that represent the temperature range expected to be encountered in the field. **EXCEPTION:** Thermistors in continuous water-quality monitors can be field-checked annually (or more frequently, if necessary) with a nonmercury NIST-certified or NIST-traceable thermometer.
  - — Fully submerge the bulb and liquid column if using a total-immersion liquid-in-glass thermometer.
  - — Keep calibration and field temperature sensors (thermistor or liquid-in-glass type) submerged throughout the calibration process.
  - — Record thermometer readings throughout the bath warming and cooling periods and while keeping the water stirred or otherwise circulated (thermistor readings will be recorded with greater frequency).
  - — Check meter batteries periodically for proper voltage when using a thermistor-type thermometer.

— Record the calibration data in the instrument log book for each thermistor thermometer (including thermistor-containing field meters), noting if a temperature sensor has been replaced.

Calibrate field thermometers every 12 months.

To calibrate field thermometers when a commercial refrigerated water bath is available:

1. Precool the sensor of the thermometer(s) being tested (field thermometer) to 0°C by immersing it in a separate ice/water bath.
2. Immerse the field and calibration temperature sensors in the refrigerated bath with a water temperature of approximately 0°C.
3. Position the temperature 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 temperature sensor(s) from the refrigerated water bath, read the field thermometer(s) to the nearest graduation (0.1 or 0.5°C) and the calibration thermometer to the nearest 0.1°C.
    a. Take three readings within a 5-minute span for each field thermometer.
    b. Calculate the mean of the three temperature readings for each field thermometer and compare its mean value with the calibration thermometer.
    c. If a liquid-filled field thermometer is found to be within ±1 percent of full scale or ±0.5°C of the calibration thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
    d. If a field thermistor is found to be within ±0.2°C of the calibration thermometer, set it aside for calibration checks at higher temperatures.
5. Repeat steps 1–4 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 “office-laboratory certified” with calibration date and certifier’s initials.

To calibrate field thermometers when a commercial refrigerated water bath is not available:

A. For the 0°C calibration

1. Freeze several ice cube trays filled with deionized water.
2. Fill a 1,000-milliliter (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 calibration thermometer into the ice/water mixture and make sure that the temperature is uniform at 0°C by stirring and checking at several locations within the bath.
3. Precool the sensor of the field thermometer(s) to 0°C by immersing in a separate ice/water bath.
4. Insert the field thermometer(s) into the ice/water mixture. Position the calibration and field thermometers 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. After the readings stabilize, compare the temperature of one field thermometer at a time with that of the calibration thermometer. Without removing the temperature sensor(s) from the test bath, read the field thermometer(s) to the nearest graduation (0.1 or 0.5°C) and the calibration thermometer to the nearest 0.1°C.
    a. Take three readings for each thermometer within a 5-minute span.
    b. Calculate the mean of the three temperature readings for each thermometer and compare its mean value with the calibration thermometer.
    c. If the field liquid-filled thermometer is found to be within ±1 percent of full scale or ±0.5°C of the calibration thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
    d. If the field thermistor is found to be within ±0.2°C of the calibration thermometer, set it aside for calibration checks at higher temperatures.

B. For the “room temperature” calibration (25°C)

1. 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 (away from drafts, vents, windows, and harsh lights).
2. Properly immerse the calibration and field thermometer(s) in the water. Cover the container and allow the water bath and thermometers to equilibrate.
3. Stir the water and, using the calibration thermometer, check the bath for temperature uniformity. Repeat this every 2 hours. It may be necessary to let the bath equilibrate overnight.
4. Compare one field thermometer at a time against the calibration thermometer, following the procedures described above in step A5 for the 0°C calibration.

C. For each temperature that is greater than 25°C

1. Warm a beaker of 1,000 mL or more of water to the desired temperature (for example, 40°C) and place it on a magnetic stirrer plate.
2. Follow the procedures described above in step A5 for the 0°C calibration.

Tag acceptable field thermometers as “office-laboratory certified” with the calibration date and certifier’s initials.

Corrections can be applied to measurements made with a thermometer that is within ±1 percent of full scale or ±0.5°C of the calibration thermometer. Corrections should be applied by using a calibration curve or table, which is plotted in the log book for the instrument. **Thermistors found to be out of calibration by more than 0.2°C must be returned to the manufacturer for repair or replacement.**

Remember to tag and date acceptable field thermometers after calibration.

6.1.3 MEASUREMENT

Air temperature, in addition to water temperature, should be measured and recorded whenever water-quality samples are collected. Water temperature must always be measured in situ and in a manner that ensures that the measurement accurately represents the intended sample conditions. Before measuring air or water temperature:

- Inspect the liquid-in-glass thermometer to be certain that the liquid column has not separated.
  - Inspect the glass bulb to be sure it is clean.
  - Inspect the protective case to be sure it is free of sand and debris.
- Check that batteries are fully charged for thermister thermometers or temperature sensors incorporated into other field meters.

6.1.3.A AIR

Measure air temperature using a dry, calibrated thermometer.

- Place or hang the thermometer about 5 feet above the ground in a shaded area that is 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 temperature of the water sample 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.

6.1.3.B SURFACE WATER

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:

- ▶ Making a cross-sectional temperature profile first, to determine the temperature variability of the stream section, is recommended—a hand-held digital thermometer works best for this purpose.
- ▶ To determine which sampling method to use (NFM 6.0), examine the cross-sectional profile and consider study objectives.
- ▶ 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 specifically represents the intended condition to be monitored).

1. Use either a liquid-in-glass thermometer or a thermistor thermometer tagged as “office-laboratory certified” and dated within the past 12 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 directly onto 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 or according to the manufacturer's guidelines 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, full-immersion thermometers—the water depth to which the thermometer is immersed 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 for liquid-in-glass and 0.2°C for thermistor readings—**do not remove the sensor from the water.**
    - When using a liquid-in-glass thermometer, check the reading three times and record on field forms the median of these values.
    - When using a thermistor thermometer, wait until the readings stabilize to within 0.2°C, then record the median of approximately the last five values.
5. Remove the temperature sensor from the water, rinse it thoroughly with deionized water, blot it dry, and store it.
6. Record the stream temperature on field forms. Determine the values as follows:
    - **In still water—median** of three or more sequential values.
    - **For equal discharge increments (EDI)—mean** value of subsections measured (use median value if measuring one vertical at the centroid of flow).
    - **For equal width increments (EWI)—mean or median** value of subsections measured.

6.1.3.C GROUND WATER

Measurements of ground-water temperature must be made downhole or with a flowthrough system at the end of purging to ensure that the temperature measured accurately represents ambient aquifer water conditions (consult NFM 6.0 for guidance). **Do not report a temperature value measured from a bailed ground-water sample.**

To measure the temperature of ground water:

- ▶ Select either the downhole or flowthrough-chamber sampling system (see NFM 6.0, fig. 6.0–4) and record the method used.
- ▶ Measure temperature with a thermometer that has been office-laboratory certified within the past 12 months and 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 pump tubing from the well to the chamber as short as possible, out of direct sunlight, and off the ground. Keep the chamber out of direct sunlight and wind.
2. Begin water withdrawal from the well. Allow the thermometer to equilibrate with ground-water temperature for no less than 60 seconds or in accordance with the manufacturer's guidelines; record the readings and time intervals throughout the period of purging.
3. Toward the end of purging, record five or more sequential measurements, spaced at increments of 3 to 5 minutes or more.
   - If the thermistor temperature is stable within the 0.2°C criterion, report the median of the final five measurements (table 6.0–1). (For a liquid-in-glass thermometer, there should be only slight fluctuation around 0.5°C.)
   - 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.
4. Remove the thermometer from the water, rinse it thoroughly with deionized water, blot it dry, and store it as described in 6.1.1.

6.1.4 TROUBLESHOOTING

Contact the instrument manufacturer if the suggestions on table 6.1-2 fail to resolve the problem, or if additional information is needed.

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 does not read accurately	• Check thermometer to see that the liquid is not separated—if separated, take back to the office laboratory to reunite column or for disposal.
Thermistor thermometer does not read accurately	• Dirty sensor—remove dirt and oil film. • Weak batteries—replace with new batteries.
Erratic thermistor thermometer readings	• 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	• Dirty sensor—clean sensor to remove dirt and oily film.

6.1.5 REPORTING

USGS temperature measurements should be stored in the National Water Information System (NWIS) data base. These data may be published electronically and (or) on paper as the verified negative or positive value measured, as described below.

- **Thermistor thermometer measurements:** Store manually recorded temperature measurements in the data base to the user-verified precision of the instrument (generally, 0.1 or 0.2°C, provided that the thermometer calibration verifies this accuracy). Electronically recorded temperature data may be stored unrounded. Unrounded temperature data in the database must be rounded when retrieved for publication.
- **Liquid-in-glass thermometer measurements:** Record temperature measurements in the data base to the nearest 0.5°C.
- Any values less than 0.1°C are highly questionable and should be published only after a complete calibration check of the equipment used.
- USGS field measurements of air and water temperature must be entered on the paper or electronic field form and stored in the NWIS data base.
  - Be sure to store all data under the correct parameter and method (if available) codes.
  - Store air and water temperature measurement data with replicate samples **only if replicate measurements were made.** Enter replicate measurements under the correct medium code for quality-control (QC) samples; alternatively, distinguish the replicate from the regular sample by using the unique time-of-sampling that was assigned to QC samples for that site and date.
  - Do not store the regular-sample measurement data with the replicate-sample data. **Enter regular-sample data only once in the NWIS data base.**
- Record the accuracy range of the instrument in the data base, if possible. Report the accuracy range with the published values.

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

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National Field Manual
for the Collection of Water-Quality Data

Chapter A6 Field Measurements

Section 6.2 DISSOLVED OXYGEN

Revised by Stewart A. Rounds, Franceska D. Wilde, and George F. Ritz

Techniques of Water-Resources Investigations Book 9–A6

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

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This National Field Manual for the Collection of Water-Quality Data (National Field Manual) responds to advances in technology and science and to the ever-developing needs for water-quality monitoring. Its aim is to provide scientifically sound guidance to U.S. Geological Survey (USGS) personnel and to document USGS requirements for collecting water-quality data. As a result, the expertise of numerous scientists has been tapped in developing the various chapters of this manual and keeping them current.

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6.2 Dissolved Oxygen

Revised by Stewart A. Rounds, Franceska D. Wilde, and George F. Ritz

The concentration of dissolved oxygen in water is affected by many factors, including ambient temperature, atmospheric pressure, and ion activity (ionic strength of the water body). Accurate dissolved-oxygen (DO) data are essential for understanding and documenting effects on environmental water resources that result from natural phenomena and human activities. Sources of DO in water include atmospheric aeration and photosynthetic activities of aquatic plants. Sinks of DO in water include respiration, aerobic decomposition processes, ammonia nitrification, and other chemical/biological reactions. Many chemical and biological reactions in groundwater and surface water depend directly or indirectly on the amount of available oxygen. The presence of DO in aquatic systems is necessary for the survival and growth of many aquatic organisms and is used as an indicator of the health and geochemical quality of surface-water and groundwater systems.

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

Standard procedures used by the U.S. Geological Survey (USGS) for determining concentrations of DO in surface water and groundwater involve the use of luminescence-based (optical sensor), amperometric (Clark cell[1]), or spectrophotometric methods of analysis. The iodometric (Winkler) method (section 6.2.3) no longer is used by the USGS for routine measurement of DO at field sites, but remains a standard method for verifying the results of DO measurements made using other methods.

The selection of field equipment and measurement methods takes into consideration (a) whether equipment will be used at varying and discrete locations and times or be deployed at a single location over a period during which it will be unattended, (b) anticipated environmental conditions, (c) the specific data-quality objectives of the data-collection program, and (d) the inherent benefits of a given technology as applied to given site characteristics and project or program objectives. The measurement methods described are employed by the USGS onsite for routine determination of DO concentrations in fresh to saline surface water and groundwater.

The primary USGS field procedure employed for DO determinations during the past two decades required the use of amperometric sensors until luminescence-based (optical) sensors became more common (around 2005). Although both optical and amperometric methods yield accurate results, optical DO sensors are considered a major technological advance over amperometric sensors because optical DO sensors are more robust in the field environment.

- ► Optical and amperometric sensor methods (section 6.2.1) are applicable to the same aqueous environmental conditions. Both sensor technologies are available in single-parameter DO meters or in multiparameter sondes and can be either handheld for discrete measurements or deployed for longer term, unattended continuous and real-time measurements.

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[1] This document refers to the “amperometric” method or sensor interchangeably with the “Clark cell” sensor. Other terms applied to amperometric methods include polarographic and galvanic technology.

- ► Spectrophotometric (colorimetric) methods (section 6.2.2) yield consistent results when applied to the determination of DO concentrations in oxygen-depleted waters (for example, in certain aquifers and deep-lake horizons). Noninstrumental colorimetric methods that are available for visually determining DO concentrations to zero milligram per liter (mg/L) can be useful for a quick reconnaissance of DO conditions and an accuracy check of DO sensor performance.
- ► The iodometric (Winkler) method (section 6.2.3) is regarded as an accurate and precise method for the calibration of DO sensors and the determination of DO concentration in water, when performed under controlled laboratory conditions. Before sensors that could be immersed directly in the water column became commonly available, USGS personnel were trained to perform Winkler titrations onsite. Standard USGS practice no longer sanctions the transport of field samples offsite for DO determination.

- **Some procedures for equipment operation as recommended in this guidance document may not apply to your equipment because of technological advances or other changes.**
- **Be sure to record any modifications made to the standard USGS procedures given in this field manual.**

6.2.1 Optical (Luminescence) and Amperometric Sensor Methods

Either the optical or amperometric sensor methods can yield accurate results for measurement of DO concentrations under most of the field conditions encountered for routine USGS data-collection activities. Both methods are relatively simple to use, whether deployed for single (discrete) or continuous (unattended) DO measurements in surface water or groundwater. Because of the advantages introduced by advances in applying luminescence technology to DO measurement, optical sensors are generally favored for most standard USGS field operations.

- ► **Optical sensors.** The technology used in optical DO sensors involves the measurement of light-emission characteristics of a luminescence-based reaction at the sensor-water interface (see TECHNICAL NOTE 1). In contrast to amperometric sensors:
  - — Oxygen is not consumed at the sensor-water interface.
  - — The optical sensor is not dependent on water flow; consequently, no stirring mechanism is required at sites with slow or stagnant waters.
  - — Optical sensors are stable. They are considerably more robust than amperometric sensors in maintaining calibration over long-term deployment and over a wide range of environmental conditions, and sensor drift over time is minimal when the sensor is kept clean.
  - — There are no known sources of interference to the luminescence method in natural aquatic systems. Optical sensors will measure accurately in the presence of hydrogen sulfide (H_2S) and also when deployed in fresh, brackish, and mildly polluted waters. Contact, however, with organic solvents can compromise sensor integrity or performance.
  - — Cleaning and maintenance are simplified. The optical sensor contains no anode or cathode to service, and uses no electrolyte solution, amperometric-type membranes, O-rings, or stirrer.

— The maintenance routine and schedule for optical sensors is less frequent than for amperometric sensors. Optical-sensor maintenance is dictated by manufacturer guidelines that are specific to the type of sensor in use and the conditions to which the sensor has been subjected.

- Optical-sensor luminophore-containing modules[2] (referred to as sensor caps, probe tips, or luminophore-coated membranes or foil, depending on the manufacturer) are rugged and resistant to punctures or other damage in storm or high-flow conditions, while amperometric (Teflon-membrane) sensors are considerably more vulnerable and require frequent replacement.
- Compared with the amperometric sensor, the frequency of a calibration check for an unattended (for example, continuously deployed) optical sensor should occur at least every 4 to 8 weeks, which depends primarily on environmental conditions and the age and condition of the luminophore, while the amperometric sensor typically requires recalibration every week or two, depending on environmental conditions.
- The manufacturers generally recommend annual to biannual replacement of the luminophore-containing module. The modules are easily replaced and should be calibrated or undergo a calibration check after being replaced.

TECHNICAL NOTE 1. The luminescence sensor employs a light-emitting diode (LED) to provide incident light of a specific wavelength, which excites a luminescent-dye molecule substrate (luminophore) of the sensor. After some dissipation of the excitation energy, longer wavelength light is emitted. The intensity of the fluorescence is proportional to the DO concentration because the presence of oxygen can quench, or suppress, the fluorescence response of the dye. Higher DO concentrations result in greater quenching and a decreased fluorescence response. More importantly, the timescale, or lifetime, of the fluorescence reaction is dependent also on the DO concentration and is not dependent on the light intensity of excitation or fluorescence, therefore allowing reliable determination of the DO concentration. Temperature stability during calibration and measurement is extremely important for optical and amperometric sensors alike.

► **Amperometric sensors** (Clark cell). The amperometric measurement method was the most commonly used field method for DO determination for USGS water data-collection efforts before introduction of the luminescence method. In this method, the DO concentration is determined using a temperature-compensating meter connected to an amperometric-membrane type of sensor or an amperometric sensor bundled with other sensors in a multiparameter sonde.

— Amperometric sensors require use of membranes and electrolyte solutions (*see* TECHNICAL NOTE 2 below).

— The method is flow-dependent, requiring that an adequate flow of water (approximately 1 foot per second (ft/s)) passes across the membrane.[3] Manual stirring is required when making handheld measurements. Use of an additional stirring mechanism fitted to the sensor or sonde is needed for discrete or continuous measurements at sites with slow or stagnant waters.

— Contact of the amperometric sensor with hydrogen sulfide (H_2S) interferes with the DO determination by degrading the electrode surfaces under the membrane.

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[2] See TECHNICAL NOTE 1 for definitions of luminescence and luminophore.

[3] The “Rapid Pulse” (YSI) sensor, however, does not require a stirrer and was designed to be virtually flow-independent for DO measurement in environmental waters. As of this writing, it is the only amperometric technology designed for this purpose and that allows a two-point calibration.

— Amperometric sensors are vulnerable to changes in temperature and the instrument must be temperature compensating. Be cognizant of the relation between sensor membranes and temperature. The permeability of the membrane changes as a function of temperature, as does the solubility of oxygen in water.

— Method performance can be negatively affected by:

- calibration drift
- a loose, wrinkled, or damaged membrane
- air bubbles in the electrolyte
- use of expired or contaminated electrolyte solution
- loose-fitting O-rings and membranes
- damaged, dirty, or otherwise contaminated electrodes under the membrane

— Extreme temperature change and (or) shock/vibration may cause a shift in the calibration, resulting in biased data.

TECHNICAL NOTE 2. Some manufacturers provide amperometric-sensor membranes of various thicknesses, the selection of which depends on the intended use of the instrument. Select the sensor membrane based on manufacturer's recommendations. Two basic types of membrane design are available: (a) individual membranes and (b) membrane-cap assemblies. Individual membranes are considerably less expensive but require more care and skill to install properly. Sensor performance can be affected by the manner in which individual membranes are installed and conditioned after installation.

6.2.1.A Equipment and Field Preparations

DO instruments (meters and sensors) are available from a number of commercial vendors. Because of differences among manufacturers in the instrument design and instructions for use, calibration, and maintenance, it is important that the user be thoroughly familiar with the instructional manual for the specific instrument system to be used in addition to the guidance given here.

Equipment Description and Maintenance

Meters, sondes, and the DO sensors used in these instruments are sophisticated electronic equipment that require care in handling and operation. Information about the equipment and supplies required for the optical and amperometric methods of determining aqueous DO concentrations is summarized in table 6.2–1.

► **Amperometric sensor.** The amperometric "instrument system" refers to the entire sensor assembly, including electrolyte solutions, membranes, and thermistors. Protect all sensors and supplies from being jostled during transportation, from sudden impacts, sudden temperature changes, and from extremes of heat and cold below 0 °C.

- ► **Optical sensor.** Guidance for when to replace the luminophore-containing cap or membrane varies among manufacturers and can be based on the specific design and materials used, the environmental conditions to which the sensor is exposed, the age of the sensor, and (or) the amount of time it is deployed. For example:
  - — Hach Company states that the need for replacement of the luminophore module depends on environmental factors to which their LDO (Luminescent Dissolved Oxygen) probe is exposed, rather than be scheduled solely on the basis of frequency or length of use. Environmental factors such as photobleaching of the luminophore surface from irradiation (for example, overexposure to sunlight), and substantial changes in water properties such as salinity or atmospheric conditions (air pressure), can affect the need for luminophore-module replacement.
  - — YSI Environmental advises annual replacement of the luminophore membrane assembly for their ROX (Reliable Oxygen) optical sensor.
  - — In-Situ, Inc. advises that the RDO (Rugged Dissolved Oxygen) sensor cap has a 2-year shelf life from the time of manufacture when not in service, but the cap must be replaced after one year of field deployment.
- ► **Storage of optical and amperometric sensors.** Become familiar with the specific manufacturer’s recommendations for short-term (field) and long-term (office) storage.
  - — Amperometric sensors should not be allowed to dry out and should be kept moist during storage.
  - — Storage of optical sensors in a humid environment differs among manufacturers; consult the manual provided for the sensor.

Table 6.2–1. Equipment and supplies for the optical and amperometric sensor methods of dissolved oxygen determination.[1]

[DO, dissolved oxygen; mg/L, milligram per liter; NFM, *National Field Manual for the Collection of Water-Quality Data*; –, minus; +, plus; °C, degrees Celsius; ±, plus or minus]

For amperometric method only
Amperometric instruments must be pressure-compensated (as well as temperature-compensated).
DO sensor membrane replacement kit includes membranes, O-rings, electrolyte (filling) solution; electrode reconditioning supplies; stirring attachment for low- or no-flow waters.
For optical and amperometric measurement methods
Instrument must be equipped with temperature compensation • DO instrument and DO sensor or multiparameter instrument with DO capability and digital temperature readout display • Operating range in water, from at least –5 °C to +45 °C • Measure concentrations from 0.05 to 20 mg/L (instrument capability can range to 50 mg/L) • Minimum scale readability (display resolution), preferably 0.01 mg/L DO • Calibrated accuracy within ±0.1 mg/L DO[2]
Calibration equipment, per manufacturer's recommendation.[3]
Pocket altimeter-barometer or DO instrument with built-in barometer; barometer measures to nearest 1 millimeter of mercury and its calibration has been checked before use.
Thermometer (see NFM 6.1 and 6.8 for calibration-check criteria) (for verification of air and water temperature and accuracy of instrument built-in thermistor).
Zero DO solution.[4] Dissolve 1 gram sodium sulfite in 1 liter of deionized water (0.008M solution, prepared fresh just before the field trip or during week of use).[5]
Flowthrough chamber for determining groundwater DO, if downhole sensor deployment is impractical.
Oxygen-solubility table (table 6.2–6), or access *http://water.usgs.gov/software/DOTABLES/*.
Waste-disposal containers.
Spare batteries. • Calibration and maintenance log books for DO instrument and barometer. • Calibrated specific conductance sensor, if working in saline or brackish systems.

[1] Modify this list to meet specific needs of the field effort.

[2] Refer to Wagner and others (2006) for long-term sensor deployment.

[3] Equipment needs and additional information specific to each calibration procedure are provided in section 6.2.1.B.

[4] Optionally, a few crystals of cobalt chloride ($CoCl_2$) can be added to the solution as a catalyst in order to speed up the reaction; however, routine USGS field operations omit the addition of $CoCl_2$, as it is a toxic substance, is regulated for proper disposal, and is not a necessary component to achieve a solution of the zero DO. If $CoCl_2$ will be used, personnel are advised to check the Material Safety Data Sheet for proper handling and disposal of the solution.

[5] Take special note of the manufacturer's guidance as applicable to your sensor. Some manufacturers supply the zero-DO solution required or document the specific instructions for preparing the zero-DO solution recommended for their sensors, including an alternative by which nitrogen gas is forced into tap or deionized water to produce a zero-DO solution (consult with the manufacturer's division of technical support).

Field trip preparations

The service performed on all equipment, whether a full calibration, calibration check, or replacement or repair of parts for the instrument, and whether performed in the office, laboratory, or field, must be accurately recorded and dated in the log book using black or blue non-erasable ink.

Field-measurement instruments are to be maintained on a regular schedule and performance-tested before field deployment, as described below:

1. Check all electrical connections and the charge on the batteries, as applicable for the instrument in use.
2. Thermistors/thermometers must be calibrated and field checked before use, as described in NFM 6.1 ("Temperature").

3. Perform a 100-percent saturation calibration check (see section 6.2.1.B). This performance check does not negate the need for onsite sensor calibration at oxygen saturation.

4. Perform a zero-DO sensor-performance check.

   a. Prepare the zero-DO sodium sulfite solution (see table 6.2–1).

   b. Before immersing sensor in the zero-DO solution, it is imperative to **remove the wiper** (or sponge) from the unit to avoid saturating it with the sodium sulfite solution. (Not all instruments have a DO sensor wiper.)

   c. Rinse sensor and wiper thoroughly and then reinstall wiper elements. Multiple and thorough rinses with deionized water are necessary to restore the sensor to proper operating condition and prevent bias to subsequent measurements.

5. Review the care and maintenance guidance provided by the manufacturer for the specific sensor being used; instructions can differ appreciably depending on the instrument type, make, and model.

   a. **Optical DO-sensor instrument:** Check the condition and (or) deployment history of the luminophore-containing sensor module, referring to the manufacturer’s guidance for replacement of the luminophore module.

      - Depending on the instrument, sensor modules are replaced annually or at least every 2 years, even if the probe is idle.

      - If the instrument reading exceeds 0.2 mg/L in the zero-DO solution, check DO again with a freshly prepared zero-DO solution; if a greater than 0.2 mg/L reading persists, contact the instrument manufacturer and inquire if the luminophore module should be replaced.

   b. **Amperometric instrument:**

      - Inspect the instrument closely, checking for loose, wrinkled, or torn membrane; air bubbles beneath the membrane; a loose O-ring, and a tarnished or discolored cathode or anode. If any of these problems are detected, do not use the sensor until it has been serviced according to the manufacturer’s guidance.

      - If the instrument reading exceeds 0.2 mg/L in the zero-DO solution, check DO again with a freshly prepared zero-DO solution; if a greater than 0.2 mg/L reading persists, replace the sensor membrane and electrolyte (if present) or repair.

      - **Membrane type** – Consult manufacturer recommendations to select a sensor membrane of the thickness required for the field operation. (Only one membrane thickness is available for some amperometric sensor makes or models.)

      - **Membrane replacement** – After replacing, the new membrane should be allowed to condition over a given period of time before sensor calibration and deployment.

        – Depending on the manufacturer and whether replacement involves using the O-ring or membrane-cap method, conditioning time depends on the type of membrane. Conditioning of membranes with O-rings, for example, generally ranges from a minimum of 2 hours up to 6 hours. For greater stability during calibration, allow the new membrane to condition overnight before calibration and use.

        – Membranes in caps are prestretched and require less conditioning.

  - For continuous monitoring applications with field-replaceable sensors, either condition the replacement sensor before the site visit, or replace the sonde with a second, clean and calibrated sonde and perform maintenance of the replaced sonde at the office.
  - When the sonde is deployed for discrete measurement, and conditions necessitate use of a new membrane before the recommended overnight conditioning time, more frequent calibration checks and possibly recalibration may be needed to ensure accurate DO measurements.[4] This is not recommended for continuous monitoring applications.

6. Remember to document field preparations and all instrument tests and adjustments in the meter log book. **Do not use an instrument that fails calibration.**

CAUTION:
Before handling sodium sulfite, cobalt chloride, or any other chemicals, refer to safety precautions on the Material Safety Data Sheet (MSDS) for that chemical.

6.2.1.B Calibration of Optical and Amperometric Sensors

Sensor-based instrument systems used to determine DO in water must be calibrated properly before being deployed. Proper calibration procedures are necessary to ensure the overall accuracy and precision of DO measurements. Amperometric sensors are more likely to require frequent calibration than optical sensors. While equipment manufacturers advise performing the calibration in the office laboratory before going onsite, USGS protocols call for onsite calibration checks and possible recalibration at the field site, as necessary to meet the specific data-quality requirements of the project.

The accuracy required by the project for sites at which DO will be determined and the capabilities of the selected instrument will govern whether a one-point calibration will be sufficient or a two-point calibration should be used. In addition, some manufacturers of the DO equipment commonly used for USGS data-collection efforts recommend testing of the equipment in a laboratory setting to determine the accuracy of room-temperature calibrations compared with measurements made under the anticipated warmer or colder field conditions. Project personnel are advised to be familiar with recommendations from the manufacturer of their equipment.

- ► **One-point calibration.** The main goal of the one-point calibration procedure is to create a 100-percent saturated oxygen environment where the DO sensor (optical or amperometric) and its regulating thermistor are at the same temperature. Amperometric sensors used in multiparameter instruments, for the most part, are capable of only a one-point calibration).[5]
  - **Procedure 1** (Air calibration chamber in air)
  - **Procedure 2** (Calibration with air-saturated water)
  - **Procedure 3** (Air calibration with a wet towel)

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[4] One sensor manufacturer recommends running the DO sensor for at least 15 minutes after a membrane change or if the electrodes were reconditioned. Check the manual or handbook of your instrument for corroboration.

[5] The “Professional Plus” multiparameter instrument (YSI Incorporated) with amperometric sensor can be calibrated at zero DO and 100 percent saturation. Other such instruments also may be in production.

- **Procedure 4** (Air calibration chamber in water). Unlike Procedures 1, 2, and 3, this procedure currently is applied to amperomeric instrument systems only. The potential applicability of this procedure to calibration of optical sensors is a topic of discussion and review that can be followed in the chapter 6 section of the NFM Comments and Errata page (*http://water.usgs.gov/owq/FieldManual/mastererrata.html*).

► **Two-point calibration (for optical sensors).** The two-point calibration typically involves calibration of the sensor at 100 percent saturation, followed by calibration at zero DO. Only specific makes and models of optical DO sensors have the capacity to be calibrated to two points. The two-point calibration adds complexity to the calibration process and is not recommended by all manufacturers of optical sensors. Be sure first to understand the instrument capabilities and then determine the best course of action for your field work.

- For routine applications, it is advisable to rely on a zero-DO performance check rather than a zero-DO recalibration, which would risk corrupting the manufacturer's zero-DO calibration.
- Use of a two-point calibration should be considered if (a) the calibration is needed to satisfy the data-quality objectives of the project,[6] (b) oxygen concentrations of less than 1 mg/L are likely to be encountered and zero-DO performance tests fail at this concentration level, or (c) the calibration is deemed necessary by experienced field personnel knowledgeable of site conditions.
- Before starting or planning for a two-point calibration, it is advisable to consult the manufacturer's instructions or technical support for the specific optical DO sensor being used.
- If using a two-point DO calibration, calibrate the DO sensor only after calibrating other field-measurement sensors to prevent possible interference of the sodium sulfite (zero-DO) solution with the calibration of the other sensors. Complete the DO calibration at 100 percent saturation before the zero calibration.

► **Sensor-performance checks.** Verifying sensor performance (calibration checks) is a required standard procedure in USGS field operations (*see* section 6.2.1.A)

- All DO sensors have the capability to undergo a performance check at zero DO as well as at saturation.[7]
- Verifying instrument performance at zero DO and using the two-point calibration can be particularly important for data accuracy when the instrument will be used to measure low DO concentrations (for example, DO less than 5 mg/L).

Do not use an instrument that fails to calibrate properly.

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[6] Although optical instruments undergo zero-calibration procedures by the manufacturer, the accuracy of factory calibrations may not satisfy the data-quality objectives of some USGS field studies.

[7] It should be underscored that manufacturers uniformly caution against zero recalibration of sensors but allow for zero DO checks, stipulating the need to thoroughly rinse the zero-solution from the sensor.

Correction for Atmospheric Pressure and Salinity

Calibration procedures include corrections for atmospheric pressure and ionic strength (ionic strength is estimated from the conductivity or salinity measurement for routine field applications). Atmospheric pressure, the temperature of the water or water vapor, and the ionic strength (estimated by conductivity or salinity) of the water must be known to determine the theoretical amount of oxygen that can be dissolved in water. **Record all calibration information in instrument log books and copy calibration data onto field forms at the time of calibration.**

TECHNICAL NOTE 3. DO sensors do not actually measure oxygen in milligrams per liter or parts per million. Both of these expressed concentrations are based on calculations that relate instrument reading with the temperature and salinity of the sample water. The actual sensor measurement is proportional to the ambient partial pressure of oxygen, which can be displayed either as percent saturation or in milligrams per liter, depending on user input.

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. National 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 may provide ambient atmospheric pressure.

- ► Determine the ambient atmospheric pressure to the nearest 1 millimeter (mm) of mercury. A calibrated pocket altimeter-barometer typically has been used to determine atmospheric pressure; however, many instruments that now are in common use include an internal barometer.
- ► Check the accuracy of all field barometers before each field trip (including barometers built into instrument systems) and record readings and adjustments in the instrument log book. If possible, check barometer accuracy while at an official weather station. If this is not an option, adjust the official weather station barometric pressure to the elevation at the field site at which the barometer reading is being recorded.
- ► 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 (fig. 6.2–1). Section 6.2.5 contains the table of oxygen solubility at various temperatures and pressures.

Most modern multiparameter instruments (see NFM 6.8) incorporate a pressure-temperature and salinity compensation algorithm in their firmware for DO measurements; the instruments have a built-in conductivity sensor that corrects the DO-concentration (in milligrams per liter) data for salinity automatically. For instruments that are not equipped with a conductivity/specific conductance (SC) sensor, a manual salinity correction of the DO data would be required.

- ► If a user-specified salinity correction is needed, **the preferred USGS method is to apply salinity correction factors after calibrating and** measuring DO concentration of the environmental water body (see section 6.2.5). Interactive tables are available for user-specified temperature, pressure, and salinity at *http://water.usgs.gov/software/DOTABLES/*.

- ► **When a manual salinity** correction is made by the user during calibration, the instrument requires recalibration for each field variation in salinity (*see* section 6.2.5).

TAKE NOTE: If using a multiparameter sonde that includes a calibrated conductivity sensor, salinity corrections to the DO concentration reading (in mg/L) are performed automatically in the sonde; that is, the DO sensor communicates with the SC sensor.

Table 6.2–2. Factors used to correct reported atmospheric pressures that have been adjusted to sea level.

[NGVD, National Geodetic Vertical Datum of 1929]

Elevation of weather station (in feet, NGVD)	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

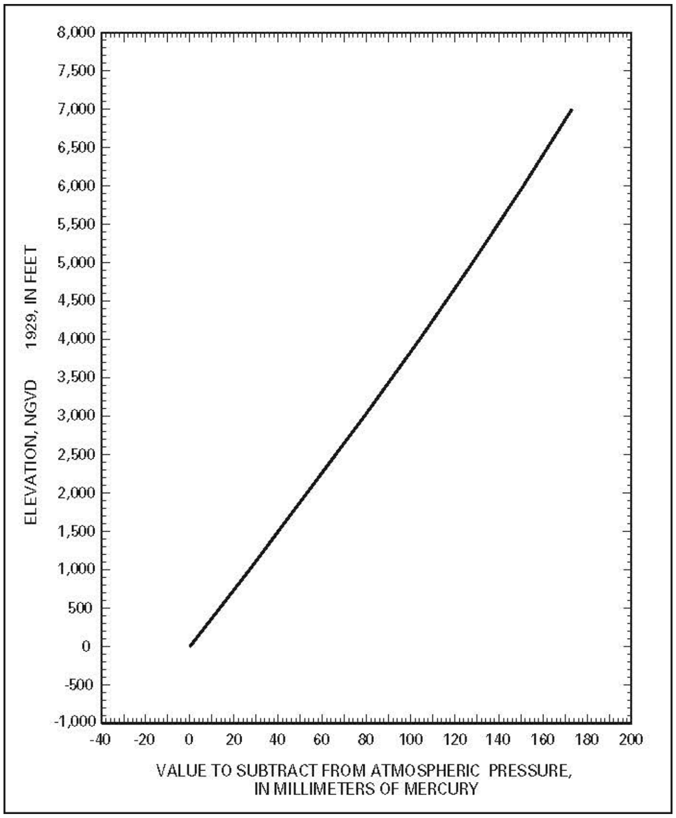

Figure 6.2–1. Factors used to correct reported atmospheric pressures that have been adjusted to sea level. NGVD 1929, National Geodetic Vertical Datum 1929.

Selection of Calibration Method

A saturated-oxygen calibration of DO sensors is recommended uniformly by manufacturers, regardless of which of the following methods is used: Air Calibration Chamber in Air (Procedure 1), Calibration in Air-Saturated Water (Procedure 2), or Air Calibration with a Wet Towel (Procedure 3). With minor modifications, these procedures can be applied to a one-point calibration of either luminescent-sensor (optical) or amperometric instruments (not all instruments allow or can accommodate a two-point calibration). A fourth method, Air Calibration Chamber in Water (Procedure 4), is described in the section on calibration for amperometric sensors. Although Procedure 4 has, in some cases, been applied when calibrating optical sensors, the pressure differentials and aqueous vapor properties at various temperatures experienced at the field site increases the potential for undetected water droplets on the thermistor and luminophore membrane and the risk for larger measurement error compared with the other calibration methods described below. It is important to refer to the manufacturer-provided guidance, as each of the procedures has inherent advantages and disadvantages and may include instrument-specific sources of error.

- ► The saturated-water method (Procedure 2) tends to be favored by manufacturers for calibrations in an office laboratory because it ensures equilibration of the temperature sensor with the DO amperometric membrane or the optical luminescence-coated sensor. Procedure 2 is considered to provide the best accuracy for calibration of optical sensors.
- ► The air calibration with a wet towel method (Procedure 3) is performed at the field site and is the method recommended most commonly by manufacturers for calibrating the amperometric (Clark cell) sensor, given advances in instrument technology. While the Wet Towel method can be used in the calibration of optical as well as amperometric sensors, the Air Calibration Chamber in Water method is applicable to amperometric sensors only. In previous versions of this field manual, the Air Calibration Chamber in Water (Procedure 4) method was published as “Procedure 3.”

- **Check DO meter calibration at each field site.**
- **Calibration of amperometric sensors should be checked each time after an instrument has been powered off and recalibrated, as necessary.**

Optical (Luminescence) DO Sensors: Calibration Procedures

The introduction of luminescence technology to DO field instruments has improved and simplified the data-collection process for field determination of DO. In addition to being more rugged, having fewer interferences, and undergoing decreased calibration drift relative to amperometric sensors, optical DO sensors tend to be more accurate, with accuracy specifications of ±0.1 mg/L or 1 percent after calibration.[8] This level of accuracy is best achieved by calibrating under controlled conditions in a laboratory or simulated laboratory environment.

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[8] USGS field scientists have corroborated the accuracy of the optical sensor to 0.05 mg/L DO by using repeated comparisons of results with the Rhodazine-D spectrophotometric method described in section 6.2.2 of this field manual (Gerolamo Casile, U.S. Geological Survey, written commun., 2012). These results can be entered into the USGS NWIS database.

TECHNICAL NOTE 4. Optical DO sensors often contain internal calibration information from the manufacturer. Although some manufacturers advise that no further calibration is warranted, the accuracy of factory calibrations do not necessarily satisfy the data-quality objectives required for USGS applications. **Because the validity of a calibration can substantially affect the overall accuracy and precision of DO measurements, users are advised to check the calibration frequently in order to meet specific data-quality objectives.**

- ► Because the optical DO sensors are not subject to drift, shock, or temperature extremes, the office-performed calibration is likely to remain stable after transport to the field; nevertheless, calibrations must be verified at the field site.[9]
- ► The Rhodazine-D spectrophotometric and iodometric methods for DO measurement described in sections 6.2.2 and 6.2.3, respectively, have been used to check the calibration of these instruments (see footnote 8).
- ► All calibration information is to be recorded in instrument-specific log books and the calibration data copied onto field forms at the time of calibration. Some instruments produce calibration reports generated by manufacturer-specific firmware; such reports that can be downloaded should be reviewed and incorporated in the instrument log book.
- ► Procedure 1 (air calibration chamber in air), Procedure 2 (calibration with air-saturated water) and Procedure 3 (air calibration with a wet towel) are described below for calibration of optical sensors at 100 percent saturation.
  - — Refer to the NFM Comments and Errata, chapter 6, for the potential applicability of the “air calibration chamber in water” method to calibration of optical sensors (*http://water.usgs.gov/owq/FieldManual/mastererrata.html)*.
  - — A description of the “air calibration chamber in water” method is given below as Procedure 4 in the section titled "Amperometric (Clark cell) DO Sensors: Calibration procedures".

Procedure 1: Air calibration chamber in air

This procedure (which is similar to Procedure 3) is commonly used for calibrating **handheld** optical DO instruments. Calibration chambers either are built into the instrument case or are provided as separate components by the manufacturer. **Use the calibration chamber that is provided or recommended by the manufacturer.**

1. Wet the inside of the calibration chamber with water and then pour out the water, leaving a few drops.
   a. Remove any water droplets on the temperature and optical sensors.
   b. Insert the sensor into the chamber (this ensures 100 percent humidity).
      - If using a screw-on calibration cup, make sure it is loose and not making an airtight seal in order to maintain ambient pressure.
      - Keep the calibration assembly in a stable temperature environment and out of direct sunlight.

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[9] Laboratory calibration is favored by manufacturers in general, who advise that DO instruments rarely should require recalibration in the field.

2. Allow 10 to 15 minutes for the air to saturate with water vapor and for the DO sensor and the air inside the calibration chamber to equilibrate. If appropriate for the instrument being used, run the instrument during the equilibration period.
3. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure checked to the nearest 1 mm of mercury.
4. Monitor the temperature and DO outputs in the calibration chamber, observing readings until the instrument readings stabilize. Read the temperature to the nearest 0.1 °C.

TECHNICAL NOTE 5. To maximize accuracy, a recommended practice is to maintain or approximate air temperatures during calibration that are within 10 °C of the ambient temperature of the water to be measured (see Procedure 3 – Wet Towel Method).

5. If calibrating to a given DO concentration rather than calibrating to a condition of 100 percent saturation, use table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*) to determine DO saturation at the calibration temperature and atmospheric pressure.
6. Following the manufacturer’s instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
    - If using an instrument that allows calibration simply to a 100-percent saturation condition, all that may be needed is to provide the ambient atmospheric pressure for the instrument to determine (with internal software) the resulting DO concentration.
7. Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study.
8. Remove the sensor from the calibration chamber to check if water droplets were on the optical tip or membrane during calibration; water droplets on the sensor tip or membrane and on the temperature sensor can cause improper calibration.
    - **Recalibrate the instrument if water droplets were present.**
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
9. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

During saturated-air calibration, it is necessary to keep water droplets off of the optical sensor module (luminescence tip or membrane) and temperature probe.

Procedure 2: Calibration with air-saturated water

This procedure, in which the DO sensor or instrument system is calibrated in water that is saturated with oxygen at a known temperature and ambient atmospheric pressure, generally is preferred by manufacturers for optical-sensor calibration.[10] Procedure 2 is considered the most accurate for optical measurements of DO because the saturated water ensures that all equipment parts equilibrate with water temperature simultaneously, and the method eliminates the need to check for water droplets on the optical tip/membrane or temperature sensor. Great care is required, however, to ensure that the water is indeed saturated with oxygen.

Equipment: Calibration with Air-Saturated Water	
1	5-gallon bucket or manufacturer-provided aeration chamber
1	10-gallon-aquarium air pump with two outlets
1	10-foot-length of aquarium pump tubing
2	Gas-diffusion (air) stones

For this procedure, producing aerated water under controlled laboratory conditions is preferred; calibrate the DO sensor in the office laboratory before departing for the field site (step 4a below).

1. In the laboratory, fill a 5-gallon bucket to three-quarters full with tap water.
2. Attach the pump tubing to the pump and then the two air stones to the ends of the tubing. Place the tubing with air stones at the bottom of the filled bucket.
3. Turn on the pump and aerate the water for a minimum of 30 minutes.[11]

   Tip: The pump could be left to operate continuously (24/7) in order to have a ready supply of air-saturated water on hand for calibration in the laboratory or for transport and calibration in the field.
4. **Calibration**—Take care to keep air bubbles off of the optical sensor (the luminescence tip or membrane).
   a. For laboratory calibration, place the DO sensor (or multiparameter sonde) in the bucket and allow 5 to 10 minutes for the sensor to come to thermal equilibrium with the aerated water. Take care not to place the sensor over or in the bubbles from the air stone!

   b. For field calibration of a handheld DO sensor:
      - Fill a 1-gallon (approximately 4-liter) container to three-quarters full with the laboratory-aerated water for transport to the field. In the field vehicle, shake the container vigorously for 2 minutes to fully aerate the water and immerse the DO sensor. Allow about 5 minutes for the sensor to come to thermal equilibrium with the aerated water.
      - Alternatively, use the Wet Towel Method (Procedure 3).
5. Read and record the temperature of the calibration water to the nearest 0.1 °C.

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[10] Some manufacturers provide the necessary aeration equipment with the instrument.

[11] Previous versions of this procedure described in this field manual specified that a sensor or sonde be immersed in the water while the water is being aerated with a battery-operated aquarium pump. Owing to uncertainties in pump quality, battery power, and possible supersaturation, this technique is not universally recommended by the manufacturers who reviewed this protocol and has been modified accordingly. If the former procedure is used, it is imperative to avoid placing the sensor in the stream of air bubbles.

6. Using a calibration-checked altimeter-barometer, determine the ambient atmospheric pressure to the nearest 1 mm of mercury.
7. Using oxygen-solubility table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*), determine the DO saturation value at the measured temperature and atmospheric pressure of the calibration water. (Refer to section 6.2.5 and table 6.2–7 for salinity corrections.)
8. Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value. Alternatively, use more stringent accuracy criteria that reflect the data-quality requirements of the study. If the field calibration or calibration check fails to meet the established criterion, (a) use a different instrument (if available), and (b) do not collect or report data using an instrument that has failed calibration.
9. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

For accurate calibration, ensure that the water is 100 percent saturated with oxygen (see step 4b above).

Procedure 3: Air calibration with a wet towel

For many multiparameter instruments a 100-percent humidity environment can be created by wrapping a moist towel around the sensor guard and inserting into a plastic bag. The Wet Towel Method is almost identical to Procedure 1, the main difference being that the sensor (or sonde) guard will be wrapped in a wet towel instead of being inserted into a calibration cup or chamber.

Equipment: Calibration with a Wet Towel	
1	Towel, sized so that it will wrap around the sensor at least two full wraps
1	Trash bag, clear or white plastic

1. Bring sensor to thermal equilibrium.
   a. If attempting to match the temperature of the water being monitored (for example, stream, lake, or groundwater), place the sensor directly in the water body (alternatively, for groundwater, into a flowthrough cell through which well water is being pumped continually).
   b. Allow 5 to10 minutes for thermal equilibration of the sensor with ambient water temperature until temperature readings have stabilized.
2. Once temperature readings are stable, soak the towel either (a) in the water for DO measurement, or (b) with tap or deionized water.

3. Remove the towel, wring it out, and then wrap the wet towel completely around the sensor guard, cup, or chamber, two full wraps or more.
    - As you wrap the sensor, ensure that no water droplets are either on the temperature sensor or on the luminescent sensor (sensor tip or membrane).
    - Place the wrapped sensor into the plastic bag and keep it out of direct sunlight in order to keep the temperature from changing.
4. Allow 10 to 15 minutes for the air to saturate with water vapor and for the DO sensor and the air inside the towel (calibration chamber) to equilibrate. Run the instrument during the equilibration period, if so directed by manufacturer instructions.
5. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure checked to the nearest 1 mm of mercury.
6. Monitor the temperature and DO outputs and observe readings until the instrument stabilizes. Read the temperature to the nearest 0.1 °C.
7. If calibrating to a DO concentration rather than to 100 percent saturation, use the oxygen-solubility table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*) to determine the DO saturation concentration at the measured temperature and atmospheric pressure.
8. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
    - If using an instrument that allows calibration only to 100 percent saturation, all that may be needed is to provide the ambient atmospheric pressure and the instrument will determine the resulting DO concentration internally.
    - Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study.
9. Remove the sensor from the towel and check if any water droplets were on the membrane. Water droplets on the membrane and temperature probe can cause improper calibration.
    - **Recalibrate the instrument if water droplets are observed.**
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
10. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Amperometric (Clark cell) Do Sensors: Calibration Procedures

The calibration and operation of amperometric instruments differ among instrument types, makes, and models—refer to the instrument manual provided by the manufacturer. Calibration for amperometric sensors typically is performed using one of the following procedures for a one-point calibration at 100 percent saturation:

- ► Procedure 1 (Air Calibration Chamber in Air)
- ► Procedure 2 (Calibration with Air-Saturated Water)
- ► Procedure 3 (Air Calibration with Wet Towel)
- ► Procedure 4 (Air Calibration Chamber in Water)

Manufacturers recommend different calibration frequencies for membrane-electrode (amperometric) DO meters. Depending on equipment capabilities, instrument performance and data quality can be enhanced by checking sensor performance; that is, making calibration checks as frequently as needed or as directed by project protocols. Sensor manufacturers generally agree that optimum performance and data quality will be obtained by frequent calibration and performance checks. Sensor performance checks at zero DO are implemented routinely by trained USGS field personnel (see section 6.2.1.B).

Tip: Many amperometric DO sensors require the meter to be powered on for 10 to 15 minutes before calibration (and use) to stabilize the probe. Refer to the manufacturer's instrument-specific guidelines for the requirements of your instrument.

Procedure 1: Air calibration chamber in air

This procedure, similar to Procedure 3, is the most commonly used method for amperometric instruments. Calibration chambers are either built into the instrument case or are provided as separate components by the manufacturer. **Use the calibration chamber provided or recommended by the manufacturer.**

1. Wet the inside of the calibration chamber with water, then pour out the water (but leave a few drops).
2. Remove any water droplets on the sensor membrane and temperature sensor, then insert the sensor into the chamber (this ensures 100 percent humidity).
    - If using a screw-on calibration cup, ensure it is loose (not making an airtight seal) to avoid causing a change in the pressure around the sensor compared to the onsite barometric pressure. Alternatively, consider using the Wet Towel Method (Procedure 3).
    - Be sure to keep the DO assembly in a stable temperature environment and out of direct sunlight, as applicable for the instrument in use.
3. Allow 10 to 15 minutes for the air to saturate and for the DO sensor and the air inside the calibration chamber to equilibrate. Apply power to the instrument during the equilibration period, as applicable for the instrument in use.
4. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure checked to the nearest 1 mm of mercury.

5. Monitor the temperature and DO outputs in the calibration chamber and observe readings until the instrument stabilizes. Read the air temperature in the chamber to the nearest 0.1 °C. To the degree possible, the temperature in the chamber should approximate the temperature of the water body in which DO will be determined within about 10 °C.

TECHNICAL NOTE 6. Most instrument manufacturers recommend calibrating at temperatures that are at least within 10 °C of the ambient water temperature. The most accurate calibration will be achieved if the temperature difference between the environmental water and the calibration chamber is minimized as much as possible (see Procedure 3, the Wet Towel Method, for additional information). In addition, the manufacturers of DO equipment that currently (2013) is in common use for USGS data-collection efforts advise testing the equipment in a laboratory setting to determine the accuracy of room-temperature calibrations compared with measurements made under the anticipated warmer or colder field conditions.

6. If calibrating to a DO concentration rather than to a 100-percent saturation condition, use the oxygen-solubility table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*) to determine the DO saturation value at the measured temperature and atmospheric pressure.

7. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.

    - If using an instrument that allows calibration simply to a 100-percent saturation condition, all that may be needed is to provide the ambient atmospheric pressure and the instrument will determine the resulting DO concentration internally.

    - Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study. If the criteria are not met, repeat the calibration procedure after checking for water droplets in step 2 above.

8. Remove the sensor from the calibration chamber and again check for water droplets on the membrane. Water droplets on the membrane and temperature sensor can cause improper calibration.

    - **Recalibrate the instrument if water droplets are observed.**

    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.

9. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Procedure 2: Calibration with air-saturated water

In this procedure, the DO sensor or instrument system is calibrated in water that is saturated with oxygen at a known temperature and ambient atmospheric pressure. **Manufacturers advise that the calibration with air-saturated water is best done in the laboratory under controlled conditions.**[12]

Equipment: Calibration with Air-Saturated Water	
1	5-gallon bucket or manufacturer-provided aeration chamber
1	10-gallon-aquarium air pump with two outlets
1	10-foot-length of aquarium pump tubing
2	Gas-diffusion (air) stones

1. In the laboratory, fill the 5-gallon bucket about three-quarters full with tap water.
2. Using two air stones, saturate the water for at least 30 minutes before use. However, some manufacturers recommend that the pump be left on continuously (24/7) so that the water is always saturated and ready to use.
3. Place the DO sensor in the water, avoiding contact with the bubble stream, and allow the sensor to come to thermal equilibrium.
4. Read the temperature of the calibration water to the nearest 0.1 °C.
5. Using a calibration-checked altimeter-barometer, determine the ambient atmospheric pressure to the nearest 1 mm of mercury.
6. **Move the sensor so as to ensure a 1 foot per second (ft/s) flow across the membrane;** alternatively, use a sensor that is equipped with a stirrer. Ensure that sufficient flow passes over the DO sensor during the saturated-water calibration method as well as when making a field measurement.
    - Move the sensor to stir the water, using either a horizontal stirring motion or a "teabag" dipping motion. Take care not to remove the sensor from the water.
    - The DO reading may rise as the water is stirred.
    - **After the DO reading has peaked and is stable, start to calibrate the DO sensor.**
    - Maintain this flow rate while monitoring measurements and adjusting the instrument calibration.

TECHNICAL NOTE 7. The various types of amperometric sensors can have different levels of flow dependency; however, the 1 ft/s flow is not detrimental to sensors with little or no flow dependence.

7. Using the oxygen-solubility table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*), determine the DO saturation value at the measured temperature and atmospheric pressure of the calibration water. (Refer to section 6.2.5 and table 6.2–7 for salinity corrections.)

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[12] Field calibrations with battery-powered pumps are not recommended by manufacturers who reviewed this report (see footnote 11). Trained USGS field personnel have, however, demonstrated success using Procedure 2 in the field.

8. Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality objectives of the study.
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
9. Record calibration information in instrument log books and transfer the calibration data into electronic records or onto paper field forms at the time of calibration.

For accurate calibration, ensure that the water is 100 percent saturated with oxygen.

Procedure 3: Calibration with a Wet Towel

This method is almost identical to Procedure 1, the main difference being that the sensor (or sonde) guard will be wrapped in a wet towel instead of being inserted into a calibration cup or chamber.

Equipment: Wet-Towel Calibration	
1	Towel, sized so that it will wrap around the sensor at least two full wraps
1	Trash bag, clear or white plastic

1. Bring the sensor to thermal equilibrium.
    - If attempting to match the temperature of the water being monitored (for example, stream, lake, or groundwater), place the sensor directly in the water body (alternatively, for groundwater, into a flowthrough cell through which well water is being pumped continually).
    - Allow 5 to10 minutes for thermal equilibration of the sensor with the ambient water temperature until temperature readings have stabilized.
2. Once temperature readings are stable, soak the towel either (a) in the environmental water for DO measurement, or (b) with tap or deionized water.
3. Remove the towel, wring it out, and wrap the wet towel completely around the sensor guard, cup, or chamber, two full wraps or more.
    - As you wrap the sensor, **ensure that no water droplets are either on the temperature sensor or on the sensor tip or membrane.**
    - Place the wrapped sensor into the plastic bag and **keep it out of direct sunlight** to keep the temperature from changing.
4. Allow 10 to 15 minutes for the air to saturate with water vapor and for the DO sensor and the air inside the towel (calibration chamber) to equilibrate. Run the instrument during the equilibration period, if so directed by manufacturer instructions.
5. Using a calibration-checked altimeter-barometer, read the ambient atmospheric pressure to the nearest 1 mm of mercury.
6. Monitor the temperature and DO outputs and observe readings until the instrument stabilizes. Read the temperature to the nearest 0.1 °C.

7. If calibrating to a specific DO concentration rather than to 100 percent saturation, use the oxygen-solubility table 6.2–6 or the online software DOTABLES (*http://water.usgs.gov/software/DOTABLES/*) to determine the DO saturation value at the measured temperature and atmospheric pressure.
8. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.
    - If using an instrument that allows calibration to 100 percent saturation, all that may be needed is to provide the ambient atmospheric pressure and the instrument will determine the resulting DO concentration internally.
    - Verify that the instrument reading is within ±0.2 mg/L or 2 percent of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study or program.
9. Remove the sensor from the towel and check if any water droplets are on the membrane. Water droplets on the membrane or temperature sensor can cause improper calibration.
    - **Recalibrate the instrument if water droplets are observed.**
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
10. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Water droplets on the DO membrane and thermistor will result in improper calibration. Recalibration is required if water droplets are observed.

Procedure 4: Air calibration chamber in water

A specialized 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; for example, at sites having field conditions with a wide disparity between ambient air and water temperature. For many multiparameter water-quality instruments, the manufacturer-provided groundwater flow cell may be modified and used as an air calibration chamber in water.[13] The modification requires the cell to be mounted on the sonde with one port of the cell tightly plugged and the other port vented to the atmosphere with tubing. The method is subject to large errors, especially in cold temperatures, if the port is not adequately vented to the environment. **Before using this method, check with the manufacturer for its applicability to the instrument to be used**.

1. Insert the sensor probe and calibration chamber into the surface water or groundwater to be measured. Once the temperature readings stabilize (allow 10 to 15 minutes), remove the sensors and calibration chamber from the water to be measured. Empty the calibration chamber, leaving a few drops of water.
    - Check for and remove any water droplets on the sensor membrane and the thermistor.
    - Insert the DO sensor into the wet chamber (this ensures 100 percent humidity).

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[13] Air calibration chambers for in-water calibrations no longer are available on the open market (for example, the YSI 5075A calibration chamber is no longer manufactured).

- Check that the port is adequately vented, that no water can leak into the calibration chamber, and that droplets of water are not adhering to the membrane and thermistor. The water droplets reduce the rate of oxygen diffusion through a membrane, producing erroneous results.

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 6 in 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.
    - For groundwater, use temperature-stabilized purge water or other clean water having a temperature that closely approximates that of the groundwater.
3. Using a calibration-checked pocket altimeter-barometer, determine the ambient atmospheric pressure to the nearest 1 mm of mercury.
4. Read the temperature within the chamber to the nearest 0.1 °C, using a calibrated thermometer (NFM 6.1).
    - The temperature inside the chamber should approximate the water temperature.
    - If the two temperatures do not match, allow additional time for equilibration of the chamber with the water temperature.
    - If the temperature of the chamber still does not approximate the water temperature, the thermistor in the DO sensor might be malfunctioning. Compare water temperature measured by the DO meter and a calibrated field thermometer. If the two measurements vary by more than ±0.5 °C, the calibration should be discontinued and the DO meter thermistor should be repaired following the manufacturer's recommendations.
5. Use table 6.2–6 (section 6.2.5) to determine the DO saturation value at the measured water temperature and atmospheric pressure. If a salinity correction will be applied during calibration, consult the instructions in section 6.2.5 and table 6.2–7.
6. Following the manufacturer's instructions, set or adjust the calibration control until the instrument reads a DO saturation value determined from oxygen solubility (table 6.2–6).
    - Verify that the instrument reading is within ±0.2 mg/L of the computed saturation value, or use more stringent accuracy criteria per the data-quality objectives of the study.
    - Verify that no water droplets are on the membrane or thermistor. **Recalibrate the instrument if water droplets are observed.**
    - Having followed all the steps above, the DO sensor is now calibrated and ready for use.
    - Remove the sensor from the calibration chamber for cleaning and storage.
7. Record calibration information in instrument log books and transfer calibration data into electronic records or onto paper field forms at the time of calibration.

Water droplets on the DO membrane and thermistor will result in improper calibration. Recalibration is required if water droplets are observed.

6.2.1.C Measurement

The solubility of oxygen in water depends on the partial pressure of oxygen in air, the temperature of the water, and the content of dissolved solids in 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 substantially within minutes after sample collection. These sample reactions are especially important when sampling groundwater that is not in equilibrium with the atmosphere.

The solubility of oxygen in water decreases as salinity increases. Correction factors for salinity normally are applied after measuring DO for single-point samples; however, for continuously deployed DO probes on multiparameter instruments that include calibrated specific-conductance sensors, it is wise to activate the instrument's internal salinity correction algorithms to account for a dynamically changing environment. Information that pertains to oxygen solubility and salinity is given in section 6.2.5, including the link to an on-line program that generates tables of DO solubility values and (or) salinity correction factors over a range of user-specified temperature, pressure, and salinity or specific conductance (*http://water.usgs.gov/software/DOTABLES/* accessed March 11, 2013).

Surface water

Standard determinations of DO in riverine surface water represent the cross-sectional median or mean concentration of dissolved oxygen at the time of observation.

- Multiparameter instruments (sondes) are in common use for USGS measurement of DO and other field properties, both for in situ discrete measurements in surface water and for short- or long-term deployment in streams, lakes and reservoirs, and other bodies of surface water. Refer to NFM 6.8, Wagner and others (2006), and manufacturer guidance for additional information regarding the siting and use of multiparameter instruments.
- Measuring the DO concentration at one distinct point in a cross section is valid only for flowing water with a cross-sectional DO variation of less than 0.5 mg/L. Discerning such variation requires a reconnaissance cross-section measurement. **Measurements made at multiple locations in the cross section are recommended as a routine practice, when possible.**
- Determining DO concentration for a single channel at the centroid of flow at the midpoint of the vertical only represents 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 to fulfill study objectives.
- Verify whether or not the instrument in use applies salinity corrections automatically. If not, apply a salinity correction to the saturation values after the DO measurement, referring to section 6.2.5 and table 6.2–7.

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

Follow the steps below to measure DO in surface water:

1. Calibration checks:
    - Check that the thermistor is accurate and that its calibration has been certified by the USGS Water Science Center within the past 12 months; more frequent calibration checks are performed in the field, depending on the field conditions encountered (see NFM 6.1.2.B for specifics).
    - Check the performance of the DO sensor at saturation and zero DO (refer to section 6.2.1.B).
    - If a calibration adjustment is necessary or if it is required to address program protocols, data-quality requirements, or site-specific conditions, calibrate the DO sensor onsite, in accordance with the procedures described in section 6.2.1.B.
2. Examine the variation in DO measured at multiple locations along the cross section (if this reconnaissance step was performed) to help 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 a calibrated temperature sensor from a bridge, cableway, or boat.
        - Do not attach the weight directly to the sensors or sensor cables, because this could damage the sensors or sensor cables.
        - To avoid damaging sensors or cables, contact the instrument manufacturer or vendor for information regarding the weights approved for use with the instrument and how to attach them.
    - **Still-water conditions**—Measure DO at multiple depths at several points in the cross section (see TECHNICAL NOTE 8).
    - **Lakes and reservoirs**—Measure DO at a series of specific depths to determine a vertical profile at each location of interest (see TECHNICAL NOTE 8).

TECHNICAL NOTE 8. For amperometric sensors: If the water velocity at the point of measurement is less than about 1 ft/s, use a stirring device to increase the flow velocity.[14]

- 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. The stir-by-hand method may not be appropriate in lakes, reservoirs, or slow-moving waters (for example, bayous); these water bodies may be stratified at the point of measurement, making accurate DO measurements impossible with a non-stirred amperometric DO probe. This could be especially problematic in areas where DO concentrations change substantially over short distances, such as near the thermocline or bottom sediments.
- High stream velocity also can cause erroneous DO measurements.

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).
4. Record the temperature without removing the sensor from the water.

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[14] Refer to footnote 3 if using a YSI “Rapid Pulse” sensor, for which a stirrer is not needed.

5. After the instrument reading has stabilized, record the median DO concentration (see NFM 6.0). The reading should stabilize to within ±0.2 mg/L.

6. For EWI, EDI, or multiple-vertical 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.

Groundwater

Before the concentration of DO in groundwater can be determined, standing water must be evacuated from the well to ensure that measurements of DO concentration in the well will be representative of formation-water concentration. An adequate well purge ensures the flow of freshwater from the formation into the well (refer to NFM 4.2 and NFM 6.0.3.A for detailed information). Measurement of ambient DO concentrations in groundwater additionally requires use of equipment and procedures that avoid aeration and mitigate losses or gains of dissolved gases in the water being sampled. A bailed sample, for example, is inadmissible for DO measurement because the field sample-decanting process exposes the sample to the atmosphere (NFM 6.0.3); this provision likewise applies to any type of sampling device from which the sample is brought in contact with air when transferred to a measurement or analysis vessel.

Project or program data-quality requirements and objectives, site characteristics, and equipment availability will dictate whether (a) measurements will be made *in situ* (DO measured downhole) or *ex situ* (DO measured above land surface, the inline-flow procedure), and if (b) optical, amperometric, or spectrophotometric methods will be used for DO measurement. This section addresses the use of optical and amperometric sensors, for which the lower threshold for measurement of aqueous DO concentrations is from 1 to 2 mg/L, depending on the instrument being used and the accuracy required.[15] **If the anticipated DO concentration is less than 1.0 mg/L, consider use of spectrophotometric methods (section 6.2.2).**[16]

► If using an optical-sensor instrument at DO less than 1.0 mg/L, first perform a zero-DO calibration check or calibration (instrument permitting), and document the results.

► When anticipating DO concentrations in the hypoxic or suboxic range on a routine or regular basis,

— Optical sensor: Readings to 0.05 mg/L should be verified using the methods described in sections 6.2.2 or 6.2.3. The presence of hydrogen sulfide, however, will not affect the accuracy of the measurement.

— Amperometric sensor: The sensor can be adversely affected by hydrogen sulfide and misread the true DO value.

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[15] The accuracy of DO measurements to 0.05 mg/L with an optical sensor has been field verified against Rhodazine-D spectrophotometric measurement on numerous occasions by USGS field-methods instructors (Gerolamo Casile, U.S. Geological Survey, oral commun., 2012).

[16] Note that spectrophotometric methods for determining DO concentration generally are not approved by the U.S. Environmental Protection Agency for regulatory assessments.

Refer to NFM sections 6.0.1 and 6.0.3 for guidance related to the selection, preparation, and procedures for in situ and ex situ measurement of field-determined properties. Study objectives and site characteristics will dictate the specific method selected. Select the field-measurement system that best fits the requirements for the data-collection effort.

- ► **Downhole (in situ) measurement** (see NFM 6.0.3.B**).** Submersible multiparameter sondes and single-parameter sensors are deployed downhole to the targeted depth interval. Deployment typically involves data collection for a single field trip. The sonde or sensor sometimes is deployed for unattended monitoring, but the appropriate conditions and protocols must be followed (see NFM 6.8). Use of the optical DO sensor makes longer-term deployment more practical, compared to that of the amperometric sensor.

- ► **Inline flowthrough cell/chamber (ex situ) measurement.** Sample is pumped directly (inline) to an airtight, transparent chamber or manufacturer-provided cell having either (1) leak-proof ports (compression fittings) that accommodate either the optical or amperometric DO single-parameter sensor (and other single-parameter sensors), or (2) a multiparameter sonde instrumented with either an optical or amperometric DO sensor. NFM 6.0, figure 6.0–3, diagrams a flowthrough cell system; figure 6.0–5 charts downhole and inline sampling processes.[17]

    - — Sample is transferred using a positive-displacement submersible pump fitted with high-density plastic or fluorocarbon-polymer tubing that is relatively gas impermeable.

    - — Use of transparent materials for the tubing and chamber is needed to allow checking for air bubbles in the water stream or adhering to the sides of the tubing and flowthrough cell or chamber (that have been introduced as an artifact of the sampling procedure, as distinguished from gas bubbles that are native to the formation water). Such air bubbles add significant error to low-level DO measurements and should be excluded (A.F. White, U.S. Geological Survey, written commun., 1993).

    - — Protect exposed sample tubing and the flow-through cell or chamber from direct sunlight.

Do not measure groundwater DO concentration in a sample extracted from a bailer or other sampling device that results in sample exposure to the atmosphere.

Follow the steps below to measure DO in groundwater:

1. Calibration checks: Check the performance of the DO sensor at saturation and zero DO (refer to section 6.2.1.B).

    - Check that the thermistor gives an accurate reading and that its calibration has been verified by the USGS Water Science Center within the past 12 months (see NFM 6.1).

    - Check the performance of the DO sensor at saturation and zero DO (refer to section 6.2.1.B).

    - If field calibration is necessary or if it is required to address program protocols, data-quality requirements, or site-specific conditions, calibrate the DO sensor in accordance with the procedures and restrictions described in section 6.2.1.B.

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[17] See section 6.0, “General Information and Guidelines,” in chapter 6 of this field manual (*http://water.usgs.gov/owq/FieldManual/Chapter6/6.0_contents.html*).

2. Install the DO equipment (see NFM 6.0 for more detailed instructions):
    - **Downhole system**—Lower the DO and temperature sensors to the measuring point, followed by the pump, to monitor DO variation during purging. When an amperometric sensor is used, water needs to flow past the sensor at a velocity of no less than 1 ft/s; attach a mechanical stirrer, if necessary, to maintain this velocity. The optical sensor is not flow dependent.
    - **Inline flowthrough system**—Refer to NFM 6.0 for installation guidelines. If sensors are to be installed in a flowthrough cell or chamber, install the DO sensor immediately downstream of the point of sample inflow. For a system using a multiparameter instrument sonde, install the sonde in the flowthrough cell provided by the manufacturer and in accordance with manufacturer instructions. Be sure to:
        - Install the DO sensor through an airtight grommet, if using a chamber instrumented with single-parameter sensors. Check that the seal around the DO sensor is intact and that the sensors are properly immersed.
        - Shield the sample tubing and flowthrough cell/chamber from direct sunlight to minimize changes to sample temperature (this step is most critical for users of amperometric sensors).
        - Dislodge and flush entrained air bubbles from the tubing walls and flowthrough chamber by tapping the tubing with a blunt tool (see TECHNICAL NOTE 9 below). Note that air bubbles are an indication of air leakage into the sampling system and should be distinguished from gas bubbles that could be native to formation water chemistry.
        - Check for and eliminate backpressure in the flowthrough chamber.
3. **If using an amperometric instrument,** be sure to maintain constant, laminar flow past the DO sensor (refer to footnote 3). Measure and record DO at regular intervals throughout purging. Allow the sensors to equilibrate with groundwater for 5 minutes or more at the flow rate to be used for sampling.
4. Check the stability (measurement 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 ±0.2 mg/L. (For each reading, monitor fluctuations for 30 to 60 seconds and record the median value, if necessary.) If the ±0.2 mg/L criterion is not met, increase the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals.
5. Report sample DO as the median of the final five DO readings recorded. Record on field forms any difficulty with stabilization.
6. Remove the sensor from the water and rinse it with deionized water.

Air bubbles in the lines and flowthrough chamber can add substantial error to DO readings in low DO or oxygen depleted groundwater.

TECHNICAL NOTE 9. Anomalously high DO measurements commonly are caused by aeration of groundwater 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).

6.2.1.D Troubleshooting for Amperometric Instruments

The troubleshooting suggestions given in table 6.2–3 are for amperometric instruments and are not exhaustive; consult the manufacturer of your amperometric instrument for additional guidance. For problems with calibration or measurement using optical sensors, periodically wipe the sensor with a wet cloth. Do not wipe the Teflon membrane; rather, remove water droplets by shaking or other means. Wiping the Teflon membrane may scratch the membrane, resulting in erroneous readings. If problems with the amperometric sensor persist, consult the manufacturer. Faulty batteries can cause erratic readings.

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

Table 6.2–3. Troubleshooting guide for amperometric instruments.

Symptom	Possible cause and corrective action
Instrument drifts or takes excessive time to stabilize	• Thermal equilibrium of water and sensor has not been reached—wait longer. • Weak batteries—replace. • DO sensor needs maintenance—recondition.
Erratic instrument readings	• Break in cable—replace cable. • Faulty connection at instrument or sensor—clean contact and tighten. • Hole in membrane—replace membrane, recondition. • Air bubble in sensor—recondition sensor. • Weak batteries—replace.
Instrument too slow to react	• Gold or silver cathode tarnished—buff with pencil eraser, manufacturer-provided polishing paper, and recondition sensor. • Fouled membrane—replace membrane and recondition sensor.
Instrument will not read zero in sodium sulfite solution	• Solution contains oxygen—make fresh solution. • Instrument still does not read zero— replace membrane and recondition sensor.
Instrument cannot be calibrated to read standards	• Unable to adjust upward—check to see if more than one membrane is on the sensor. • Unable to adjust downward (membrane is probably too tight or too thin)—replace membrane.
Instrument reads inaccurate temperature	• Faulty thermistor or cable—repair or replace.

6.2.2 Spectrophotometric (Rhodazine-D and Indigo-Carmine) Methods

Various spectrophotometric methods (*see* TECHNICAL NOTE 10) are available for determining DO over a broad range of concentrations. The information given in this section, however, is limited to the application of spectrophotometric analysis of Rhodazine-D[18] and Indigo-Carmine reagents for determining DO concentrations in relatively oxygen-deficient (hypoxic) and anoxic[19] waters; that is, DO concentration from about 2 to zero mg/L.[20] The option to measure DO by spectrophotometry in the higher concentration ranges generally is selected when field conditions limit use of optical or amperometric sensor methods. (Non-instrumental analyses of Rhodazine-D and Indigo-Carmine reagent indicators also are available for measuring aqueous DO concentrations, but the analysis can be subject to considerable operator variability, is not applicable to standard USGS field protocols, and is thus beyond the scope of this guidance.)

TECHNICAL NOTE 10. The purpose of photometry is to measure light in a way that takes the sensitivity of human visual system into account. Photometry only measures in the visible spectral region from 360 nm to 830 nm, where human eyes are sensitive. Spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength. The National Institute of Standards and Technology (NIST) maintains the national scales for reflectance and transmittance in the ultraviolet, visible, and near-infrared spectral regions; that is, 250 nm to 2,500 nm (*see* *http://www.nist.gov/pml/div685/grp03/photometry.cfm,* and *http://www.nist.gov/pml/div685/grp03/spectrophotometry.cfm*).

Spectrophotometric methods for DO measurement have been used in USGS field work for measuring DO in oxygen-depleted groundwater and can be adapted for work in oxygen-depleted zones of lakes and reservoirs, but are not approved by the U.S. Environmental Protection Agency for application to regulatory assessments. The Rhodazine-D spectrophotometric method for determining DO in groundwater was introduced by White and others (1990) as a means for obtaining accurate DO data for groundwater at a time when sensor methods lacked the capability of in situ measurement.

- ► The Rhodazine-D spectrophotometric method is applicable to a range from 0.1 to 1.0 mg/L dissolved oxygen in aqueous environments. The Rhodazine-D (phenzone dye) compound, in reduced form, reacts with dissolved oxygen to form a deep rose to red-purple reaction product.
- ► Low-level Indigo-Carmine spectrophotometric methods are applicable to DO concentration ranges from either 0.006 to 0.8 or 0.2 to 2.0 mg/L, depending on the specific manufacturer kit ("ampul" or "ampoule" kit) being used for the range of interest. Indigo Carmine reacts with the dissolved oxygen present in the sample to form a highly colored blue reaction product.
- ► As mentioned previously, USGS technical staff have documented optical sensor measurements[21] at DO concentrations of 0.05 mg/L and Rhodazine-D spectrophotometric readings to be of comparable accuracy. To date, these findings have not been published or verified using different types of optical sensors. Before measuring and reporting hypoxic to anoxic DO concentration data from optical

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[18] Rhodazine-D™ is a proprietary product of CHEMetrics, Inc. (White and others, 1990).

[19] Hypoxic: *Hypoxia* – "A condition in which natural waters have a low concentration of dissolved oxygen (about 2 milligrams per liter compared with a normal level of 8 to 10 milligrams per liter). Stevenson and Wyman (1991); *http://toxics.usgs.gov/definitions/hypoxia.html*. ***Anoxic***, in this document, refers to water that has a very low concentration of dissolved oxygen (that is, less than 0.5 milligrams per liter) (U.S. Geological Survey, 2010; *http://toxics.usgs.gov/definitions/anoxic.html*), or total deprivation of oxygen (U.S. Environmental Protection Agency, 2009).

[20] The information for the concentration range of the spectrophotometric methods discussed was provided from and reviewed by technical specialists representing CHEMetrics, Inc. and the Hach Company. See *http://www.chemetrics.com and www.hach.com*.

[21] Unpublished data. Comparisons were made using an In-Situ Inc. TROLL 9500 Profiler equipped with a rugged dissolved oxygen (RDO) optical sensor (Gerolamo Casile, U.S. Geological Survey, oral commun., 2012).

sensors, the capability and accuracy of the optical sensor in this low DO-concentration range needs to be documented by making side-by-side measurements onsite to compare results with values obtained using a spectrophotometric method.

6.2.2.A Equipment and Supplies

The Rhodazine-D and Indigo-Carmine spectrophotometric methods were designed to minimize atmospheric interaction with the water sampled. Two sampling systems commonly are used: (1) an in situ (submersible or downhole) sampler, such as the assemblies discussed in White and others (1990), and (2) a plastic overflow cell through which sample water is pumped (see equipment and supplies in table 6.2–4).

The sampling system is configured to utilize a self-filling ampoule system with the Rhodazine-D or Indigo Carmine reagent vacuum-sealed inside. DO concentration is determined instrumentally on the resultant solution using a spectrophotometer or photometer. The ampoule kits and spectrophotometer (or photometer) are available commercially. The spectrophotometer (or photometer) selected must be able to be adjusted, either manually or automatically, to the appropriate wavelength of incident light needed for the determination of DO in the resultant colored sample, based on the reagent used. Applicable spectrophotometers, photometers, and ampoule kits are available commercially from various companies and for a variety of concentration ranges.

- ► The accuracy of commercially available reagent kits may not be included with the equipment or supplies purchased. Always check with the manufacturer regarding the accuracy of the specific test kit(s) of interest.
- ► The accuracy of the test kits will typically be a function of the concentration range of DO in the sample.
- ► A spectrophotometer is used to measure the amount of light that a sample absorbs. The instrument operates by passing a beam of light through a sample and measuring the intensity of light received by a detector (*http://www.chm.davidson.edu/vce/spectrophotometry/Spectrophotometry.html*).
- ► Some spectrophotometers are precalibrated specifically for the products or kits developed by the kit manufacturer. If using a spectrophotometer that is not precalibrated for the products being used, calculate the DO concentration using the regression equations provided by the manufacturer of the reagent kit.

Table 6.2–4. Equipment and supplies for the spectrophotometric method of dissolved-oxygen determination using Rhodazine-D™ and Indigo Carmine reagents.

[mm, millimeter; DO, dissolved-oxygen concentration; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Portable spectrophotometer (or photometer)
Appropriate reagent kits for the expected DO range of the environmental condition
Blank ampoule (zero DO), included in each kit
Submersible sampling tool, used in situ, to meet criteria described in White and others (1990). For example, • Manganous sulfate reagent • Plastic sampler device (overflow cell), length of C-flex tubing, and sample pump
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
Lint-free wipes to remove moisture from surface of the ampoule

6.2.2.B Calibration and Interferences

DO is measured as percent absorbance by the spectrophotometer. A calibration chart typically is provided with each chemical reagent kit, along with a regression formula to convert absorbance to micrograms per liter (µg/L) of DO for use with a spectrophotometer that does not perform the conversion in its firmware. Most current spectrophotometers and photometers available for measurement of dissolved oxygen are precalibrated for direct readout of DO concentration in milligrams per liter.

- ► Ensure that an appropriate blank ampoule is used to zero the spectrophotometer (or photometer).
- ► Additional calibration is needed if the method will be used to determine DO in heavily contaminated or acidic waters. This can be done 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.

These chemical reagent-based methods are not subject to salinity or dissolved-gas interferences (ASTM D5543-09, ASTM D 888-12, White and others, 1990; Gilbert and others, 1982). Interferences from total salinity, major dissolved inorganic species, dissolved gases, or temperature are typically negligible with this method. However, color and turbidity in the environmental sample may interfere with both the Rhodazine-D and Indigo-Carmine methods, causing positively biased results. If using these methods in colored or turbid water, first conduct an assessment of the amount of bias attributable to such effects.

- ► Rhodazine-D. The spectrophotometric method using Rhodazine-D reagent is affected by the presence of oxidizing agents, including chlorine, ferric and cupric ions, and hexavalent chromium, resulting in high-biased DO readings (White and others, 1990).[22]
  - — The presence of cupric copper and ferric iron at a concentration less than 50 µg/L may cause a bias of less than 1 µg/L; at 100 µg/L concentration, cupric copper may cause a bias of 5 µg/L, and ferric iron may cause a bias of 7 µg/L.
  - — Sample pH at or below a pH of 2 may cause erroneous results.

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[22] See also *http://www.chemetrics.com/*products/pdf/oxygen_rhodazined.pdf, accessed September 20, 2012.

  - — A hydroquinone concentration greater than 200 µg/L is a positive interferent and its oxidation byproduct, benzoquinone, causes a false positive result. The effect from oxidizing agents can be corrected if the concentrations of the interfering species are known (White and others, 1990).

- ► Indigo Carmine. The spectrophotometric method using Indigo Carmine reagent[23] is affected by ferric iron, hypochlorite (chlorine), and chromate, which can cause a false positive at concentrations equal to or greater than 10 mg/L.
  - — Cupric copper interferes positively at or above 100 mg/L.
  - — Seawater may cause the reagent to precipitate.

6.2.2.C Measurement

USGS spectrophotometric measurement procedures have been tested and quality assured for the determination of DO concentration using the Rhodazine-D and Indigo-Carmine reagents provided in commercially available kits supplied by the CHEMetrics and Hach companies, respectively.[24] While the instructions provided by the manufacturers generally should be followed, augmented instructions and information are provided below to ensure that DO measurement meets USGS standards for accuracy and reproducibility. USGS personnel are advised to make the adjustments described here to the manufacturer-provided instructions.

Rhodazine-D and Indigo-Carmine reagents react with DO to produce an oxidized complex characterized by deep-rose or brightly blue-colored reaction products, respectively. The color intensity is proportional to the concentration of the initial DO present. **Timing is very important for colorimetric analyses made with a spectrophotometer.** Follow the explicit instructions for the waiting time after the sample mixes with the reagent. The reaction with the reagents occurs almost instantaneously for both the Rhodazine-D and Indigo-Carmine methods. Color development continues after the time interval specified for these methods because oxygen from the atmosphere continuously diffuses into the sample through the broken ampule tip.

- ► Do not extend the waiting times specified in the Rhodazine-D and Indigo-Carmine methods, but adhere to them strictly.
- ► Excessive mixing of the ampule before reading the spectrophotometer also may introduce atmospheric oxygen, which can bias the results, resulting in erroneous readings.

Follow the steps below to measure DO using the spectrophotometric method:

1. Familiarize yourself with instructions from the manufacturer for the kit to be used and adjust the instructions to incorporate the procedures that follow, as applicable.
2. Accounting for site characteristics and study objectives, purge the well following guidelines in NFM 4.2.
3. Set the spectrophotometer to an appropriate wavelength for the kit being used. When using a manufacturer-designated DO photometer (or spectrophotometer), verify whether or not introduction of the ampoule provided in the kit will trigger the correct wavelength setting automatically.

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[23] ASTM D 888-12; ASTM D 5543-09; Gilbert and others (1982).

[24] Instructions from the Hach Company and CHEMetrics Inc. for selected colorimetry-based methods at DO concentration ranges relevant to routine USGS sampling were selected for testing because USGS field personnel currently use the equipment and reagent kits from these companies.

4. Zero the spectrophotometer using the blank provided in the kit (follow the manufacturer's instructions).[25]

5. When collecting the sample:

    - Prevent sample aeration. Use a positive-displacement submersible pump and high-density plastic or fluorocarbon polymer sample tubing that is relatively gas impermeable, if possible, throughout measurement.

    - Operate equipment to mitigate losses or gains of dissolved gases. (Consult NFM 6.0 for proper downhole and inline flowthrough-chamber sampling procedures.)

6. Select your sample-collection method: Use either a downhole or overflow-sampler device.

    - *Go to Step 7* for the downhole sampling tool method,[26] *or*

    - *Go to Step 8* for the plastic overflow-sampler device with a suitable pump method.

7. **Downhole system**: After purging the well (NFM 4.2), follow steps 7a through d.

    a. Carefully immerse a reagent-containing ampoule on the sampling tool that is attached to a wire line.

    b. At the desired depth of sample collection (in a well or in surface water), break the scored tip of the ampoule by 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 ampoule tip.

    c. Withdraw the ampoule from the sampling device and invert once to mix the contents of the ampoule, allowing the bubble to travel from end to end; follow the kit-specific instructions regarding the number of ampoule inversions.[27]

    - Take care that this process does not introduce atmospheric oxygen into the ampoule.

    - Make sure the time required to bring the ampoule to the surface does not exceed the waiting times specified by the method. (This method may work best for shallow wells).

    d. Wipe all liquid from the exterior of the ampoule, using a lint-free tissue. Skip to step 9.

8. **Overflow device**: After purging the well (NFM 4.2), follow steps 8a through f.

    a. Connect the plastic overflow-sampling device (table 6.2–4) to the outlet of the pump tubing with C-flex tubing 3 feet (ft) or less in length. The overflow device is used to break the ampoule in the flowing stream of water.

    - If using the **Rhodazine-D** method, the kit is equipped with the appropriate overflow sampling device needed to crack the ampoule.

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[25] Native water may be used if this option is provided by the kit manufacturer.

[26] A downhole sampling tool is described by White and others (1990).

[27] Instructions provided by kit manufacturers specify inverting the ampoule several times with the bubble traveling from end to end to facilitate mixing of reagent and sample. USGS field observations, however, indicate that vigorous or repeated mixing can introduce atmospheric oxygen and bias the measurement (Gerolamo Casile, U.S. Geological Survey, written commun., 2013).

- If using the **Indigo-Carmine** method, adapt the Rhodazine-D instructions as follows, instead of using the directions provided[28]:
  - – Obtain a plastic funnel with a funnel size of approximately 1 cup.
  - – Adapt the funnel to the end of a length of C-flex tubing. This funnel, while overflowing, will allow the tip of the Indigo-Carmine ampoule to be broken very close to where the sample water flows in.

TECHNICAL NOTE 11. Use optically clear materials to enable seeing whether bubbles are entrained in the tubing or flow cell (chamber). Air bubbles that adhere to the sides of the tubing and chamber will add significant error to low-level DO measurements (A.F. White, U.S. Geological Survey, written commun., 1993).

b. Reduce the pumping rate to achieve an even, nonturbulent, laminar rate of flow (for groundwater, about 500 milliliters per minute) that is used for sample collection. While pumping, allow the sampling device to overflow during sample collection.
   - Check for air bubbles in or adhering to the tubing and flowthrough cell (chamber).
   - Tap the tubing with a blunt tool to dislodge entrained air bubbles.

c. Insert the glass ampoule, tip first, into the overflowing sampling device so that the tapered tip is at the bottom of the device, close to the point of water inflow.

d. Snap the tip by gently pressing the upper end of the ampoule toward the wall of the sampling device.
   - The vacuum ampoule will draw in the sample water, leaving a small bubble at one end.
   - Ensure that the ampoule is full before proceeding to step e; this will prevent entraining excess atmospheric oxygen and thereby producing erroneous readings.

e. Withdraw the ampoule from the sampling device and invert to mix the contents of the ampoule, allowing the bubble to travel from end to end; follow the kit-specific instructions regarding the number of ampoule inversions (see footnote 27).

f. Wipe all liquid from the exterior of the ampoule, using a lint-free tissue.

9. Insert the ampoule directly into the spectrophotometer cell holder, either immediately after retrieval or as specified in the kit-specific instructions.
10. Read concentration or absorbance:

    a. Make spectrophotometer readings, adhering as strictly as possible to the manufacturer-specified time interval.
       - **Rhodizine-D**—Record the reading within the time interval directed by the kit manufacturer (for example, within 30 seconds when using the CHEMetrics ampoule kit).

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[28] The Hach Company Indigo Carmine kit instructs placing the sample tube at the bottom of an overflowing beaker, then breaking the ampoule near the sample tubing at the bottom of the beaker. Tests conducted by USGS personnel indicated that substituting the directions in step 8a substantially improve measurement accuracy and reproducibility. (Gerolamo Casile, U.S. Geological Survey, written communication, 2013).

- **Indigo-Carmine**—Record the reading within the time interval directed by the kit manufacturer.

b. If using a spectrophotometer that does not convert absorbance values of DO measurements to milligrams per liter for the kit being used, use regression equations to make the conversion (see White and others, 1990).

11. **Quality control**: Consider utilizing multiple determinations to document the precision and (or) accuracy of the DO concentration to be reported.
    - Repeat steps 9 and 10 twice in rapid succession to document measurement precision.
    - To document the variability of DO concentrations within the water system being measured, repeat steps 4 through 10 on three sequentially collected samples.

Do not exceed the time interval specified for completion of color development.

6.2.3 Iodometric (Winkler) Method

The USGS currently uses the Alsterberg-Azide modification to the Winkler titration procedure for iodometric determination of DO. The precision of measurements using the iodometric method should be within at least ±0.05 mg/L[29] when performed by experienced analysts (American Public Health Association, 2005).

► The iodometric (Winkler) method no longer is being used routinely as a standard field method for measurement of DO in USGS investigations because (1) the accuracy and reproducibility achievable are dependent on the experience and expertise of the data collector, (2) potential environmental interferences (for example, the presence of nitrite, ferrous and ferric iron, and organic matter) require advanced knowledge of the chemistry of the sample, and (3) field conditions can make preventing exposure of the sample to atmospheric oxygen difficult. Nevertheless, the iodometric method is recognized as a reliable standard for producing accurate results when correctly implemented.

► The iodometric (Winkler) method is widely accepted in the scientific community and is used to check the calibration of, and the measurements made with, electrometric DO instrument systems.

— The Winkler method was used to verify the accuracy of optically and amperometrically determined DO concentrations reported by the USGS in an oil spill investigation, in accordance with a request by the U.S. Environmental Protection Agency (Wilde and Skrobialowski, 2011).

— Checking the calibration of electrometric instruments using the Winkler procedure is performed in a controlled (that is, laboratory) environment. The DO instrument is calibrated with air-saturated deionized water in which the DO concentration has been determined by the Winkler method; the DO instrument is then adjusted to the concentration determined from the titration.

— If a saline solution is used to approximate the environmental water, do not apply a salinity correction factor.

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[29] Based on a standard deviation (SD) of ±0.02 mg/L for a three SD accuracy of ±0.06 mg/L.

6.2.3.A Equipment and Supplies

Equipment and supplies needed for the iodometric method are listed in table 6.2–5. The procedure involves the use of reagents available in premeasured pillow packets from commercial suppliers. Alternatively, reagents may be prepared by a chemist or titration technician, as described in American Public Health Association (2005).

- ► The accuracy of commercially obtained reagent packets may differ among manufacturers and other preparers of the reagents and should be recorded in field notes.
- ► Clean all equipment before use.

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

[mL, milliliter; *N*, normal; µS/cm, microsiemens per centimeter at 25 degrees Celsius; NFM, *National Field Manual for the Collection of Water-Quality Data*]

Beaker, 2,000 mL, glass or Teflon
Bottles for biochemical 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
Chemical reagents:[1] • Alkaline iodide-azide reagent • Manganous sulfate reagent • Sulfamic acid granules • Sodium thiosulfate, 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 µS/cm)
Bottle, squeeze dispenser, for deionized water
Thermometer, calibrated (see NFM 6.1 for selection and calibration criteria)
Pocket altimeter-barometer, calibrated, or DO-measurement equipment that includes barometer

[1] Use either commercially prepared reagent pillow packets or analyst-prepared reagents, depending on the data-quality requirements of the study.

6.2.3.B Measurement

This section describes how to make an iodometric determination of DO concentration.

- ► When the purpose of using the Winkler method is to check calibration of an amperometric or luminescent-sensor instrument, start at step 1 below and continue to the end. For quality control, steps 5 and 6 are written so as to verify the Winkler determination in duplicate. This is standard practice and should be followed.
- ► If making a Winkler determination for the DO concentration of an environmental sample, start at step 5, substituting the sample water for deionized water (DIW). Collect the sample and perform the titration as described below on at least two subsamples to provide the appropriate quality control. When filling the BOD bottles, a minimum of three bottle volumes of sample should pass through the bottle to collect the final volume.
  - — **In surface water:** To fill the bottles, use of a sewage sampler is recommended. If a hand-held method is needed, fill the bottles in the water body by tilting them slightly to allow the bottle to slowly fill in a manner so as to avoid turbulence, bubbling, or otherwise entraining air. Keep the filled bottles submerged (in the surface-water body) for about 30 seconds. Next, while the bottle is submerged, insert the stopper firmly in the bottle, taking care not to trap air bubbles.
  - — **In groundwater:** A laminar-flow sample is pumped inline from the well into the bottle, from the bottom to overflowing the top of the bottle and in a manner so as to avoid any turbulence and bubbles. Allow the sample to overflow for at least 30 seconds. Next, while still overflowing, insert the stopper firmly into the bottle, taking care not to trap air bubbles.
  - — Pour off excess water that is trapped on the lip of the stoppered bottle.
  - — Follow step 6 procedures as described below, substituting the sample-filled biochemical oxygen demand (BOD) bottles.
- ► Results of two iodometric titrations should agree within 0.1 mg/L. If they do not agree, repeat the titration on one or more additional subsamples until this quality-assurance criterion is met.

Follow the steps below to check calibration of an optical or amperometric DO instrument using the Winkler Alsterberg-Azide titration:

1. Fill a clean 2,000-mL beaker with deionized water that is near DO saturation. The water temperature should be close to the ambient (field or laboratory) temperature.
2. Prepare the DO-sensing instrument for operation, in accordance with the manufacturer’s instructions.
3. Place the DO sensor in a beaker of DIW. If using an amperometric sensor, maintain a water velocity of at least 1 ft/s flowing passed the sensor. If the sensor is not equipped with a stirring mechanism, use a magnetic stirrer.
4. Monitor the DO concentrations of the DIW with the DO instrument and record the value after the readings have stabilized.
5. Carefully fill two clean BOD bottles with three or more bottle volumes of DIW from the beaker, taking care not to introduce any air bubbles by slowly overflowing the bottles adequately to remove any trapped air bubbles.
6. Determine the DO concentration of the DIW in each BOD bottle, as follows:

a. Add one each of the following dry reagent pillow packets[30]
   - Alkaline iodide-azide (white powder).
   - Manganous sulfate (pinkish-colored powder).

b. Recap the bottle **to prevent air bubbles from being trapped in the bottle.**

c. Invert the bottle 25 times or more to completely dissolve the reagents.
   - An orange-brown flocculent indicates the presence of DO.
   - Allow the flocculent to settle halfway down the bottle (approximately 5 minutes).
   - Invert the bottle 25 times again; let the flocculent settle again until the upper half of the solution is clear.

d. Add one reagent pillow of sulfamic acid (see footnote 30).

e. Recap the bottle without introducing air or air bubbles. Invert the bottle 25 times until all of the flocculent and granules are dissolved, leaving a yellow color.

f. Fill a clean 25-mL buret with 0.025 *N (Normal)* sodium thiosulfate titrant. Remove any air bubbles from the delivery tube beneath the stopcock and zero the meniscus.

g. Using either a clean 200-mL pipet or a 200-mL volumetric flask, measure 200 mL of the sample and dispense the sample into a clean, wide-mouth Erlenmeyer flask.

h. Place the flask on a magnetic stirrer. Carefully insert a clean Teflon stirring bar and stir the sample at a moderate rate without aerating the sample.

i. Add increments of sodium thiosulfate titrant until the color turns pale straw-yellow.

j. Add 1 to 2 mL of starch indicator solution. (This causes the sample to turn dark blue.)

k. Very slowly add more sodium thiosulfate titrant until the sample just turns clear. (A white background behind or below the flask will help to see the color change.)

l. Record the volume of sodium thiosulfate 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,

$$DO\ (mg/L) = \left(\frac{200}{sample\ volume}\right) \times titrant\ added,\ in\ mL \tag{1}$$

m. Record the DO value. Rinse the equipment thoroughly with deionized water.

7. **Quality control**. Titration values for the duplicate samples should agree within 0.1 mg/L.
   - If they do not agree, repeat the titration process (steps 5 and 6a through 6m, above) on one or more additional subsamples until this quality-assurance criterion is met.
   - Record the final, quality-assured value for DO concentration.

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[30] Laboratory-prepared reagents might be prepared instead, depending on data-quality requirements, if titration will be performed by an analyst.

8. Recheck the field instrument for proper functioning, following the manufacturer's recommendations and instructions.
    - Consult the manufacturer if the field instrument does not calibrate properly.
    - Do not use an instrument that fails calibration.

6.2.4 Reporting

USGS personnel are instructed to enter the DO value on the field form indicating method (optical, amperometric, spectrophotometric, or iodometric) used for DO determination.

- ► DO concentrations for the amperometric and optical-sensor methods are measured to the nearest 0.01 mg/L, but currently are reported to the nearest 0.1 mg/L.
- ► DO concentrations for the spectrophotometric/Rhodazine-D and Indigo-Carmine methods are reported to the nearest 0.01 mg/L.
- ► **Note that the percentage of DO saturation in water can be greater than 100.** When the concentration exceeds 20 mg/L, check manufacturer's specifications and:
    - — Report ">20 mg/L" if the manufacturer's instrument range specifications do not exceed 20 mg/L.
    - — Report concentration values up to the maximum specified limit if the manufacturer's instrument range specifications exceed 20 mg/L.
    - — Report "> the listed numerical limit" if the concentration exceeds the manufacturer's specified instrument range.

6.2.5 Correction Factors for Oxygen Solubility Concentrations and Salinity

Solubility concentrations of oxygen in freshwater at various temperatures and pressures (table 6.2–6) and correction factors for salinity based on specific conductance (table 6.2–7) were generated from the equations of Benson and Krause (1980, 1984) and can be customized to cover the range and decimal places needed; see U.S. Geological Survey Office of Water Quality Technical Memorandum 2011.03 (Myers, 2011). **By accessing "DOTABLES," the interactive software that generated tables 6.2–6 and 6.2–7, the user can self-generate individual values or tables of a specific range of oxygen-solubility and salinity correction factors: http://water.usgs.gov/software/DOTABLES/.**[31]

- ► To adjust freshwater oxygen-saturation values for the effects of salinity, use correction factors based on chloride concentration or specific conductance. Refer to the manufacturer's instructions for the DO instrument before applying a salinity correction.
- ► Correcting DO solubility for saline waters (greater than 2,000 microsiemens per centimeter or 1,000 mg/L chloride) varies with instrument type, calibration method, and the salts in solution.

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[31] DOTABLES is an online program that generates tables of dissolved oxygen (DO) solubility values and (or) salinity correction factors over a range of user-specified values for water temperature, barometric pressure, and salinity or specific conductance. In addition to generating tables, DOTABLES can compute a single-value of oxygen solubility and percent saturation for a specific instance of temperature, pressure, and salinity.

- — The correction based on specific conductance (table 6.2–7) is more useful because accurate conductivity can be determined easily from a field measurement.
- — Salinity correction factors based on chloride can be calculated using information provided in U.S. Geological Survey Quality of Water Branch Technical Memorandum 79.10 (Pickering, 1979).

► DO instruments either use an automatic internal salinity correction, a manual salinity control knob for internal correction, or the calibration control knob for manual correction of salinity. Check that instruments with automatic internal salinity correction use approved salinity correction factors.

Example of salinity correction

Suppose a DO measurement is made in water with a temperature of 20.0 degrees Celsius, an atmospheric pressure of 750 millimeters of mercury, and a specific conductance of 8,000 microsiemens per centimeter (µS/cm). The freshwater oxygen solubility from table 6.2–6 is 8.97 mg/L for that temperature and pressure; the salinity correction factor from table 6.2–7 is 0.9733 for that temperature and specific conductance. The solubility of oxygen under these conditions then is:

$$8.97\ mg/L\ x\ 0.97331 = 8.73\ mg/L \tag{2}$$

The presence of more dissolved ions in the saline water decreases the oxygen solubility.

► If calibrating an instrument that does not have an internal salinity compensation algorithm, you could adjust the DO instrument to read 8.73 mg/L for a 100 percent saturation condition.

► If the DO measurement made with an amperometric or optical sensor under the above conditions were 7.50 mg/L and the DO probe did not have an internal salinity compensation algorithm, then the actual DO concentration should be reported as 7.50 mg/L multiplied by 0.9733, which equals 7.30 mg/L.

► **Do not use a salinity correction factor for measurements made with the iodometric (Winkler) or spectrophotometric methods.**

Example of percent saturation calculation

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

$$DO\ (percent\ saturation) = \frac{measured\ DO\ (mg\,/\,L)}{DO\ (mg\,/\,L\ at\ 100\ percent\ saturation)} \times 100 \tag{3}$$

For a salinity-corrected DO measurement of 7.30 mg/L for a sample in which the oxygen solubility (salinity corrected) is 8.73 mg/L as in the above example, the percent DO saturation would be the dividend of 7.30 divided by 8.73, multiplied by 100, which equals 83.6 percent. Note that for measurements with the iodometric (Winkler) or spectrophotometric methods, salinity correction factors are not applied to the measurement concentration.

Table 6.2–6. Solubility of oxygen infreshwater at various temperatures and pressures.

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius; Values for atmospheric pressures from 600 to 695 millimeters of mercury begin several pages forward]

Temp. (deg C)	Atmospheric pressure, in millimeters of mercury																			
	700	705	710	715	720	725	730	735	740	745	750	755	760	765	770	775	780	785	790	795
0.0	13.46	13.56	13.65	13.75	13.85	13.94	14.04	14.14	14.23	14.33	14.43	14.52	14.62	14.72	14.81	14.91	15.01	15.10	15.20	15.30
0.5	13.27	13.37	13.46	13.56	13.65	13.75	13.84	13.94	14.03	14.13	14.23	14.32	14.42	14.51	14.61	14.70	14.80	14.89	14.99	15.08
1.0	13.09	13.18	13.28	13.37	13.46	13.56	13.65	13.75	13.84	13.93	14.03	14.12	14.22	14.31	14.40	14.50	14.59	14.69	14.78	14.87
1.5	12.91	13.00	13.09	13.19	13.28	13.37	13.46	13.56	13.65	13.74	13.84	13.93	14.02	14.11	14.21	14.30	14.39	14.48	14.58	14.67
2.0	12.73	12.82	12.91	13.01	13.10	13.19	13.28	13.37	13.46	13.56	13.65	13.74	13.83	13.92	14.01	14.10	14.20	14.29	14.38	14.47
2.5	12.56	12.65	12.74	12.83	12.92	13.01	13.10	13.19	13.28	13.37	13.46	13.55	13.64	13.73	13.82	13.91	14.00	14.10	14.19	14.28
3.0	12.39	12.48	12.57	12.66	12.75	12.84	12.93	13.02	13.10	13.19	13.28	13.37	13.46	13.55	13.64	13.73	13.82	13.91	14.00	14.09
3.5	12.23	12.31	12.40	12.49	12.58	12.67	12.75	12.84	12.93	13.02	13.11	13.19	13.28	13.37	13.46	13.55	13.63	13.72	13.81	13.90
4.0	12.07	12.15	12.24	12.33	12.41	12.50	12.59	12.67	12.76	12.85	12.93	13.02	13.11	13.20	13.28	13.37	13.46	13.54	13.63	13.72
4.5	11.91	11.99	12.08	12.17	12.25	12.34	12.42	12.51	12.59	12.68	12.77	12.85	12.94	13.02	13.11	13.20	13.28	13.37	13.45	13.54
5.0	11.75	11.84	11.92	12.01	12.09	12.18	12.26	12.35	12.43	12.52	12.60	12.69	12.77	12.86	12.94	13.03	13.11	13.19	13.28	13.36
5.5	11.60	11.69	11.77	11.86	11.94	12.02	12.11	12.19	12.27	12.36	12.44	12.52	12.61	12.69	12.78	12.86	12.94	13.03	13.11	13.19
6.0	11.46	11.54	11.62	11.70	11.79	11.87	11.95	12.04	12.12	12.20	12.28	12.37	12.45	12.53	12.61	12.70	12.78	12.86	12.94	13.03
6.5	11.31	11.39	11.48	11.56	11.64	11.72	11.80	11.88	11.97	12.05	12.13	12.21	12.29	12.37	12.46	12.54	12.62	12.70	12.78	12.86
7.0	11.17	11.25	11.33	11.41	11.49	11.58	11.66	11.74	11.82	11.90	11.98	12.06	12.14	12.22	12.30	12.38	12.46	12.54	12.62	12.70
7.5	11.03	11.11	11.19	11.27	11.35	11.43	11.51	11.59	11.67	11.75	11.83	11.91	11.99	12.07	12.15	12.23	12.31	12.39	12.47	12.55
8.0	10.90	10.98	11.06	11.14	11.21	11.29	11.37	11.45	11.53	11.61	11.69	11.76	11.84	11.92	12.00	12.08	12.16	12.24	12.32	12.39
8.5	10.77	10.84	10.92	11.00	11.08	11.16	11.23	11.31	11.39	11.47	11.54	11.62	11.70	11.78	11.86	11.93	12.01	12.09	12.17	12.24
9.0	10.64	10.71	10.79	10.87	10.94	11.02	11.10	11.18	11.25	11.33	11.41	11.48	11.56	11.64	11.71	11.79	11.87	11.94	12.02	12.10
9.5	10.51	10.59	10.66	10.74	10.81	10.89	10.97	11.04	11.12	11.19	11.27	11.35	11.42	11.50	11.57	11.65	11.73	11.80	11.88	11.95
10.0	10.39	10.46	10.54	10.61	10.69	10.76	10.84	10.91	10.99	11.06	11.14	11.21	11.29	11.36	11.44	11.51	11.59	11.66	11.74	11.81
10.5	10.26	10.34	10.41	10.49	10.56	10.64	10.71	10.78	10.86	10.93	11.01	11.08	11.16	11.23	11.30	11.38	11.45	11.53	11.60	11.68
11.0	10.15	10.22	10.29	10.37	10.44	10.51	10.59	10.66	10.73	10.81	10.88	10.95	11.03	11.10	11.17	11.25	11.32	11.39	11.47	11.54
11.5	10.03	10.10	10.17	10.25	10.32	10.39	10.47	10.54	10.61	10.68	10.76	10.83	10.90	10.97	11.05	11.12	11.19	11.26	11.34	11.41
12.0	9.91	9.99	10.06	10.13	10.20	10.27	10.35	10.42	10.49	10.56	10.63	10.71	10.78	10.85	10.92	10.99	11.06	11.14	11.21	11.28
12.5	9.80	9.87	9.94	10.02	10.09	10.16	10.23	10.30	10.37	10.44	10.51	10.58	10.66	10.73	10.80	10.87	10.94	11.01	11.08	11.15
13.0	9.69	9.76	9.83	9.90	9.97	10.04	10.11	10.19	10.26	10.33	10.40	10.47	10.54	10.61	10.68	10.75	10.82	10.89	10.96	11.03
13.5	9.59	9.65	9.72	9.79	9.86	9.93	10.00	10.07	10.14	10.21	10.28	10.35	10.42	10.49	10.56	10.63	10.70	10.77	10.84	10.91
14.0	9.48	9.55	9.62	9.69	9.76	9.82	9.89	9.96	10.03	10.10	10.17	10.24	10.31	10.37	10.44	10.51	10.58	10.65	10.72	10.79

Table 6.2–6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius; Values for atmospheric pressures from 600 to 695 millimeters of mercury begin several pages forward]

Temp. (deg C)	Atmospheric pressure, in millimeters of mercury																			
	700	705	710	715	720	725	730	735	740	745	750	755	760	765	770	775	780	785	790	795
14.5	9.38	9.44	9.51	9.58	9.65	9.72	9.78	9.85	9.92	9.99	10.06	10.13	10.19	10.26	10.33	10.40	10.47	10.53	10.60	10.67
15.0	9.27	9.34	9.41	9.48	9.54	9.61	9.68	9.75	9.81	9.88	9.95	10.02	10.08	10.15	10.22	10.29	10.35	10.42	10.49	10.56
15.5	9.18	9.24	9.31	9.38	9.44	9.51	9.58	9.64	9.71	9.78	9.84	9.91	9.98	10.04	10.11	10.18	10.24	10.31	10.38	10.44
16.0	9.08	9.14	9.21	9.28	9.34	9.41	9.47	9.54	9.61	9.67	9.74	9.80	9.87	9.94	10.00	10.07	10.13	10.20	10.27	10.33
16.5	8.98	9.05	9.11	9.18	9.24	9.31	9.37	9.44	9.50	9.57	9.64	9.70	9.77	9.83	9.90	9.96	10.03	10.09	10.16	10.22
17.0	8.89	8.95	9.02	9.08	9.15	9.21	9.28	9.34	9.41	9.47	9.54	9.60	9.66	9.73	9.79	9.86	9.92	9.99	10.05	10.12
17.5	8.80	8.86	8.92	8.99	9.05	9.12	9.18	9.24	9.31	9.37	9.44	9.50	9.57	9.63	9.69	9.76	9.82	9.89	9.95	10.01
18.0	8.70	8.77	8.83	8.90	8.96	9.02	9.09	9.15	9.21	9.28	9.34	9.40	9.47	9.53	9.59	9.66	9.72	9.78	9.85	9.91
18.5	8.62	8.68	8.74	8.80	8.87	8.93	8.99	9.06	9.12	9.18	9.24	9.31	9.37	9.43	9.50	9.56	9.62	9.69	9.75	9.81
19.0	8.53	8.59	8.65	8.72	8.78	8.84	8.90	8.96	9.03	9.09	9.15	9.21	9.28	9.34	9.40	9.46	9.53	9.59	9.65	9.71
19.5	8.44	8.50	8.57	8.63	8.69	8.75	8.81	8.87	8.94	9.00	9.06	9.12	9.18	9.25	9.31	9.37	9.43	9.49	9.55	9.62
20.0	8.36	8.42	8.48	8.54	8.60	8.66	8.73	8.79	8.85	8.91	8.97	9.03	9.09	9.15	9.21	9.28	9.34	9.40	9.46	9.52
20.5	8.28	8.34	8.40	8.46	8.52	8.58	8.64	8.70	8.76	8.82	8.88	8.94	9.00	9.06	9.12	9.18	9.25	9.31	9.37	9.43
21.0	8.19	8.25	8.31	8.37	8.43	8.49	8.55	8.61	8.67	8.73	8.79	8.85	8.92	8.98	9.04	9.10	9.16	9.22	9.28	9.34
21.5	8.11	8.17	8.23	8.29	8.35	8.41	8.47	8.53	8.59	8.65	8.71	8.77	8.83	8.89	8.95	9.01	9.07	9.13	9.19	9.25
22.0	8.04	8.09	8.15	8.21	8.27	8.33	8.39	8.45	8.51	8.57	8.63	8.68	8.74	8.80	8.86	8.92	8.98	9.04	9.10	9.16
22.5	7.96	8.02	8.08	8.13	8.19	8.25	8.31	8.37	8.43	8.48	8.54	8.60	8.66	8.72	8.78	8.84	8.89	8.95	9.01	9.07
23.0	7.88	7.94	8.00	8.06	8.11	8.17	8.23	8.29	8.35	8.40	8.46	8.52	8.58	8.64	8.69	8.75	8.81	8.87	8.93	8.98
23.5	7.81	7.86	7.92	7.98	8.04	8.09	8.15	8.21	8.27	8.33	8.38	8.44	8.50	8.56	8.61	8.67	8.73	8.79	8.84	8.90
24.0	7.73	7.79	7.85	7.90	7.96	8.02	8.08	8.13	8.19	8.25	8.30	8.36	8.42	8.48	8.53	8.59	8.65	8.70	8.76	8.82
24.5	7.66	7.72	7.77	7.83	7.89	7.94	8.00	8.06	8.11	8.17	8.23	8.28	8.34	8.40	8.45	8.51	8.57	8.62	8.68	8.74
25.0	7.59	7.65	7.70	7.76	7.81	7.87	7.93	7.98	8.04	8.10	8.15	8.21	8.26	8.32	8.38	8.43	8.49	8.54	8.60	8.66
25.5	7.52	7.58	7.63	7.69	7.74	7.80	7.85	7.91	7.97	8.02	8.08	8.13	8.19	8.24	8.30	8.35	8.41	8.47	8.52	8.58
26.0	7.45	7.51	7.56	7.62	7.67	7.73	7.78	7.84	7.89	7.95	8.00	8.06	8.11	8.17	8.22	8.28	8.33	8.39	8.44	8.50
26.5	7.38	7.44	7.49	7.55	7.60	7.66	7.71	7.77	7.82	7.88	7.93	7.99	8.04	8.10	8.15	8.20	8.26	8.31	8.37	8.42
27.0	7.32	7.37	7.43	7.48	7.53	7.59	7.64	7.70	7.75	7.81	7.86	7.91	7.97	8.02	8.08	8.13	8.19	8.24	8.29	8.35
27.5	7.25	7.30	7.36	7.41	7.47	7.52	7.57	7.63	7.68	7.74	7.79	7.84	7.90	7.95	8.01	8.06	8.11	8.17	8.22	8.27
28.0	7.19	7.24	7.29	7.35	7.40	7.45	7.51	7.56	7.61	7.67	7.72	7.77	7.83	7.88	7.93	7.99	8.04	8.10	8.15	8.20
28.5	7.12	7.18	7.23	7.28	7.33	7.39	7.44	7.49	7.55	7.60	7.65	7.71	7.76	7.81	7.87	7.92	7.97	8.02	8.08	8.13

Table 6.2–6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius; Values for atmospheric pressures from 600 to 695 millimeters of mercury begin several pages forward]

Temp. (deg C)	Atmospheric pressure, in millimeters of mercury																			
	700	705	710	715	720	725	730	735	740	745	750	755	760	765	770	775	780	785	790	795
29.0	7.06	7.11	7.16	7.22	7.27	7.32	7.38	7.43	7.48	7.53	7.59	7.64	7.69	7.74	7.80	7.85	7.90	7.95	8.01	8.06
29.5	7.00	7.05	7.10	7.15	7.21	7.26	7.31	7.36	7.42	7.47	7.52	7.57	7.62	7.68	7.73	7.78	7.83	7.89	7.94	7.99
30.0	6.94	6.99	7.04	7.09	7.14	7.20	7.25	7.30	7.35	7.40	7.46	7.51	7.56	7.61	7.66	7.71	7.77	7.82	7.87	7.92
30.5	6.88	6.93	6.98	7.03	7.08	7.13	7.19	7.24	7.29	7.34	7.39	7.44	7.49	7.55	7.60	7.65	7.70	7.75	7.80	7.85
31.0	6.82	6.87	6.92	6.97	7.02	7.07	7.12	7.17	7.23	7.28	7.33	7.38	7.43	7.48	7.53	7.58	7.63	7.69	7.74	7.79
31.5	6.76	6.81	6.86	6.91	6.96	7.01	7.06	7.11	7.16	7.21	7.27	7.32	7.37	7.42	7.47	7.52	7.57	7.62	7.67	7.72
32.0	6.70	6.75	6.80	6.85	6.90	6.95	7.00	7.05	7.10	7.15	7.20	7.25	7.30	7.36	7.41	7.46	7.51	7.56	7.61	7.66
32.5	6.64	6.69	6.74	6.79	6.84	6.89	6.94	6.99	7.04	7.09	7.14	7.19	7.24	7.29	7.34	7.39	7.44	7.49	7.54	7.59
33.0	6.59	6.64	6.69	6.74	6.79	6.84	6.89	6.93	6.98	7.03	7.08	7.13	7.18	7.23	7.28	7.33	7.38	7.43	7.48	7.53
33.5	6.53	6.58	6.63	6.68	6.73	6.78	6.83	6.88	6.93	6.98	7.02	7.07	7.12	7.17	7.22	7.27	7.32	7.37	7.42	7.47
34.0	6.48	6.53	6.57	6.62	6.67	6.72	6.77	6.82	6.87	6.92	6.97	7.02	7.06	7.11	7.16	7.21	7.26	7.31	7.36	7.41
34.5	6.42	6.47	6.52	6.57	6.62	6.67	6.71	6.76	6.81	6.86	6.91	6.96	7.01	7.06	7.10	7.15	7.20	7.25	7.30	7.35
35.0	6.37	6.42	6.47	6.51	6.56	6.61	6.66	6.71	6.76	6.80	6.85	6.90	6.95	7.00	7.05	7.09	7.14	7.19	7.24	7.29
35.5	6.32	6.36	6.41	6.46	6.51	6.56	6.60	6.65	6.70	6.75	6.80	6.84	6.89	6.94	6.99	7.04	7.08	7.13	7.18	7.23
36.0	6.26	6.31	6.36	6.41	6.45	6.50	6.55	6.60	6.65	6.69	6.74	6.79	6.84	6.88	6.93	6.98	7.03	7.08	7.12	7.17
36.5	6.21	6.26	6.31	6.35	6.40	6.45	6.50	6.54	6.59	6.64	6.69	6.73	6.78	6.83	6.88	6.92	6.97	7.02	7.07	7.11
37.0	6.16	6.21	6.26	6.30	6.35	6.40	6.44	6.49	6.54	6.59	6.63	6.68	6.73	6.77	6.82	6.87	6.92	6.96	7.01	7.06
37.5	6.11	6.16	6.20	6.25	6.30	6.35	6.39	6.44	6.49	6.53	6.58	6.63	6.67	6.72	6.77	6.81	6.86	6.91	6.95	7.00
38.0	6.06	6.11	6.15	6.20	6.25	6.29	6.34	6.39	6.43	6.48	6.53	6.57	6.62	6.67	6.71	6.76	6.81	6.85	6.90	6.95
38.5	6.01	6.06	6.10	6.15	6.20	6.24	6.29	6.34	6.38	6.43	6.47	6.52	6.57	6.61	6.66	6.71	6.75	6.80	6.84	6.89
39.0	5.96	6.01	6.05	6.10	6.15	6.19	6.24	6.29	6.33	6.38	6.42	6.47	6.52	6.56	6.61	6.65	6.70	6.75	6.79	6.84
39.5	5.91	5.96	6.01	6.05	6.10	6.14	6.19	6.23	6.28	6.33	6.37	6.42	6.46	6.51	6.56	6.60	6.65	6.69	6.74	6.78
40.0	5.87	5.91	5.96	6.00	6.05	6.09	6.14	6.19	6.23	6.28	6.32	6.37	6.41	6.46	6.50	6.55	6.59	6.64	6.69	6.73

Table 6.2–6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius]

Temp.	Atmospheric pressure, in millimeters of mercury																			
(deg C)	600	605	610	615	620	625	630	635	640	645	650	655	660	665	670	675	680	685	690	695
0.0	11.53	11.62	11.72	11.82	11.91	12.01	12.11	12.20	12.30	12.40	12.49	12.59	12.69	12.78	12.88	12.98	13.07	13.17	13.27	13.36
0.5	11.36	11.46	11.56	11.65	11.75	11.84	11.94	12.03	12.13	12.22	12.32	12.41	12.51	12.60	12.70	12.80	12.89	12.99	13.08	13.18
1.0	11.21	11.30	11.39	11.49	11.58	11.68	11.77	11.86	11.96	12.05	12.15	12.24	12.34	12.43	12.52	12.62	12.71	12.81	12.90	12.99
1.5	11.05	11.14	11.24	11.33	11.42	11.52	11.61	11.70	11.79	11.89	11.98	12.07	12.17	12.26	12.35	12.44	12.54	12.63	12.72	12.81
2.0	10.90	10.99	11.08	11.18	11.27	11.36	11.45	11.54	11.63	11.72	11.82	11.91	12.00	12.09	12.18	12.27	12.37	12.46	12.55	12.64
2.5	10.75	10.84	10.93	11.02	11.11	11.20	11.29	11.39	11.48	11.57	11.66	11.75	11.84	11.93	12.02	12.11	12.20	12.29	12.38	12.47
3.0	10.61	10.70	10.79	10.88	10.96	11.05	11.14	11.23	11.32	11.41	11.50	11.59	11.68	11.77	11.86	11.95	12.03	12.12	12.21	12.30
3.5	10.47	10.55	10.64	10.73	10.82	10.91	10.99	11.08	11.17	11.26	11.35	11.43	11.52	11.61	11.70	11.79	11.87	11.96	12.05	12.14
4.0	10.33	10.42	10.50	10.59	10.68	10.76	10.85	10.94	11.02	11.11	11.20	11.28	11.37	11.46	11.54	11.63	11.72	11.81	11.89	11.98
4.5	10.19	10.28	10.36	10.45	10.54	10.62	10.71	10.79	10.88	10.97	11.05	11.14	11.22	11.31	11.39	11.48	11.57	11.65	11.74	11.82
5.0	10.06	10.15	10.23	10.32	10.40	10.48	10.57	10.65	10.74	10.82	10.91	10.99	11.08	11.16	11.25	11.33	11.42	11.50	11.59	11.67
5.5	9.93	10.02	10.10	10.18	10.27	10.35	10.43	10.52	10.60	10.68	10.77	10.85	10.94	11.02	11.10	11.19	11.27	11.35	11.44	11.52
6.0	9.80	9.89	9.97	10.05	10.14	10.22	10.30	10.38	10.47	10.55	10.63	10.71	10.80	10.88	10.96	11.04	11.13	11.21	11.29	11.37
6.5	9.68	9.76	9.84	9.93	10.01	10.09	10.17	10.25	10.33	10.42	10.50	10.58	10.66	10.74	10.82	10.91	10.99	11.07	11.15	11.23
7.0	9.56	9.64	9.72	9.80	9.88	9.96	10.04	10.12	10.20	10.29	10.37	10.45	10.53	10.61	10.69	10.77	10.85	10.93	11.01	11.09
7.5	9.44	9.52	9.60	9.68	9.76	9.84	9.92	10.00	10.08	10.16	10.24	10.32	10.40	10.48	10.56	10.64	10.72	10.80	10.87	10.95
8.0	9.33	9.40	9.48	9.56	9.64	9.72	9.80	9.88	9.95	10.03	10.11	10.19	10.27	10.35	10.43	10.51	10.58	10.66	10.74	10.82
8.5	9.21	9.29	9.37	9.44	9.52	9.60	9.68	9.76	9.83	9.91	9.99	10.07	10.14	10.22	10.30	10.38	10.46	10.53	10.61	10.69
9.0	9.10	9.18	9.25	9.33	9.41	9.48	9.56	9.64	9.71	9.79	9.87	9.95	10.02	10.10	10.18	10.25	10.33	10.41	10.48	10.56
9.5	8.99	9.07	9.14	9.22	9.29	9.37	9.45	9.52	9.60	9.67	9.75	9.83	9.90	9.98	10.05	10.13	10.21	10.28	10.36	10.43
10.0	8.88	8.96	9.03	9.11	9.18	9.26	9.33	9.41	9.49	9.56	9.64	9.71	9.79	9.86	9.94	10.01	10.09	10.16	10.24	10.31
10.5	8.78	8.85	8.93	9.00	9.08	9.15	9.23	9.30	9.37	9.45	9.52	9.60	9.67	9.75	9.82	9.89	9.97	10.04	10.12	10.19
11.0	8.68	8.75	8.82	8.90	8.97	9.04	9.12	9.19	9.26	9.34	9.41	9.48	9.56	9.63	9.71	9.78	9.85	9.93	10.00	10.07
11.5	8.58	8.65	8.72	8.79	8.87	8.94	9.01	9.08	9.16	9.23	9.30	9.38	9.45	9.52	9.59	9.67	9.74	9.81	9.88	9.96
12.0	8.48	8.55	8.62	8.69	8.77	8.84	8.91	8.98	9.05	9.12	9.20	9.27	9.34	9.41	9.48	9.56	9.63	9.70	9.77	9.84
12.5	8.38	8.45	8.52	8.59	8.67	8.74	8.81	8.88	8.95	9.02	9.09	9.16	9.23	9.31	9.38	9.45	9.52	9.59	9.66	9.73
13.0	8.29	8.36	8.43	8.50	8.57	8.64	8.71	8.78	8.85	8.92	8.99	9.06	9.13	9.20	9.27	9.34	9.41	9.48	9.55	9.62
13.5	8.19	8.26	8.33	8.40	8.47	8.54	8.61	8.68	8.75	8.82	8.89	8.96	9.03	9.10	9.17	9.24	9.31	9.38	9.45	9.52
14.0	8.10	8.17	8.24	8.31	8.38	8.45	8.52	8.58	8.65	8.72	8.79	8.86	8.93	9.00	9.07	9.14	9.20	9.27	9.34	9.41

Table 6.2–6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius]

Temp. (deg C)	Atmospheric pressure, in millimeters of mercury																			
	600	**605**	**610**	**615**	**620**	**625**	**630**	**635**	**640**	**645**	**650**	**655**	**660**	**665**	**670**	**675**	**680**	**685**	**690**	**695**
14.5	8.01	8.08	8.15	8.22	8.29	8.35	8.42	8.49	8.56	8.63	8.69	8.76	8.83	8.90	8.97	9.04	9.10	9.17	9.24	9.31
15.0	7.93	7.99	8.06	8.13	8.20	8.26	8.33	8.40	8.47	8.53	8.60	8.67	8.74	8.80	8.87	8.94	9.00	9.07	9.14	9.21
15.5	7.84	7.91	7.97	8.04	8.11	8.17	8.24	8.31	8.37	8.44	8.51	8.57	8.64	8.71	8.77	8.84	8.91	8.97	9.04	9.11
16.0	7.76	7.82	7.89	7.95	8.02	8.09	8.15	8.22	8.28	8.35	8.42	8.48	8.55	8.61	8.68	8.75	8.81	8.88	8.95	9.01
16.5	7.67	7.74	7.80	7.87	7.93	8.00	8.07	8.13	8.20	8.26	8.33	8.39	8.46	8.52	8.59	8.65	8.72	8.79	8.85	8.92
17.0	7.59	7.66	7.72	7.79	7.85	7.92	7.98	8.05	8.11	8.17	8.24	8.30	8.37	8.43	8.50	8.56	8.63	8.69	8.76	8.82
17.5	7.51	7.58	7.64	7.70	7.77	7.83	7.90	7.96	8.03	8.09	8.15	8.22	8.28	8.35	8.41	8.47	8.54	8.60	8.67	8.73
18.0	7.43	7.50	7.56	7.62	7.69	7.75	7.81	7.88	7.94	8.01	8.07	8.13	8.20	8.26	8.32	8.39	8.45	8.51	8.58	8.64
18.5	7.36	7.42	7.48	7.55	7.61	7.67	7.73	7.80	7.86	7.92	7.99	8.05	8.11	8.18	8.24	8.30	8.36	8.43	8.49	8.55
19.0	7.28	7.34	7.41	7.47	7.53	7.59	7.66	7.72	7.78	7.84	7.90	7.97	8.03	8.09	8.15	8.22	8.28	8.34	8.40	8.47
19.5	7.21	7.27	7.33	7.39	7.45	7.52	7.58	7.64	7.70	7.76	7.82	7.89	7.95	8.01	8.07	8.13	8.20	8.26	8.32	8.38
20.0	7.13	7.20	7.26	7.32	7.38	7.44	7.50	7.56	7.62	7.68	7.75	7.81	7.87	7.93	7.99	8.05	8.11	8.17	8.24	8.30
20.5	7.06	7.12	7.18	7.24	7.31	7.37	7.43	7.49	7.55	7.61	7.67	7.73	7.79	7.85	7.91	7.97	8.03	8.09	8.15	8.21
21.0	6.99	7.05	7.11	7.17	7.23	7.29	7.35	7.41	7.47	7.53	7.59	7.65	7.71	7.77	7.83	7.89	7.95	8.01	8.07	8.13
21.5	6.92	6.98	7.04	7.10	7.16	7.22	7.28	7.34	7.40	7.46	7.52	7.58	7.64	7.70	7.76	7.82	7.88	7.94	7.99	8.05
22.0	6.85	6.91	6.97	7.03	7.09	7.15	7.21	7.27	7.33	7.39	7.45	7.50	7.56	7.62	7.68	7.74	7.80	7.86	7.92	7.98
22.5	6.79	6.85	6.90	6.96	7.02	7.08	7.14	7.20	7.26	7.31	7.37	7.43	7.49	7.55	7.61	7.67	7.72	7.78	7.84	7.90
23.0	6.72	6.78	6.84	6.90	6.95	7.01	7.07	7.13	7.19	7.24	7.30	7.36	7.42	7.48	7.53	7.59	7.65	7.71	7.77	7.82
23.5	6.66	6.71	6.77	6.83	6.89	6.94	7.00	7.06	7.12	7.17	7.23	7.29	7.35	7.40	7.46	7.52	7.58	7.63	7.69	7.75
24.0	6.59	6.65	6.71	6.76	6.82	6.88	6.94	6.99	7.05	7.11	7.16	7.22	7.28	7.33	7.39	7.45	7.51	7.56	7.62	7.68
24.5	6.53	6.59	6.64	6.70	6.76	6.81	6.87	6.93	6.98	7.04	7.10	7.15	7.21	7.27	7.32	7.38	7.44	7.49	7.55	7.61
25.0	6.47	6.52	6.58	6.64	6.69	6.75	6.81	6.86	6.92	6.97	7.03	7.09	7.14	7.20	7.25	7.31	7.37	7.42	7.48	7.53
25.5	6.41	6.46	6.52	6.57	6.63	6.69	6.74	6.80	6.85	6.91	6.96	7.02	7.08	7.13	7.19	7.24	7.30	7.35	7.41	7.46
26.0	6.35	6.40	6.46	6.51	6.57	6.62	6.68	6.73	6.79	6.84	6.90	6.95	7.01	7.07	7.12	7.18	7.23	7.29	7.34	7.40
26.5	6.29	6.34	6.40	6.45	6.51	6.56	6.62	6.67	6.73	6.78	6.84	6.89	6.95	7.00	7.06	7.11	7.16	7.22	7.27	7.33
27.0	6.23	6.28	6.34	6.39	6.45	6.50	6.56	6.61	6.67	6.72	6.77	6.83	6.88	6.94	6.99	7.05	7.10	7.15	7.21	7.26
27.5	6.17	6.23	6.28	6.33	6.39	6.44	6.50	6.55	6.60	6.66	6.71	6.77	6.82	6.87	6.93	6.98	7.04	7.09	7.14	7.20
28.0	6.12	6.17	6.22	6.28	6.33	6.38	6.44	6.49	6.54	6.60	6.65	6.70	6.76	6.81	6.87	6.92	6.97	7.03	7.08	7.13
28.5	6.06	6.11	6.17	6.22	6.27	6.33	6.38	6.43	6.49	6.54	6.59	6.64	6.70	6.75	6.80	6.86	6.91	6.96	7.02	7.07

Table 6.2–6. Solubility of oxygen in freshwater at various temperatures and pressures.—Continued

[Solubility shown in milligrams per liter. Values based on published equations by Benson and Krause (1980 and 1984). Temp. deg C, temperature in degrees Celsius]

Temp.	Atmospheric pressure, in millimeters of mercury																			
(deg C)	600	605	610	615	620	625	630	635	640	645	650	655	660	665	670	675	680	685	690	695
29.0	6.01	6.06	6.11	6.16	6.22	6.27	6.32	6.37	6.43	6.48	6.53	6.59	6.64	6.69	6.74	6.80	6.85	6.90	6.95	7.01
29.5	5.95	6.00	6.06	6.11	6.16	6.21	6.27	6.32	6.37	6.42	6.47	6.53	6.58	6.63	6.68	6.74	6.79	6.84	6.89	6.95
30.0	5.90	5.95	6.00	6.05	6.11	6.16	6.21	6.26	6.31	6.37	6.42	6.47	6.52	6.57	6.63	6.68	6.73	6.78	6.83	6.88
30.5	5.85	5.90	5.95	6.00	6.05	6.10	6.16	6.21	6.26	6.31	6.36	6.41	6.46	6.52	6.57	6.62	6.67	6.72	6.77	6.82
31.0	5.79	5.85	5.90	5.95	6.00	6.05	6.10	6.15	6.20	6.25	6.31	6.36	6.41	6.46	6.51	6.56	6.61	6.66	6.71	6.77
31.5	5.74	5.79	5.84	5.90	5.95	6.00	6.05	6.10	6.15	6.20	6.25	6.30	6.35	6.40	6.45	6.50	6.55	6.61	6.66	6.71
32.0	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.10	6.15	6.20	6.25	6.30	6.35	6.40	6.45	6.50	6.55	6.60	6.65
32.5	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.09	6.14	6.19	6.24	6.29	6.34	6.39	6.44	6.49	6.54	6.59
33.0	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.09	6.14	6.19	6.24	6.29	6.34	6.39	6.44	6.49	6.54
33.5	5.54	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.09	6.14	6.19	6.24	6.28	6.33	6.38	6.43	6.48
34.0	5.50	5.54	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.99	6.04	6.08	6.13	6.18	6.23	6.28	6.33	6.38	6.43
34.5	5.45	5.50	5.55	5.59	5.64	5.69	5.74	5.79	5.84	5.89	5.94	5.98	6.03	6.08	6.13	6.18	6.23	6.28	6.32	6.37
35.0	5.40	5.45	5.50	5.55	5.59	5.64	5.69	5.74	5.79	5.84	5.88	5.93	5.98	6.03	6.08	6.13	6.18	6.22	6.27	6.32
35.5	5.35	5.40	5.45	5.50	5.55	5.59	5.64	5.69	5.74	5.79	5.84	5.88	5.93	5.98	6.03	6.08	6.12	6.17	6.22	6.27
36.0	5.31	5.36	5.40	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.79	5.83	5.88	5.93	5.98	6.02	6.07	6.12	6.17	6.22
36.5	5.26	5.31	5.36	5.41	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.78	5.83	5.88	5.93	5.97	6.02	6.07	6.12	6.16
37.0	5.22	5.27	5.31	5.36	5.41	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.78	5.83	5.88	5.93	5.97	6.02	6.07	6.11
37.5	5.17	5.22	5.27	5.31	5.36	5.41	5.45	5.50	5.55	5.60	5.64	5.69	5.74	5.78	5.83	5.88	5.92	5.97	6.02	6.06
38.0	5.13	5.18	5.22	5.27	5.32	5.36	5.41	5.46	5.50	5.55	5.60	5.64	5.69	5.73	5.78	5.83	5.87	5.92	5.97	6.01
38.5	5.09	5.13	5.18	5.22	5.27	5.32	5.36	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.83	5.87	5.92	5.97
39.0	5.04	5.09	5.13	5.18	5.23	5.27	5.32	5.36	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.82	5.87	5.92
39.5	5.00	5.05	5.09	5.14	5.18	5.23	5.27	5.32	5.37	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.82	5.87
40.0	4.96	5.00	5.05	5.09	5.14	5.18	5.23	5.28	5.32	5.37	5.41	5.46	5.50	5.55	5.59	5.64	5.69	5.73	5.78	5.82

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

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	0	1000	2000	3000	4000	5000	6000	7000	8000	9000	10000	11000	12000	13000	14000
0.0	1.0000	0.9961	0.9922	0.9882	0.9843	0.9804	0.9764	0.9724	0.9684	0.9644	0.9604	0.9564	0.9524	0.9483	0.9443
1.0	1.0000	0.9961	0.9923	0.9884	0.9845	0.9805	0.9766	0.9727	0.9687	0.9648	0.9608	0.9568	0.9528	0.9488	0.9448
2.0	1.0000	0.9962	0.9923	0.9885	0.9846	0.9807	0.9768	0.9729	0.9690	0.9651	0.9611	0.9572	0.9532	0.9493	0.9453
3.0	1.0000	0.9962	0.9924	0.9886	0.9847	0.9809	0.9770	0.9732	0.9693	0.9654	0.9615	0.9576	0.9536	0.9497	0.9458
4.0	1.0000	0.9962	0.9925	0.9887	0.9849	0.9811	0.9772	0.9734	0.9696	0.9657	0.9618	0.9579	0.9541	0.9502	0.9462
5.0	1.0000	0.9963	0.9925	0.9888	0.9850	0.9812	0.9774	0.9736	0.9698	0.9660	0.9622	0.9583	0.9545	0.9506	0.9467
6.0	1.0000	0.9963	0.9926	0.9889	0.9851	0.9814	0.9776	0.9739	0.9701	0.9663	0.9625	0.9587	0.9549	0.9510	0.9472
7.0	1.0000	0.9963	0.9927	0.9890	0.9853	0.9816	0.9778	0.9741	0.9703	0.9666	0.9628	0.9590	0.9552	0.9514	0.9476
8.0	1.0000	0.9964	0.9927	0.9891	0.9854	0.9817	0.9780	0.9743	0.9706	0.9669	0.9631	0.9594	0.9556	0.9519	0.9481
9.0	1.0000	0.9964	0.9928	0.9892	0.9855	0.9819	0.9782	0.9745	0.9708	0.9672	0.9634	0.9597	0.9560	0.9523	0.9485
10.0	1.0000	0.9964	0.9928	0.9893	0.9856	0.9820	0.9784	0.9747	0.9711	0.9674	0.9637	0.9601	0.9564	0.9527	0.9489
11.0	1.0000	0.9965	0.9929	0.9893	0.9858	0.9822	0.9786	0.9750	0.9713	0.9677	0.9640	0.9604	0.9567	0.9530	0.9494
12.0	1.0000	0.9965	0.9930	0.9894	0.9859	0.9823	0.9787	0.9752	0.9716	0.9680	0.9643	0.9607	0.9571	0.9534	0.9498
13.0	1.0000	0.9965	0.9930	0.9895	0.9860	0.9825	0.9789	0.9754	0.9718	0.9682	0.9646	0.9610	0.9574	0.9538	0.9502
14.0	1.0000	0.9965	0.9931	0.9896	0.9861	0.9826	0.9791	0.9756	0.9720	0.9685	0.9649	0.9613	0.9578	0.9542	0.9506
15.0	1.0000	0.9966	0.9931	0.9897	0.9862	0.9827	0.9793	0.9758	0.9723	0.9687	0.9652	0.9617	0.9581	0.9545	0.9510
16.0	1.0000	0.9966	0.9932	0.9898	0.9863	0.9829	0.9794	0.9760	0.9725	0.9690	0.9655	0.9620	0.9584	0.9549	0.9513
17.0	1.0000	0.9966	0.9932	0.9898	0.9864	0.9830	0.9796	0.9761	0.9727	0.9692	0.9657	0.9622	0.9587	0.9552	0.9517
18.0	1.0000	0.9967	0.9933	0.9899	0.9865	0.9831	0.9797	0.9763	0.9729	0.9695	0.9660	0.9625	0.9591	0.9556	0.9521
19.0	1.0000	0.9967	0.9933	0.9900	0.9866	0.9833	0.9799	0.9765	0.9731	0.9697	0.9663	0.9628	0.9594	0.9559	0.9524
20.0	1.0000	0.9967	0.9934	0.9901	0.9867	0.9834	0.9800	0.9767	0.9733	0.9699	0.9665	0.9631	0.9597	0.9562	0.9528
21.0	1.0000	0.9967	0.9934	0.9902	0.9868	0.9835	0.9802	0.9769	0.9735	0.9701	0.9668	0.9634	0.9600	0.9566	0.9531
22.0	1.0000	0.9968	0.9935	0.9902	0.9869	0.9836	0.9803	0.9770	0.9737	0.9704	0.9670	0.9636	0.9603	0.9569	0.9535
23.0	1.0000	0.9968	0.9935	0.9903	0.9870	0.9838	0.9805	0.9772	0.9739	0.9706	0.9672	0.9639	0.9605	0.9572	0.9538
24.0	1.0000	0.9968	0.9936	0.9904	0.9871	0.9839	0.9806	0.9774	0.9741	0.9708	0.9675	0.9642	0.9608	0.9575	0.9541
25.0	1.0000	0.9968	0.9936	0.9904	0.9872	0.9840	0.9808	0.9775	0.9743	0.9710	0.9677	0.9644	0.9611	0.9578	0.9545
26.0	1.0000	0.9968	0.9937	0.9905	0.9873	0.9841	0.9809	0.9777	0.9744	0.9712	0.9679	0.9647	0.9614	0.9581	0.9548
27.0	1.0000	0.9969	0.9937	0.9906	0.9874	0.9842	0.9810	0.9778	0.9746	0.9714	0.9681	0.9649	0.9616	0.9584	0.9551
28.0	1.0000	0.9969	0.9938	0.9906	0.9875	0.9843	0.9812	0.9780	0.9748	0.9716	0.9684	0.9651	0.9619	0.9586	0.9554
29.0	1.0000	0.9969	0.9938	0.9907	0.9876	0.9844	0.9813	0.9781	0.9750	0.9718	0.9686	0.9654	0.9621	0.9589	0.9557

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

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	15000	16000	17000	18000	19000	20000	21000	22000	23000	24000	25000	26000	27000	28000	29000
0.0	0.9402	0.9361	0.9321	0.9280	0.9239	0.9198	0.9157	0.9116	0.9074	0.9033	0.8992	0.8950	0.8909	0.8867	0.8826
1.0	0.9408	0.9367	0.9327	0.9286	0.9246	0.9205	0.9164	0.9124	0.9083	0.9042	0.9001	0.8960	0.8918	0.8877	0.8836
2.0	0.9413	0.9373	0.9333	0.9293	0.9252	0.9212	0.9172	0.9131	0.9091	0.9050	0.9009	0.8969	0.8928	0.8887	0.8846
3.0	0.9418	0.9378	0.9339	0.9299	0.9259	0.9219	0.9179	0.9139	0.9099	0.9058	0.9018	0.8978	0.8937	0.8897	0.8856
4.0	0.9423	0.9384	0.9345	0.9305	0.9266	0.9226	0.9186	0.9146	0.9107	0.9067	0.9027	0.8986	0.8946	0.8906	0.8866
5.0	0.9428	0.9389	0.9350	0.9311	0.9272	0.9233	0.9193	0.9154	0.9114	0.9075	0.9035	0.8995	0.8955	0.8915	0.8875
6.0	0.9433	0.9395	0.9356	0.9317	0.9278	0.9239	0.9200	0.9161	0.9122	0.9082	0.9043	0.9004	0.8964	0.8924	0.8885
7.0	0.9438	0.9400	0.9361	0.9323	0.9284	0.9246	0.9207	0.9168	0.9129	0.9090	0.9051	0.9012	0.8973	0.8933	0.8894
8.0	0.9443	0.9405	0.9367	0.9329	0.9290	0.9252	0.9213	0.9175	0.9136	0.9098	0.9059	0.9020	0.8981	0.8942	0.8903
9.0	0.9447	0.9410	0.9372	0.9334	0.9296	0.9258	0.9220	0.9182	0.9143	0.9105	0.9067	0.9028	0.8989	0.8951	0.8912
10.0	0.9452	0.9415	0.9377	0.9340	0.9302	0.9264	0.9226	0.9188	0.9150	0.9112	0.9074	0.9036	0.8998	0.8959	0.8921
11.0	0.9457	0.9419	0.9382	0.9345	0.9308	0.9270	0.9233	0.9195	0.9157	0.9119	0.9082	0.9044	0.9006	0.8968	0.8929
12.0	0.9461	0.9424	0.9387	0.9350	0.9313	0.9276	0.9239	0.9201	0.9164	0.9126	0.9089	0.9051	0.9014	0.8976	0.8938
13.0	0.9465	0.9429	0.9392	0.9355	0.9319	0.9282	0.9245	0.9208	0.9171	0.9133	0.9096	0.9059	0.9021	0.8984	0.8946
14.0	0.9470	0.9433	0.9397	0.9361	0.9324	0.9287	0.9251	0.9214	0.9177	0.9140	0.9103	0.9066	0.9029	0.8992	0.8954
15.0	0.9474	0.9438	0.9402	0.9366	0.9329	0.9293	0.9257	0.9220	0.9183	0.9147	0.9110	0.9073	0.9036	0.8999	0.8962
16.0	0.9478	0.9442	0.9406	0.9370	0.9334	0.9298	0.9262	0.9226	0.9190	0.9153	0.9117	0.9080	0.9044	0.9007	0.8970
17.0	0.9482	0.9446	0.9411	0.9375	0.9340	0.9304	0.9268	0.9232	0.9196	0.9160	0.9123	0.9087	0.9051	0.9014	0.8978
18.0	0.9486	0.9451	0.9415	0.9380	0.9345	0.9309	0.9273	0.9238	0.9202	0.9166	0.9130	0.9094	0.9058	0.9022	0.8985
19.0	0.9490	0.9455	0.9420	0.9385	0.9349	0.9314	0.9279	0.9243	0.9208	0.9172	0.9136	0.9101	0.9065	0.9029	0.8993
20.0	0.9493	0.9459	0.9424	0.9389	0.9354	0.9319	0.9284	0.9249	0.9214	0.9178	0.9143	0.9107	0.9071	0.9036	0.9000
21.0	0.9497	0.9463	0.9428	0.9394	0.9359	0.9324	0.9289	0.9254	0.9219	0.9184	0.9149	0.9114	0.9078	0.9043	0.9007
22.0	0.9501	0.9467	0.9432	0.9398	0.9363	0.9329	0.9294	0.9260	0.9225	0.9190	0.9155	0.9120	0.9085	0.9049	0.9014
23.0	0.9504	0.9470	0.9436	0.9402	0.9368	0.9334	0.9299	0.9265	0.9230	0.9196	0.9161	0.9126	0.9091	0.9056	0.9021
24.0	0.9508	0.9474	0.9440	0.9406	0.9372	0.9338	0.9304	0.9270	0.9236	0.9201	0.9167	0.9132	0.9097	0.9063	0.9028
25.0	0.9511	0.9478	0.9444	0.9411	0.9377	0.9343	0.9309	0.9275	0.9241	0.9207	0.9172	0.9138	0.9104	0.9069	0.9034
26.0	0.9515	0.9481	0.9448	0.9415	0.9381	0.9347	0.9314	0.9280	0.9246	0.9212	0.9178	0.9144	0.9110	0.9075	0.9041
27.0	0.9518	0.9485	0.9452	0.9419	0.9385	0.9352	0.9318	0.9285	0.9251	0.9217	0.9183	0.9149	0.9115	0.9081	0.9047
28.0	0.9521	0.9488	0.9455	0.9422	0.9389	0.9356	0.9323	0.9289	0.9256	0.9222	0.9189	0.9155	0.9121	0.9087	0.9053
29.0	0.9524	0.9492	0.9459	0.9426	0.9393	0.9360	0.9327	0.9294	0.9261	0.9228	0.9194	0.9161	0.9127	0.9093	0.9060

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

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	30000	31000	32000	33000	34000	35000	36000	37000	38000	39000	40000	41000	42000	43000	44000
0.0	0.8784	0.8742	0.8701	0.8659	0.8617	0.8575	0.8533	0.8491	0.8449	0.8407	0.8365	0.8323	0.8281	0.8239	0.8197
1.0	0.8795	0.8753	0.8712	0.8670	0.8629	0.8587	0.8546	0.8504	0.8462	0.8421	0.8379	0.8337	0.8296	0.8254	0.8212
2.0	0.8805	0.8764	0.8723	0.8682	0.8641	0.8599	0.8558	0.8517	0.8476	0.8434	0.8393	0.8351	0.8310	0.8268	0.8227
3.0	0.8815	0.8775	0.8734	0.8693	0.8652	0.8611	0.8570	0.8529	0.8488	0.8447	0.8406	0.8365	0.8324	0.8283	0.8242
4.0	0.8825	0.8785	0.8745	0.8704	0.8664	0.8623	0.8582	0.8542	0.8501	0.8460	0.8419	0.8379	0.8338	0.8297	0.8256
5.0	0.8835	0.8795	0.8755	0.8715	0.8675	0.8635	0.8594	0.8554	0.8513	0.8473	0.8433	0.8392	0.8351	0.8311	0.8270
6.0	0.8845	0.8805	0.8766	0.8726	0.8686	0.8646	0.8606	0.8566	0.8526	0.8485	0.8445	0.8405	0.8365	0.8325	0.8284
7.0	0.8855	0.8815	0.8776	0.8736	0.8697	0.8657	0.8617	0.8577	0.8538	0.8498	0.8458	0.8418	0.8378	0.8338	0.8298
8.0	0.8864	0.8825	0.8786	0.8746	0.8707	0.8668	0.8628	0.8589	0.8549	0.8510	0.8470	0.8431	0.8391	0.8351	0.8311
9.0	0.8873	0.8834	0.8796	0.8757	0.8718	0.8678	0.8639	0.8600	0.8561	0.8522	0.8482	0.8443	0.8404	0.8364	0.8325
10.0	0.8882	0.8844	0.8805	0.8766	0.8728	0.8689	0.8650	0.8611	0.8572	0.8533	0.8494	0.8455	0.8416	0.8377	0.8338
11.0	0.8891	0.8853	0.8815	0.8776	0.8738	0.8699	0.8661	0.8622	0.8583	0.8545	0.8506	0.8467	0.8428	0.8389	0.8351
12.0	0.8900	0.8862	0.8824	0.8786	0.8748	0.8709	0.8671	0.8633	0.8594	0.8556	0.8517	0.8479	0.8440	0.8402	0.8363
13.0	0.8908	0.8871	0.8833	0.8795	0.8757	0.8719	0.8681	0.8643	0.8605	0.8567	0.8529	0.8490	0.8452	0.8414	0.8375
14.0	0.8917	0.8879	0.8842	0.8804	0.8767	0.8729	0.8691	0.8654	0.8616	0.8578	0.8540	0.8502	0.8464	0.8426	0.8388
15.0	0.8925	0.8888	0.8851	0.8813	0.8776	0.8739	0.8701	0.8664	0.8626	0.8588	0.8551	0.8513	0.8475	0.8437	0.8400
16.0	0.8933	0.8896	0.8859	0.8822	0.8785	0.8748	0.8711	0.8674	0.8636	0.8599	0.8561	0.8524	0.8486	0.8449	0.8411
17.0	0.8941	0.8905	0.8868	0.8831	0.8794	0.8757	0.8720	0.8683	0.8646	0.8609	0.8572	0.8535	0.8497	0.8460	0.8423
18.0	0.8949	0.8913	0.8876	0.8840	0.8803	0.8766	0.8730	0.8693	0.8656	0.8619	0.8582	0.8545	0.8508	0.8471	0.8434
19.0	0.8957	0.8921	0.8884	0.8848	0.8812	0.8775	0.8739	0.8702	0.8666	0.8629	0.8592	0.8556	0.8519	0.8482	0.8445
20.0	0.8964	0.8928	0.8892	0.8856	0.8820	0.8784	0.8748	0.8711	0.8675	0.8639	0.8602	0.8566	0.8529	0.8493	0.8456
21.0	0.8972	0.8936	0.8900	0.8864	0.8828	0.8793	0.8757	0.8720	0.8684	0.8648	0.8612	0.8576	0.8539	0.8503	0.8467
22.0	0.8979	0.8943	0.8908	0.8872	0.8837	0.8801	0.8765	0.8729	0.8693	0.8658	0.8622	0.8585	0.8549	0.8513	0.8477
23.0	0.8986	0.8951	0.8915	0.8880	0.8845	0.8809	0.8774	0.8738	0.8702	0.8667	0.8631	0.8595	0.8559	0.8523	0.8487
24.0	0.8993	0.8958	0.8923	0.8888	0.8853	0.8817	0.8782	0.8747	0.8711	0.8676	0.8640	0.8605	0.8569	0.8533	0.8497
25.0	0.9000	0.8965	0.8930	0.8895	0.8860	0.8825	0.8790	0.8755	0.8720	0.8685	0.8649	0.8614	0.8578	0.8543	0.8507
26.0	0.9006	0.8972	0.8937	0.8903	0.8868	0.8833	0.8798	0.8763	0.8728	0.8693	0.8658	0.8623	0.8588	0.8552	0.8517
27.0	0.9013	0.8979	0.8944	0.8910	0.8875	0.8841	0.8806	0.8771	0.8736	0.8702	0.8667	0.8632	0.8597	0.8562	0.8527
28.0	0.9019	0.8985	0.8951	0.8917	0.8883	0.8848	0.8814	0.8779	0.8745	0.8710	0.8675	0.8641	0.8606	0.8571	0.8536
29.0	0.9026	0.8992	0.8958	0.8924	0.8890	0.8856	0.8821	0.8787	0.8753	0.8718	0.8684	0.8649	0.8615	0.8580	0.8545

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

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius; salinity correction factors for 30 to 35 degrees Celsius begin several pages forward]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	45000	46000	47000	48000	49000	50000	51000	52000	53000	54000	55000	56000	57000	58000	59000
0.0	0.8155	0.8112	0.8070	0.8028	0.7986	0.7944	0.7901	0.7859	0.7817	0.7775	0.7733	0.7691	0.7648	0.7606	0.7564
1.0	0.8170	0.8128	0.8086	0.8045	0.8003	0.7961	0.7919	0.7877	0.7835	0.7793	0.7751	0.7709	0.7668	0.7626	0.7584
2.0	0.8185	0.8144	0.8102	0.8061	0.8019	0.7978	0.7936	0.7894	0.7853	0.7811	0.7770	0.7728	0.7686	0.7645	0.7603
3.0	0.8200	0.8159	0.8118	0.8077	0.8035	0.7994	0.7953	0.7911	0.7870	0.7829	0.7788	0.7746	0.7705	0.7664	0.7623
4.0	0.8215	0.8174	0.8133	0.8092	0.8051	0.8010	0.7969	0.7928	0.7887	0.7846	0.7805	0.7764	0.7723	0.7682	0.7641
5.0	0.8230	0.8189	0.8148	0.8108	0.8067	0.8026	0.7986	0.7945	0.7904	0.7863	0.7823	0.7782	0.7741	0.7700	0.7660
6.0	0.8244	0.8204	0.8163	0.8123	0.8082	0.8042	0.8002	0.7961	0.7921	0.7880	0.7840	0.7799	0.7759	0.7718	0.7678
7.0	0.8258	0.8218	0.8178	0.8138	0.8098	0.8057	0.8017	0.7977	0.7937	0.7897	0.7857	0.7816	0.7776	0.7736	0.7696
8.0	0.8272	0.8232	0.8192	0.8152	0.8112	0.8073	0.8033	0.7993	0.7953	0.7913	0.7873	0.7833	0.7793	0.7753	0.7713
9.0	0.8285	0.8246	0.8206	0.8167	0.8127	0.8088	0.8048	0.8008	0.7969	0.7929	0.7889	0.7850	0.7810	0.7770	0.7731
10.0	0.8299	0.8259	0.8220	0.8181	0.8141	0.8102	0.8063	0.8023	0.7984	0.7945	0.7905	0.7866	0.7826	0.7787	0.7748
11.0	0.8312	0.8273	0.8234	0.8195	0.8156	0.8117	0.8077	0.8038	0.7999	0.7960	0.7921	0.7882	0.7843	0.7804	0.7764
12.0	0.8324	0.8286	0.8247	0.8208	0.8170	0.8131	0.8092	0.8053	0.8014	0.7975	0.7936	0.7898	0.7859	0.7820	0.7781
13.0	0.8337	0.8299	0.8260	0.8222	0.8183	0.8145	0.8106	0.8067	0.8029	0.7990	0.7952	0.7913	0.7874	0.7836	0.7797
14.0	0.8349	0.8311	0.8273	0.8235	0.8197	0.8158	0.8120	0.8082	0.8043	0.8005	0.7966	0.7928	0.7890	0.7851	0.7813
15.0	0.8362	0.8324	0.8286	0.8248	0.8210	0.8172	0.8134	0.8095	0.8057	0.8019	0.7981	0.7943	0.7905	0.7867	0.7828
16.0	0.8374	0.8336	0.8298	0.8260	0.8223	0.8185	0.8147	0.8109	0.8071	0.8033	0.7995	0.7958	0.7920	0.7882	0.7844
17.0	0.8385	0.8348	0.8310	0.8273	0.8235	0.8198	0.8160	0.8123	0.8085	0.8047	0.8010	0.7972	0.7934	0.7896	0.7859
18.0	0.8397	0.8360	0.8322	0.8285	0.8248	0.8210	0.8173	0.8136	0.8098	0.8061	0.8023	0.7986	0.7948	0.7911	0.7873
19.0	0.8408	0.8371	0.8334	0.8297	0.8260	0.8223	0.8186	0.8149	0.8112	0.8074	0.8037	0.8000	0.7963	0.7925	0.7888
20.0	0.8419	0.8383	0.8346	0.8309	0.8272	0.8235	0.8198	0.8161	0.8124	0.8087	0.8050	0.8013	0.7976	0.7939	0.7902
21.0	0.8430	0.8394	0.8357	0.8321	0.8284	0.8247	0.8211	0.8174	0.8137	0.8100	0.8064	0.8027	0.7990	0.7953	0.7916
22.0	0.8441	0.8405	0.8368	0.8332	0.8296	0.8259	0.8223	0.8186	0.8150	0.8113	0.8076	0.8040	0.8003	0.7967	0.7930
23.0	0.8451	0.8415	0.8379	0.8343	0.8307	0.8271	0.8234	0.8198	0.8162	0.8126	0.8089	0.8053	0.8016	0.7980	0.7943
24.0	0.8462	0.8426	0.8390	0.8354	0.8318	0.8282	0.8246	0.8210	0.8174	0.8138	0.8102	0.8065	0.8029	0.7993	0.7957
25.0	0.8472	0.8436	0.8400	0.8365	0.8329	0.8293	0.8257	0.8222	0.8186	0.8150	0.8114	0.8078	0.8042	0.8006	0.7970
26.0	0.8482	0.8446	0.8411	0.8375	0.8340	0.8304	0.8269	0.8233	0.8197	0.8162	0.8126	0.8090	0.8054	0.8018	0.7983
27.0	0.8491	0.8456	0.8421	0.8386	0.8350	0.8315	0.8280	0.8244	0.8209	0.8173	0.8138	0.8102	0.8066	0.8031	0.7995
28.0	0.8501	0.8466	0.8431	0.8396	0.8361	0.8326	0.8290	0.8255	0.8220	0.8184	0.8149	0.8114	0.8078	0.8043	0.8007
29.0	0.8510	0.8476	0.8441	0.8406	0.8371	0.8336	0.8301	0.8266	0.8231	0.8196	0.8160	0.8125	0.8090	0.8055	0.8019

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

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	0	**1000**	**2000**	**3000**	**4000**	**5000**	**6000**	**7000**	**8000**	**9000**	**10000**	**11000**	**12000**	**13000**	**14000**
30.0	1.0000	0.9969	0.9939	0.9908	0.9877	0.9845	0.9814	0.9783	0.9751	0.9720	0.9688	0.9656	0.9624	0.9592	0.9560
31.0	1.0000	0.9970	0.9939	0.9908	0.9877	0.9846	0.9815	0.9784	0.9753	0.9721	0.9690	0.9658	0.9626	0.9595	0.9563
32.0	1.0000	0.9970	0.9939	0.9909	0.9878	0.9847	0.9817	0.9785	0.9754	0.9723	0.9692	0.9660	0.9629	0.9597	0.9565
33.0	1.0000	0.9970	0.9940	0.9909	0.9879	0.9848	0.9818	0.9787	0.9756	0.9725	0.9694	0.9662	0.9631	0.9600	0.9568
34.0	1.0000	0.9970	0.9940	0.9910	0.9880	0.9849	0.9819	0.9788	0.9757	0.9727	0.9696	0.9665	0.9633	0.9602	0.9571
35.0	1.0000	0.9970	0.9940	0.9911	0.9880	0.9850	0.9820	0.9790	0.9759	0.9728	0.9698	0.9667	0.9636	0.9605	0.9573

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	15000	**16000**	**17000**	**18000**	**19000**	**20000**	**21000**	**22000**	**23000**	**24000**	**25000**	**26000**	**27000**	**28000**	**29000**
30.0	0.9527	0.9495	0.9463	0.9430	0.9397	0.9364	0.9332	0.9299	0.9266	0.9232	0.9199	0.9166	0.9133	0.9099	0.9066
31.0	0.9530	0.9498	0.9466	0.9434	0.9401	0.9369	0.9336	0.9303	0.9270	0.9237	0.9204	0.9171	0.9138	0.9105	0.9071
32.0	0.9533	0.9501	0.9469	0.9437	0.9405	0.9373	0.9340	0.9308	0.9275	0.9242	0.9209	0.9176	0.9143	0.9110	0.9077
33.0	0.9536	0.9505	0.9473	0.9441	0.9409	0.9376	0.9344	0.9312	0.9279	0.9247	0.9214	0.9181	0.9149	0.9116	0.9083
34.0	0.9539	0.9508	0.9476	0.9444	0.9412	0.9380	0.9348	0.9316	0.9284	0.9251	0.9219	0.9186	0.9154	0.9121	0.9088
35.0	0.9542	0.9511	0.9479	0.9448	0.9416	0.9384	0.9352	0.9320	0.9288	0.9256	0.9224	0.9191	0.9159	0.9126	0.9094

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	30000	**31000**	**32000**	**33000**	**34000**	**35000**	**36000**	**37000**	**38000**	**39000**	**40000**	**41000**	**42000**	**43000**	**44000**
30.0	0.9032	0.8998	0.8964	0.8931	0.8897	0.8863	0.8829	0.8795	0.8760	0.8726	0.8692	0.8658	0.8623	0.8589	0.8554
31.0	0.9038	0.9005	0.8971	0.8937	0.8904	0.8870	0.8836	0.8802	0.8768	0.8734	0.8700	0.8666	0.8632	0.8597	0.8563
32.0	0.9044	0.9011	0.8977	0.8944	0.8910	0.8877	0.8843	0.8809	0.8776	0.8742	0.8708	0.8674	0.8640	0.8606	0.8572
33.0	0.9050	0.9017	0.8984	0.8950	0.8917	0.8884	0.8850	0.8817	0.8783	0.8749	0.8716	0.8682	0.8648	0.8614	0.8580
34.0	0.9056	0.9023	0.8990	0.8957	0.8923	0.8890	0.8857	0.8824	0.8790	0.8757	0.8723	0.8690	0.8656	0.8622	0.8588
35.0	0.9061	0.9028	0.8996	0.8963	0.8930	0.8897	0.8864	0.8830	0.8797	0.8764	0.8731	0.8697	0.8664	0.8630	0.8597

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

[Factors are dimensionless. Values based on published equations by Benson and Krause (1984). Temp. deg C, temperature in degrees Celsius]

Temp. (deg C)	Specific conductance, in microsiemens per centimeter at 25 degrees Celsius														
	45000	**46000**	**47000**	**48000**	**49000**	**50000**	**51000**	**52000**	**53000**	**54000**	**55000**	**56000**	**57000**	**58000**	**59000**
30.0	0.8520	0.8485	0.8450	0.8416	0.8381	0.8346	0.8311	0.8276	0.8241	0.8207	0.8172	0.8137	0.8102	0.8066	0.8031
31.0	0.8529	0.8494	0.8460	0.8425	0.8391	0.8356	0.8321	0.8287	0.8252	0.8217	0.8182	0.8148	0.8113	0.8078	0.8043
32.0	0.8537	0.8503	0.8469	0.8435	0.8400	0.8366	0.8331	0.8297	0.8262	0.8228	0.8193	0.8159	0.8124	0.8089	0.8054
33.0	0.8546	0.8512	0.8478	0.8444	0.8410	0.8375	0.8341	0.8307	0.8272	0.8238	0.8204	0.8169	0.8135	0.8100	0.8066
34.0	0.8555	0.8521	0.8487	0.8453	0.8419	0.8385	0.8351	0.8317	0.8282	0.8248	0.8214	0.8180	0.8145	0.8111	0.8077
35.0	0.8563	0.8529	0.8496	0.8462	0.8428	0.8394	0.8360	0.8326	0.8292	0.8258	0.8224	0.8190	0.8156	0.8122	0.8087

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pH 6.4

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

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pH 6.4

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

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

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

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

By definition,

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

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

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

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

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

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

6.4.1 EQUIPMENT AND SUPPLIES

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

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

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

Table 6.4–1. Equipment and supplies used for measuring pH[1]

[mL, milliliters; mV, millivolt; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; +, plus: ±, plus or minus; MSDS, Material Safety Data Sheets]

✓ pH meter and pH electrodes
  - Battery powered, solid state, with automatic temperature compensation (for multiparameter instruments, see NFM 6.8)
  - Range of at least 2 to 12 pH, preferably 0 to 14 pH
  - Accuracy of at least ±0.01 units
  - Temperature range of at least 0 to +45°C
  - Millivolt readout with accuracy of ±1.0 mV

✓ 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)

✓ pH electrode storage solution

✓ Thermistor (or thermometer), calibrated

✓ Buffer solutions for pH 4, 7, and 10; temperature correction chart(s) for buffers; labeled with expiration dates

✓ Stand for holding pH electrode

✓ Bottle, delivery (squeeze), to dispense deionized water

✓ Deionized water, maximum conductivity of 1 µS/cm

✓ Beakers or measurement vessels, polyethylene or Teflon® preferable, assorted volumes of 50 to 150 mL, clean but not acid rinsed

✓ Flowthrough chamber (for ground-water measurements)

✓ Minnow bucket (or mesh bag) with tether or equivalent, used for temperature equilibration of buffer solutions

✓ Waste-disposal container

✓ pH-meter/electrode logbook for recording calibrations, maintenance, and repairs

✓ MSDS for all pH buffers and other reagents to be used

[1] This list pertains to single-parameter instruments for measuring pH. Refer to NFM 6.8 for information on and general use of multiparameter instruments. This list may be modified to meet the specific needs of the field effort.

CAUTION: Keep Material Safety Data Sheets (MSDS) readily available and refer to them to ensure that pH buffers or other chemicals are handled safely.

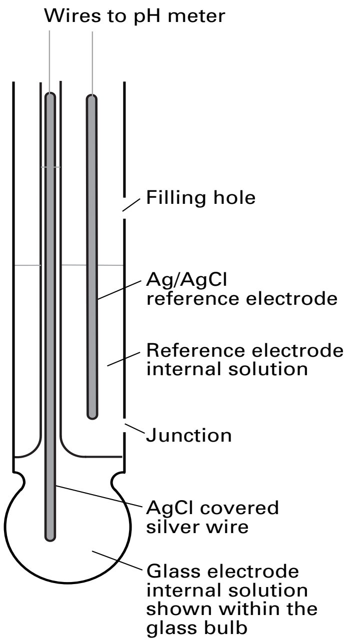
6.4.1.A pH METERS

A pH meter is a high-impedance voltmeter that measures the very small, direct current potential (in millivolts (mV)) generated between a glass pH electrode and a pH reference electrode. The potentiometric measurement is displayed as a pH value. The meter uses potentiometric differences to generate these pH values and is programmed with (1) the ideal Nernstian response relating hydrogen-ion activity (concentration) and electrical response (59.16 mV/unit pH), and (2) an automatic temperature compensation (ATC) factor. Since the ideal Nernstian slope response from the electrode varies with temperature, the meter's software adjusts the slope to be in accordance with the Nernst equation at the corresponding environmental temperature during calibration and measurement (refer to section 6.4.3 for an explanation of the Nernst equation).

6.4.1.B pH ELECTRODES

The pH electrode is a special type of ion selective electrode (ISE) that is designed specifically for the measurement of hydrogen-ion concentration in a dilute aqueous solution.

- ▶ Diodes or triodes (combination electrodes) are used in most USGS field studies.
  - — Combination electrodes are housed either in a glass or an epoxy body. Diodes contain a pH reference electrode and pH measurement electrode. Triodes contain the reference and measurement electrodes plus a thermistor. In either case, the basic electrode operation is the same (IC Controls, 2005a).
  - — All combination pH electrodes have a glass membrane, a reference and a measurement electrode, an ionic (filling) solution, and a reference junction (shown on fig. 6.4–1); these are described below.



The active part of the electrode is the glass "membrane" or bulb. The glass body of the tube has thick walls, whereas the bulb is made to be as thin as possible. The surface of the glass bulb is protonated by both internal and external solution until equilibrium is achieved. Both sides of the glass are charged by the adsorbed protons; this charge is responsible for potential difference (described by the Nernst equation) and is directly proportional to the difference in pH between the solutions on both sides of the glass bulb.

Figure 6.4–1. Diagram of a combination (single-junction) pH electrode. Modified from pH-meter.info (2005).

- Electrode performance naturally degrades over time with normal use. However, field personnel need to be alert to those chemical environments that can cause serious and more rapid degradation of electrode performance (IC Controls, 2005a). Many such environments are coincident with industrial, mined, and urban areas (table 6.4–2).
  - — Field personnel should be aware of the effect on the pH measurement when deploying the electrode in such environments: document field conditions on field forms.
  - — When measuring pH under specific adverse chemical conditions, the use of electrodes with properties designed to withstand such conditions is recommended (table 6.4–2).

Table 6.4–2. pH electrodes recommended for water having elevated concentrations of sodium and other monovalent major cations, sulfide, cyanide, and ferric chloride.

[H^+, hydrogen ion; Na^+, sodium ion; >, greater than; ≥, greater than or equal to]

Chemical condition	Description of water	Degradation effect on a common combination pH electrode	Recommended pH electrode
Basic ions dominant in solution	pH high (>10 pH units); low H^+ activity results in measurement of other monovalent ions in solution.	Sluggish response to changes in pH, resulting from dehydration of the glass membrane.	Glass pH electrode designed for measuring high values of pH.
	Sodium effect: Elevated Na^+ at pH ≥11.0, H^+ activity is low. The electrode senses Na^+ activity as if it were H^+ because of the similar charge and structure of the Na^+ and H^+ ions.	The pH measurement is negatively biased.	Glass pH electrode designed for measuring high values of pH.
Elevated concentrations of sulfide or cyanide	Elevated concentrations of sulfides or cyanides are found in industrial, mined, or urban areas.	Sulfide or cyanide contamination of the internal reference electrode.	Double-junction electrodes and plasticized reference electrodes.
Elevated concentration of ferric chloride	Ferric chloride is used as a flocculating agent in wastewater treatment plants, for example.	Ferric chloride attacks the glass membrane of the pH electrode, deactivating many of the sensing sites on the glass surface.	Consult the manufacturer for (1) selecting pH electrodes that can withstand this environment; and (or) (2) specific cleaning procedures for the glass membrane.

Glass membrane. The most essential and vulnerable element of the pH electrode is the sensitive glass membrane, which permits the sensing of hydrogen-ion activity in most natural waters. When the pH electrode is immersed in a solution (for example, a calibration buffer or a sample solution), ions from the glass diffuse into a thin layer on the outside of the membrane, while hydrogen ions diffuse through this layer until an equilibrium is reached between the internal and external ionic concentrations. In this way, an electrical potential is developed across the sensing surface, which is proportional to the concentration of hydrogen ions in the surrounding solution (pH-meter.info, 2005).

A clean, undamaged glass membrane is necessary for performing an accurate measurement of pH.

Reference and measurement electrodes. Contained within the pH-sensor body are a reference electrode (that generates a constant electrical potential) and a pH-measurement electrode. The measurement electrode generates a separate electrical potential that is proportional to the concentration of hydrogen ions in the sample solution. The electrodes together form a complete electrical circuit; when the diffusion of hydrogen ions reaches equilibrium, no electrical current is present, and the difference in electrical potential that exists between the reference and the measurement electrodes is an indication of the hydrogen-ion concentration in the solution. The pH meter, sensing this minute difference in electrical potentials, converts this difference into a pH value based on the latest calibration of the pH electrode.

Ionic (filling) solutions. An ionic solution used to fill the space within the pH electrode is the source of mobile, chemical ions that serve to complete the electrical circuit between the internal reference and pH-measurement electrodes.The pH electrode may be filled either with an ionic liquid solution (liquid-filled pH electrode) or an ionic gel solution (gel-filled pH electrode). Typically, these ionic solutions contain a chloride salt (usually silver or potassium) of a known and specific molarity (strength). For liquid-filled electrodes, maintaining a sufficient volume and the correct molarity of the filling solution within the electrode is very important to achieving meaningful measurements. Most standard pH electrodes are designed to function well when the electrode filling solution strength is similar to the sample ionic strength, typically having a relatively high ionic strength of 3 molar (M) or greater. Using low ionic-strength or high ionic-strength pH electrodes and a filling solution of appropriate composition and molarity—as recommended by the electrode manufacturer—is recommended when working with environmental samples having conductivities less than 100 µS/cm or greater than 20,000 µS/cm, respectively.

Reference junction. The liquid reference junction (sometimes called the "salt bridge") is an electrically conductive bridge within the pH electrode, between the reference ionic solution and the sample being measured. This junction is necessary for the proper functioning of the pH-sensing electrical cell; it must allow free movement of electrons, but at the same time, isolate the ionic solution from the bulk environmental sample. Typically, this junction is made of a porous material such as ceramic, Teflon, or glass fiber, and may clog and malfunction if not maintained properly. The function of the reference junction is characterized by a chemical memory. In a correctly functioning pH electrode, a small amount of time lapses before the appropriate ionic bridge is formed between the electrode reference ionic solution and the external environmental sample or external calibration-buffer solution. The length of time necessary for the establishment of this ionic equilibrium is a primary reason for the requirement that pH be measured in a quiescent sample solution. (Sections 6.4.4 and 6.4.5 provide further discussion.)

Remember to check that the junction on the pH electrode is not clogged; a clogged electrode will not function properly.

Electrode performance naturally deteriorates over time under normal operating conditions. However, use of the electrode in severe chemical environments can cause more rapid deterioration (table 6.4–2). Many of these environments are coincident with industrial and urban locations: immersing a pH electrode in such environments should be avoided or minimized to the extent possible (IC Controls, 2005a). Whenever the pH electrode is exposed to conditions such as those listed on table 6.4–2, this information should be recorded in the pH-meter/electrode logbook and documented in field notes.

pH BUFFER SOLUTIONS 6.4.1.C

pH buffer solutions (buffers) are ionic solutions that are used to calibrate the pH instrument system. Buffers maintain constant pH values because of their ability to resist changes to the specific pH value for which they are produced. **Measurements of pH are only as accurate as the buffers used to calibrate the electrode.**

- ▶ Use only buffers that have been certified traceable to an NIST standard reference material.
- ▶ Select the buffer molarity that is appropriate for the ionic strength of the water to be measured and the instrument system that will be used.
  - — For pH measurements of dilute waters with conductivities less than 100 µS/cm, use of buffers having lower-than-standard molarity and a low ionic-strength pH electrode is recommended (refer to section 6.4.3.B).
  - — For pH measurements in high ionic-strength waters with conductivities greater than 20,000 µS/cm, use of buffers having a higher-than-standard molarity is recommended (refer to section 6.4.3.C).
- ▶ Label pH buffer containers with the acquisition date and the expiration date. Copy the expiration date and the buffer lot number onto any reagent containers into which the buffer is transferred. Copy the temperature-correction information onto the respective buffer container or keep a copy of this information with the buffers being transported to the field.
- ▶ **Discard the pH buffer on its expiration date**. The pH of a buffer can be altered substantially because of temperature fluctuation, carbon dioxide (CO_2) absorption, mold growth, or evaporation.

Use the following precautions and protocols to help ensure the accuracy of the pH measurement *(modified from Busenberg and Plummer, 1987):*

- Cap buffer bottles firmly after use to prevent evaporation and contamination from atmospheric CO_2. The pH 10 buffer has the greatest sensitivity to CO_2 contamination, whereas the pH 4 buffer is the least sensitive. Buffers are stable for the short exposure time during electrode calibration.
- Never pour used buffer back into a bottle containing the stock buffer solution.
- Do not insert an electrode or other material into a bottle containing stock buffer solution — **always pour the buffer into a separate container** and discard the solution after use.
- Take care not to contaminate the buffer with another buffer or with other fluids.
- **Do not let the buffer become diluted** (this can happen, for example, if deionized water used to clean the electrode drips into the buffer).
- **Protect buffers against wide temperature variations**, whether in transit, during use, or in storage. Never expose buffers to extreme heat or freezing temperatures. If buffers experience these conditions, their pH values can no longer be assumed to be valid. Discard buffer solutions and any other reagents appropriately.
- Before using buffers in the calibration sequence, bring them to the temperature of the sample solution as much as possible. Since buffer composition differs among manufacturers; check the temperature-correction factors provided by the manufacturer in order to assign the correct pH value to the buffer for the temperature of the buffer at the time of calibration.

In order of greatest to least sensitivity of standard buffers to CO_2 contamination: pH 10 buffer > pH 7 buffer > pH 4 buffer. In order of greatest to least variation of buffer pH with change in temperature: pH 10 buffer > pH 7 buffer > pH 4 buffer.

6.4.2 MAINTENANCE OF pH INSTRUMENTS

Proper care of pH meters, and particularly of the electrode, is essential for maintaining the accuracy and precision required for pH measurements and promotes the longevity of the equipment. pH instrument maintenance includes adhering to the manufacturer's instructions for the use and care of the instrument, and routine use of appropriate electrode cleaning, reconditioning, and storage requirements. As always, follow the manufacturer's instructions for the specific type of electrode in use.

Electrode performance must be monitored before every water-quality field trip and again while at the field site.

6.4.2.A ELECTRODE CARE AND CLEANING

USGS field personnel should integrate the following guidance for the care and cleaning of pH electrodes into their routine field-measurement procedures.

- Never handle the glass bulb with fingers. Oily film or scratches on the bulb will interfere with the design characteristics of the glass membrane and affect subsequent pH measurements.
- Inspect the electrode and electrode cable for physical damage. For example, check for
    - Cut or frayed cable(s).
    - Broken connectors and mismatched or missing parts.
    - A visibly scratched or broken bulb, cracked electrode body, and broken or damaged internal electrode (reference and measurement electrodes).
- Gel-filled electrodes do not require filling and typically require less maintenance than liquid-filled electrodes. Do not store gel-filled electrodes in dilute water, even temporarily, as salts may leach from the gel into the dilute water and produce a large junction potential, resulting in errors in pH measurement.

To prepare and care for liquid-filled electrodes:

1. Remove salt crystal deposits from the electrode, membranes, and junctions by rinsing with deionized water (DIW). Visually check that the reference junction is not blocked or caked with salt. Thorough rinsing with DIW should remove these deposits. Be sure to unplug the fill hole before making pH measurements, as suction pressure may affect the proper movement of ions in the filling solution and the correct operation of the reference junction. Re-plug the fill hole after use.
   - If using an electrode after it has been in a storage solution, uncap the fill hole and suspend the electrode in the air for about 15 minutes. This will allow the filling solution to flush residual storage solution through the porous reference junction and thoroughly wet the junction.
   - After 15 minutes, visually inspect the junction for liquid or new salt accumulation. Ensure that the filling solution is flowing freely. Refer to the manufacturer’s instructions.
2. Check the filling solution level and replenish it if necessary. The solution should reach the bottom of the fill hole. **Filling solutions differ in molarity and composition—always check that the correct filling solution required by the manufacturer for a particular electrode is being used.**
3. Drain and flush the reference chamber of refillable electrodes, and routinely refill them with the correct filling solution (check the manufacturer's recommendations).
4. Keep a record of the electrode and meter operation and maintenance and repairs in the pH-meter/electrode logbook.
   - Record in the calibration logbook the operational history of each pH electrode.
   - Record the Nernst slope reading and the millivolt readings at pH 4, 7, 10, or other pertinent pH buffer values (based on field study objectives) during calibration. Properly working electrodes should give 95 to 102 percent response of that expected from the theoretical Nernst relationship (Busenberg and Plummer, 1987).

> **TECHNICAL NOTE:** The theoretical Nernst response is 59.16 mV/pH unit at 25°C, but varies based on temperature. Adequate adjustment of the Nernstian relation requires manual or automatic temperature compensation (ATC). Most modern pH meters have the ATC feature. A slope of 95 percent or less signals probable electrode deterioration and the need to monitor closely any further decline in slope percent. Consider replacing the electrode if calibration slope values cannot be brought to greater than 95 percent. **Do not use an electrode with a slope of less than 95 percent.**

5. Keep the electrode bulb moist and capped when not in use. Use only the wetting solution recommended by the manufacturer.

For routine cleaning of the pH electrode:

Keeping electrodes clean and the liquid junction free-flowing is necessary for producing accurate pH measurements. Because of the variety of electrodes available, check the manufacturer's instructions for specific tips and precautions.

1. **Before and after each use—**rinse the electrode body thoroughly, using only DIW. Dispense the DIW from a squeeze bottle.
2. Do not wipe or wick moisture from electrodes with paper towels or ChemWipes® as these can scratch the pH glass membrane. Wiping the electrode body with paper also may cause a static charge (polarization) on the exterior of the pH electrode, which can also adversely affect the pH measurement.

6.4.2.B RECONDITIONING OF LIQUID-FILLED ELECTRODES

If problems persist during calibration of a liquid-filled electrode, or if there is reason to doubt that the electrode is in good working condition, check the manufacturer's instructions for how to test and recondition the electrode. Reconditioning procedures should be implemented only if the electrode's slope response has deteriorated to less than 95 percent. Document in the pH-meter/electrode logbook if the electrode has been reconditioned or replaced.

The following general procedures can be used to attempt to bring the liquid-filled electrode back into proper working condition:

1. Remove the old filling solution from the electrode.
   a. Place the needle of a 1- or 3-milliliter (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 fill 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.
2. Flush the pH electrode with DIW.
   a. Use a syringe or squeeze bottle to partially fill the pH electrode chamber with DIW.
   b. With a syringe, remove the DIW from the pH electrode chamber.
   c. As a result of changes in pressure, temperature, and evaporation, visible crystals may form in the pH electrode. If these are present, continue to flush with DIW until all the crystals have been dissolved and removed from the pH electrode.
3. Fill the electrode with fresh filling solution. Flush the electrode chamber with fresh filling solution using a syringe or a plastic squeeze bottle.
   a. Partially fill the pH electrode chamber with the filling solution.
   b. Tilt the pH electrode so that the filling solution will contact all of the internal electrode surfaces.
   c. Remove and discard the filling solution to a waste container.
   d. Refill the electrode chamber with fresh filling solution until the filling-solution level is just below the fill hole. **Be sure to use the appropriate type and molarity of filling solution.**
   e. Rinse any excess filling solution from the outside of the electrode with DIW.
4. After following the reconditioning procedures, retest the electrode**. If the procedures fail to remedy the problem, discard the electrode.**

ELECTRODE STORAGE 6.4.2.C

Electrodes must be clean before they are stored for any length of time. Refer to the manufacturer's instructions for the proper short-term (used daily or weekly) and long-term (2 to 4 months) storage requirements of the electrode.

General guidelines for short-term storage:

1. Storage solutions are specific to the type of electrode; check the manufacturer's manual for each electrode. **Do not store glass hydrogen-ion electrodes in DIW** unless instructed to do so by the manufacturer.
2. Storage solutions have a limited shelf life. Label storage solution containers with the expiration date and discard expired solutions on that date and in a proper manner.
3. Do not place a small piece of cotton or paper towel in the electrode cap to help keep it moist, as this can scratch the glass membrane sensor.
4. Store liquid-filled pH electrodes upright.
5. Store liquid-filled electrodes wet between uses to maximize their accuracy and response time.
   - The glass membrane (bulb) should be fully immersed in the proper electrode storage solution.
   - Between field sites, replace the plug on the fill hole and cover the electrode bulb with the cap.
   - Fill the cap with enough storage solution to keep the bulb wet.
6. Gel-filled electrodes should be stored according to the manufacturer's instructions.

General guidelines for long-term storage:

1. Liquid-filled electrodes may need to be drained of filling solution; follow the manufacturer's instructions.
2. Clean the electrode contacts and connector (with alcohol, if necessary). Allow the contacts to dry and seal and store them in a plastic bag.
3. Store every component of the pH measuring system in an area that is clean, dry, and protected from extremely hot or cold temperatures.

6.4.3 CALIBRATION OF THE pH INSTRUMENT SYSTEM

Proper calibration of the pH instrument system is crucial to accurate pH measurement of environmental samples. During calibration, the pH electrodes are immersed in buffer solutions of known pH (section 6.4.1.C). The buffers are designed to produce a corresponding electrical response potential (usually in millivolts) for the specific pH buffer (for example, pH = 4, 7, or 10 buffer solution) within the pH electrode. These potentials are measured by the pH meter. The Nernst equation gives the expected (theoretical) response potential of the pH buffer at the specific temperature of the calibration (Hem, 1989; see TECHNICAL NOTE below). Note that the measured temperature must be programmed into the pH meter unless the meter has incorporated automatic temperature compensation. The calibration returns the actual, measured potential.

TECHNICAL NOTE: pH electrodes operate on the principle that differing concentrations of the H^+, in buffers or environmental samples, produce differing potentiometric responses (measured in millivolts). The Nernst equation is used to establish the calibration of the pH instrument system by determining the slope of electrical potential versus pH at a given temperature. At 25°C, this Nernstian relation (the slope along any two points on the line plotted for electrical potential versus pH) is known to be 59.16 mV/pH units. To calculate the slope between two points along the line of measured potentials versus pH:

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

where

S = slope

E = electrode pair potential, in mV, and

E^0 = standard potential, in mV.

Thus, using two buffers of known pH (pH_1 and pH_2),

$$E_1=E^0- S(pH_1) \quad and \quad E_2=E^0- S(pH_2).$$

Rearrange as:

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

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

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

where

t = temperature in degrees Celsius, and

S_t = slope at a given temperature.

The primary concept in accurate calibration of the pH electrode is to select pH buffers with values that bracket the expected pH of the environmental sample; this is known as a two-point calibration. Before field calibration of the pH instrument system, it is useful to estimate (or to anticipate from historical site data, if available) the pH and conductivity of the waters to be encountered at the field sites. If no data are available from which to estimate sample pH, then pH indicator paper can be used onsite as a gross indicator of the pH of the system. (**Under no circumstances should a pH value from indicator paper be recorded as site pH.)** For three-point or other multipoint calibrations, follow the manufacturer’s instructions for (a) which buffers to use and (b) the sequence of buffer use.

> **EXAMPLE:** When measuring pH in a stream that is within the normal range of specific electrical conductivity,
>
> a. If pH values are expected to be between 7 and 8, then the standard pH 7 and pH 10 buffers should be selected.
>
> b. If pH values are expected to be less than 7, then the standard pH 7 and pH 4 buffers should be selected.
>
> c. If the anticipated pH range in pH is large, a check of electrode performance using a third standard buffer value is advisable.

The following guidelines and standard procedures apply in general whenever a pH instrument system is to be calibrated. Because calibration and operating procedures can differ with differing instrument systems, check the manufacturer’s recommended calibration procedures and calibration solutions. Digital pH meters automatically compensate for buffer temperatures and indicate appropriate Nernst values (in millivolts). When using these instruments, follow the manufacturer's calibration instructions precisely—**do not take shortcuts**.

- ▶ Before each field trip and field calibration, check pH meter/electrode logbook records for electrode performance. **Remember—**any noted calibration slope of 95 percent or less indicates probable electrode deterioration; at 94-percent slope or less, the electrode should not be used.
- ▶ Use at least two pH buffer solutions of documented, traceable pH value for adequate calibration of the pH instrument system.
- ▶ Pour the amount needed of each buffer from the source container into a clean, polyethylene bottle dedicated for the respective buffer, and label the bottle with the buffer’s pH value, lot number, expiration date, and the temperature-adjusted pH values provided by the manufacturer for that buffer.
- ▶ The temperature of the buffer solutions should be near the same temperature as the water to be sampled. A calibration check of the temperature sensor must be performed at least annually (NFM 6.1).

> **TECHNICAL NOTE:** Temperature has two effects on the pH measurement of a sample—temperature can affect meter and electrode potentials (Nernstian slope effect), and it can change hydrogen-ion activity (chemical effect) within the sample. 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 will be minimized if the electrodes, buffers, and container are allowed to equilibrate to the same temperature.

Do not use pH buffers that have exceeded their date of expiration.

6.4.3.A CALIBRATION PROCEDURE UNDER STANDARD AQUEOUS CONDITIONS

“Standard aqueous conditions” refers to environmental water with an ionic strength that is within the range in which a standard buffer solution and combination pH electrode can be appropriately used to achieve an accurate pH measurement. For routine USGS water-quality measurements, ionic strengths ranging from 100 to 20,000 μS/cm are considered standard.

When calibrating the pH electrode:

1. Bring the pH buffers to the ambient temperature of the stream or ground water to be measured, to the degree possible under the prevailing field conditions. The temperature sensor (liquid-in-glass or thermistor thermometer), measurement vessel, and electrode also should be at or near the ambient temperature of the environmental sample. **Maintain each buffer as close to sample temperature as possible when calibrating the electrode.**
   - Surface water and ground water—When equilibrating the buffer temperature to ambient surface-water temperature, one method is to place the buffer bottles in a minnow bucket or mesh bag and suspend them in the body of surface water. Alternatively, place the buffers into a bucket or insulated cooler (a) containing surface water, or (b) being filled with ground water.
   - **When immersing buffer bottles in water, ensure that the bottle is firmly capped and that the water level remains below the cap so that water cannot enter the bottle and contaminate the buffer**.
2. Inspect the pH electrode.
   a. Check for damage to the electrode bulb, body, or cables.
   b. Rinse any mineral precipitate off the electrode with DIW.
   c. Uncover (unplug) the fill hole.
   d. If you can visually see small bubbles within the electrode solution, **gently** tap the electrode body to dislodge them. Bubbles trapped in the sensing tip of the electrode will affect the physical conditions necessary for correct operation of the electrode. **Do not wipe moisture from the electrode.**
3. Power up the pH meter. The meter will perform an internal self-test. Note any discrepancies displayed by the meter and record these in the pH-meter/electrode logbook. Malfunctioning meters usually require manufacturer attention; do not try to fix malfunctioning meters in the field. Having backup meters for field trips is necessary for this reason.
4. Record in the ph-meter/instrument logbook the internal self-test information displayed by the pH meter. A calibration log is **mandatory** for all calibrations.

5. Initiate the calibration process by pushing the required calibration display sequences for the particular pH meter and electrode. **Standard USGS procedure for calibration of a single-parameter pH meter-and-electrode system requires a two- or three-point calibration.**
   - Some types of pH-instrument systems may use a different multipoint calibration procedure; in such cases, follow the instructions provided in the instrument manual.
   - A single-point calibration, recommended by some manufacturers, is not acceptable for USGS field measurement of pH.
6. Record in the pH-meter/electrode logbook: pH value, measured temperature, lot number, and expiration date of the first buffer. Typically, the meter will initially indicate the pH 7 buffer (isoelectric point).
7. Begin calibration procedures:
   a. Note that the electrode and thermistor must be rinsed with DIW at least three times between uses of each buffer.

   b. Rinse the electrode twice with the first buffer (usually the pH 7 buffer). Do not allow the glass membrane of the electrode to come in contact with the sides or bottom of the beaker or other measurement vessel.

      i. **First rinse—**Pour enough buffer into a small beaker or other vessel so that it covers the electrode reference junction; swirl the buffer to rinse the electrode body from above the reference junction to the bottom of the bulb. Discard buffer appropriately.

      ii. **Second rinse—**Pour the next aliquot of buffer into the vessel and immerse the electrode in the buffer for 1 minute. Discard buffer appropriately.

   c. Pour another aliquot of buffer into the vessel. Immerse the electrode for 1 minute, without swirling the buffer solution.

   d. Record the pH measurement shown on the meter display in the pH meter/electrode logbook, along with the buffer temperature reading and the pH value from the buffer and temperature table.
      - For pH meters displaying millivolt values, the meter will display the value associated with the pH 7 buffer, as compensated for the buffer temperature.
      - **For properly functioning electrodes, the pH 7 millivolt value should be between +10 and -10 mV. Record the millivolt data in the pH-meter/electrode logbook.**

   e. Press “Cal” or other display instructions to lock in the pH 7 calibration.

TECHNICAL NOTE: During the calibration sequence, after the DIW and buffer rinses and when the specific buffer value is ready to be locked in to the calibration, some meters provide the opportunity to adjust the initially displayed pH value to a corrected pH value for that buffer solution.

- **If this adjustment is equal to or less than 0.05 pH units**, proceed with the adjustment, but specifically note this in the pH meter/electrode logbook.
- **If the adjustment would exceed 0.05 pH units**, the pH electrode is not functioning optimally; consider reconditioning the electrode or using another electrode until the cause of the substandard performance can be determined.

8. **Return to step 6 above, followed by step 7**, repeating each of the procedures just followed but using either the pH 4 or pH 10 buffer, whichever buffer solution, along with the pH 7 buffer, brackets the pH values of the environmental water to be sampled. Record all the calibration data, including the millivolt data, in the pH meter/electrode logbook (see step 7 to test the adequacy of the calibration using the slope test or millivolt test).

9. **At this point, the electrode should be calibrated**. Check the adequacy of the calibration and that the electrode is functioning properly, using the slope test or (and) the millivolt test. Some instruments have the capability to display the slope value; this datum should be recorded in the pH-meter/electrode logbook.

   - **The slope test.** Values ranging from 95 to 102 percent slope are acceptable—if the slope-percent value is outside of this range: clean the electrode and check the level of the filling solution, that the fill hole is open, and that the junction is free-flowing; then, recalibrate.

TECHNICAL NOTE: Since the theoretical Nernstian relation between electrical response and pH at the calibration temperature is programmed into the pH meter software, the calibration process provides the Nernstian response from the electrode/meter system being calibrated. The actual calibration slope is calculated and the **displayed slope value** represents the actual slope of the electrical potential (millivolt)– pH line that this calibration has produced.

   - **The millivolt test.** For pH meters that display and store only millivolt readings (do not display the slope percent), use the following guidelines to ascertain adequate calibration:
     - — pH 7 buffer: Displays between -10 to +10 mV
     - — pH 4 buffer: Displays between +165 to +195 mV
     - — pH 10 buffer: Displays between -165 to -195 mV
   - If using buffers other than the standard pH 4, 7, and 10 buffers, refer to the information provided with the specific buffer lot to determine the correct, temperature-compensated millivolt potential for that buffer.

10. **Replace the electrode** if, after recalibration, the slope remains outside the acceptable range of 95 to 102 percent or if the acceptable range of the millivolt response is not met at any of the calibration points.

CALIBRATION FOR LOW IONIC-STRENGTH WATER 6.4.3.B

Calibration of pH instrument systems with standard buffers does not guarantee accurate and (or) timely pH measurement in low ionic-strength waters (conductivity less than 100 µS/cm) and in very low ionic-strength waters (conductivity less than 50 µS/cm). As sample ionic strength decreases, the efficiency of the standard pH instrument system also decreases. Low or very low ionic-strength waters have little buffering capacity and may readily absorb atmospheric CO_2, resulting in the formation of carbonic acid in the sample. A continuous change in pH values can occur from the varying reaction rates of the sample water with CO_2, resulting in an unstable measurement.

Standard pH electrodes do not respond well in waters with low ionic strength.

- ▶ Standard combination pH electrodes respond more slowly, the response is characterized by continual drift, and calibration is difficult to maintain. Equilibration with the sample water may not be completely achieved or the equilibration time may be on the order of hours.
- ▶ Standard pH electrodes exhibit a jumpy response and are more sensitive to conditions of flow and agitation, and measurement accuracy decreases (Wood, 1981).

When preparing to measure pH in low ionic-strength waters, the response time, accuracy, and reproducibility of the measurement can be improved by modifying the type of electrode and buffer.

To measure pH in water of low ionic strength:

1. Use a specific, low ionic-strength electrode. The pH electrode for low ionic-strength solutions typically is characterized by
   - A thin, responsive glass membrane;
   - A reference junction that allows rapid electrolyte flow; and
   - A pH-neutral ionic additive within the reference filling solution.
2. Use corresponding low ionic-strength pH buffers.
   - The low ionic-strength buffer should contain the same type of pH-neutral ionic additive as that in the electrode reference filling solution (the amount of pH neutral ionic additive must be the same in the electrode and buffer, so that the net pH effect is standardized).
   - Low ionic-strength buffers may not be of the standard pH buffer values (pH = 4, 7, 10). Check that your pH meter can accept these “nonstandard” buffer values for calibration.

Calibration of the pH instrument system and measurements made in low ionic-strength solutions should involve a specific combination of low ionic-strength buffers and low ionic-strength electrodes.

6.4.3.C CALIBRATION FOR HIGH IONIC-STRENGTH WATER

USGS studies increasingly involve pH measurement and sampling of high ionic-strength waters (ionic strength greater than 3 *M* or conductivity greater than 20,000 μS/cm) from sources such as industrial effluent (for example, from paper mills, oil refineries, carbonate processing or other mining activities that have corrosive properties), combined sewer/storm water from urban systems, seawater, and brines. Using standard buffers or standard equipment may not yield an accurate pH measurement for such waters.

- ▶ The high ionic strength of some industrial effluents or brines often are of greater or equal ionic strength than that of the filling solution in the standard pH electrode. This results in an ionic gradient toward the reference junction and into the pH electrode, which compromises the design parameters of the electrode and therefore the soundness of the calibration and the pH measurement.
- ▶ Standard buffers are not of an ionic strength that approximates or exceeds the ionic strength of the sample solution, and standard filling solutions in pH electrodes similarly may have too low of an ionic strength to be calibrated properly for measurement of pH in high ionic-strength waters.

When selecting the measurement system to be used to determine the pH of high ionic-strength waters, consider the following options:

1. Obtain high ionic-strength (conductivity greater than 20,000 μS/cm) pH buffer solutions from commercial sources, if available. Follow the guidelines for maintenance and use of pH buffers previously described in section 6.4.1.C, paying close attention to the effect of temperature on buffer values.
2. Obtain high ionic-strength pH glass electrodes, if available. These may be characterized by filling solutions of greater than 3 *M* ionic strength and more solution-specific glass sensors. Note specific uses recommended by the manufacturer and follow the manufacturer's instructions.
3. If no suitable pH glass electrode/buffer system is available for pH measurement in high ionic-strength environments, investigate the suitability of alternative instrumentation and methods, such as those that employ spectrophotometric or optical methods, with respect to the site-specific conditions to be encountered and study data-quality objectives (Bellerby and others, 1995; Farquharson and others, 1992; Sedjil and Lu, 1998).
   - Spectrophotometric methods typically involve the constant-rate introduction of acid-base indicator dyes into the sample; pH measurement is accomplished by measurement of the resultant spectra of the dye. An important limitation to this system is that acid-base indicator dyes are typically sensitive over very narrow pH ranges (Raghuraman and others, 2006).
   - Spectrophotometric measurement of pH in environmental samples is a methodology designed for specific environments; follow the guidelines provided by the equipment manufacturer.
   - As part of USGS studies, any pH data obtained by spectrophotometry or other nontraditional pH measurement method must be entered under the unique parameter and (or) method code designated in the USGS National Water Information System (NWIS) water-quality database.

CALIBRATION FOR THE pH SENSOR IN MULTIPARAMETER INSTRUMENTS 6.4.3.D

Before beginning calibration of the pH electrode in a multiparameter instrument sonde, read and follow carefully the instrument manual and manufacturer's instructions. Guidelines that incorporate USGS protocols for pH calibration and measurement are described in NFM 6.8.

General procedures for calibration of the pH sensor in a multiparameter sonde:

1. Select the pH 7 and one additional buffer solution that will bracket the anticipated pH of the sample. Equilibrate the temperature of the buffers to the temperature of the environmental sample.
2. Rinse the sonde and electrode thoroughly three times with DIW before and between use of each buffer solution.
3. Rinse the pH and temperature sensors three times with separate aliquots of the first pH buffer, using the "pour-swirl-discard, pour-sit-discard, pour-sit-measure" method described in section 6.4.3.A. Allow enough time for the sensors to equilibrate to buffer temperature before locking in the first calibration point.
4. Repeat step 3, using the second pH buffer, and lock in the second calibration point. (Depending on site conditions and study objectives, it might be useful to check the calibration range of the pH sensor using a third buffer; if appropriate, lock in a value.)
5. Always record temperature information with calibration information in the pH-meter/electrode logbook and on the field sheet.

MEASUREMENT 6.4.4

The pH of sample water is to be measured as soon as possible after removal of the sample from its environmental source. The pH of a water sample can change substantially within hours or even minutes after sample collection as a result of temperature change; degassing (loss of sample oxygen, carbon dioxide, hydrogen sulfide, ammonia); in-gassing (gain of sample oxygen, carbon dioxide, hydrogen sulfide, ammonia); mineral precipitation (formation of calcium carbonate, iron hydroxides); metabolic respiration by microorganisms; and other chemical, physical, and biological reactions (Hem, 1989). Field conditions, including rain, wind, cold, dust, direct sunlight, and direct exposure to vehicle exhaust can cause measurement problems.[2] Always protect the instrument system and the measurement process from the effects of harsh weather and transportation damage.

The pH value of an aqueous system should be determined by taking the median of three or more separate and stable measurements that are recorded in a quiescent sample. Recording a median value ensures that the reported pH value represents a true measurement, instead of a computed measurement, and avoids the mathematical procedure required to compute a mean pH from logarithmic operations.

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[2] The effects of field conditions on the quality of field measurements, water-quality samples, and data integrity must be anticipated by field personnel and protocols to minimize sample contamination as described in NFM 4 and 5 are to be implemented as standard operating procedure.

TECHNICAL NOTE: The pH value of a given sample always is recorded in the USGS database as a median of a series of stable measurements. For applications that require reporting pH over time (for example, an annual average pH) or space, however, computation of the mean of the hydrogen ion activity may be useful. To compute a series of pH measurements collected over time or space:

a. Take the antilog of each pH measurement, using the following equation: Activity = 10^{-pH}.
b. Add all the antilog values and divide the sum by the total number of values.
c. Convert the calculated mean activity back to pH units, using the equation, pH = (-log10) (mean H^+ activity).

If reporting pH as a computed mean, document this information and the procedure used. **Do not enter a mean pH value in the USGS NWIS database under the parameter code for a median or direct determination of pH.**

6.4.4.A pH MEASUREMENT IN SURFACE WATER

When using a single-parameter pH electrode/meter instrument system, the pH of surface water is determined ex situ, from a quiescent, non-stirred sample that is withdrawn from a churn or cone splitter or other approved sample-compositing device. Although referred to as a single-parameter method, most modern pH meters are equipped with a thermistor used to determine the temperature of the sample. Each pH measurement must be accompanied with a concurrent temperature measurement.

- ▶ It is not advisable to immerse the pH electrode into flowing surface water for the following reasons:
  - — Placing the pH electrode into moving water risks damage to the delicate glass membrane (scratching, pitting, coating), which will inhibit the correct functioning of the electrode. In addition, proper functioning of the glass membrane is affected when ionic equilibrium is not achieved with the surrounding sample solution.
  - — Calibration of the electrode was accomplished in a quiescent sample, not in flowing or stirred water. Adequate calibration of the instrument system cannot be assumed to extend to moving water.
  - — USGS methodology in surface-water measurement usually involves the collection of depth- and width-integrated samples. In situ measurements of pH in a moving water system, either at a singular point in the waterway or across a section, do not meet these requirements.
  - — Reference-junction equilibrium cannot be achieved in moving water; thus, correct electrode functioning will again be inhibited.
  - — It is difficult to have electrode temperature come to equilibrium with sample temperature in moving water; correct pH instrument system functioning will be inhibited.
- ▶ The determination of pH in situ, using a multiparameter instrument system, is described in NFM 6.0 and 6.8. The system selected depends on the data-quality objectives of the study and on site-specific conditions.

Before collecting the sample and making ex situ measurements, it is advisable to determine the range of pH values in the cross section, or estimate the magnitude of lateral mixing of the waterway at the field site, using an in situ measurement method (for example, with a multiparameter sonde).

When making an ex situ pH measurement:

Set up the pH instrument system close to the sampling site in order to minimize the time lapse between sample collection and pH measurement.

1. The glass membrane of the electrode should not contact the sides or bottom of the beaker or other measurement vessel. Use only a clean measurement vessel.
2. Fill the measurement vessel with sufficient sample to ensure that the electrode reference junction is fully immersed, taking care not to aerate the sample.
3. After calibration (or measuring the pH of a different sample), rinse the electrode and thermistor three times with DIW. This crucial step must always be completed between differing solutions.
4. **Rinse the electrode and thermistor sensors two times with the sample**, as follows:
   a. **First rinse—**Pour an aliquot of sample onto the sensors and swirl the sample water around the electrode sensors. Discard the sample appropriately.
   b. **Second rinse—**Pour an aliquot of sample onto the sensors and allow the sensors to sit in the solution for 1 minute (do not swirl). Discard the sample appropriately.
5. **Measure pH**, as follows:
   a. Pour a third aliquot of sample into the vessel. **Allow the sensors to sit in a quiescent sample** for 1 minute or until the pH value stabilizes within the established criterion. Record the pH value on the electronic or paper field-notes form.
   b. Repeat the procedure in (a) above on at least two additional aliquots of the sample, recording the pH measurement for each aliquot on the field form(s).
6. **Calculate a final sample pH as the median** of the values measured for the sample aliquots and document the calculation on field forms.
7. **Record** the final pH value of the sample to the nearest 0.01 pH unit, along with the sample temperature, in paper and (or) electronic field forms, including forms that accompany samples being shipped to the laboratory.
8. The pH value should be reported to the nearest 0.1 pH unit when published and when recorded in the NWIS database.

Always record the temperature of the sample concurrently with each pH measurement.

6.4.4.B pH MEASUREMENT IN GROUND WATER

The pH of ground water should be measured under no-flow (quiescent sample) conditions. When using a single-parameter meter, the measurement can be made either with the pH electrode and temperature sensor inserted (a) into an airtight flowthrough cell or chamber to which the sample is pumped, or (b) in a vessel that contains an aliquot of sample either collected from pump discharge or withdrawn from a sampling device, such as a bailer (figs. 6.4–2 and 6.4–3, respectively). (See NFM 6.8 for pH measurement using a multiparameter sonde).

The central concept for measuring pH in ground water is to use equipment that minimizes aeration, chemical change, and temperature change. If possible, operate equipment in a manner that helps to mitigate losses and gains of dissolved gases in solution.

- The flowthrough cell/chamber method yields accurate pH data when implemented appropriately.
- Bailed or other methods for collecting discrete samples for pH measurement must be implemented carefully to avoid temperature change, turbulence, and sample aeration from decanting and mixing of the bailed water.
- Downhole deployment of a submersible sensor or sonde risks losing the equipment if it becomes lodged in the well.

Document on electronic or paper field forms the methodology used to obtain samples for pH measurement.

Unless specifically required by study objectives or environmental constraints, in situ measurement of pH by putting the sensor system directly into the well (downhole method) should be avoided for the following reasons:

- Placing the pH electrode directly into the borehole risks damage to the delicate glass membrane (scratching, pitting, coating), which will inhibit the correct functioning of the electrode. Any accretions or coatings on the inside of the borehole may be transferred to the pH sensor and damage, or alter, the membrane.
- Pumps, wiring, and (or) other equipment within the borehole may damage or degrade the pH sensor and the sonde.
- Any static electrical charge on the inside of the well casing or borehole may be transferred to the pH electrode, a condition sometimes referred to as a "ground loop," which also compromises accurate pH measurement.

Always measure and record sample temperature concurrently with pH measurements.

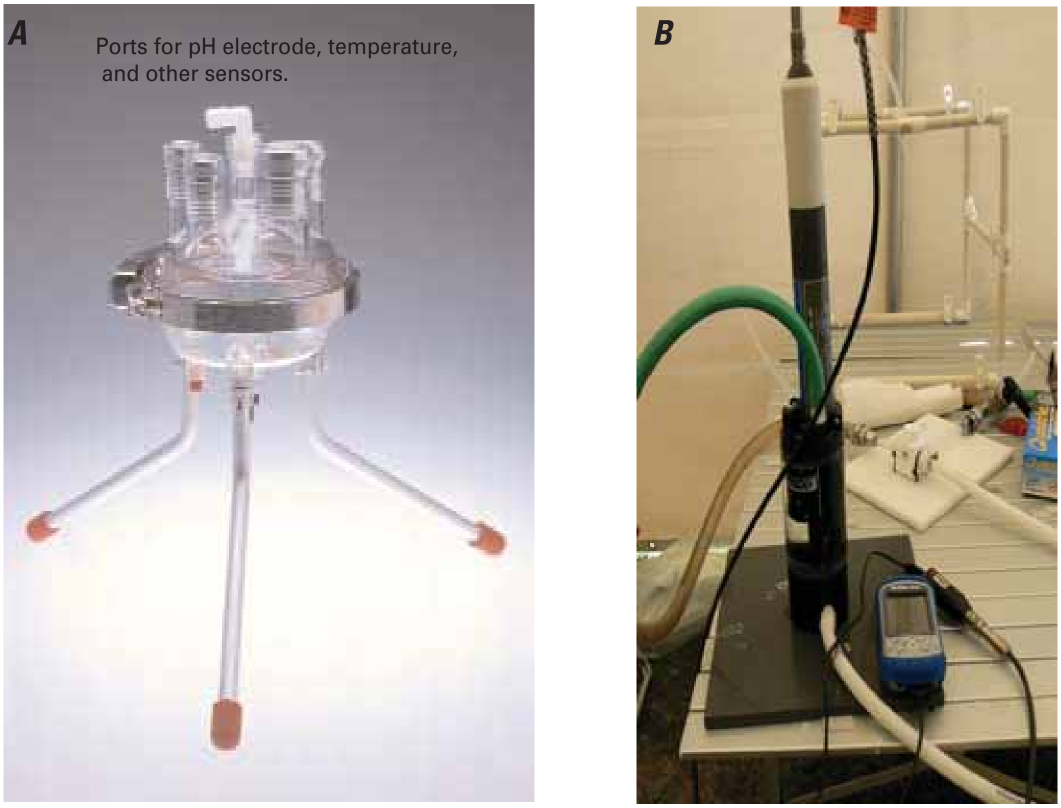

Figure 6.4–2. Photographs of (***A***) a flowthrough cell/chamber for use with single-parameter field-measurement sensors, shown without sensors installed; and (***B***) a flowthrough cell attached to a multiparameter sonde. Photograph ***A*** courtesy of Geotech Environmental. Photograph ***B*** is a USGS stock image.

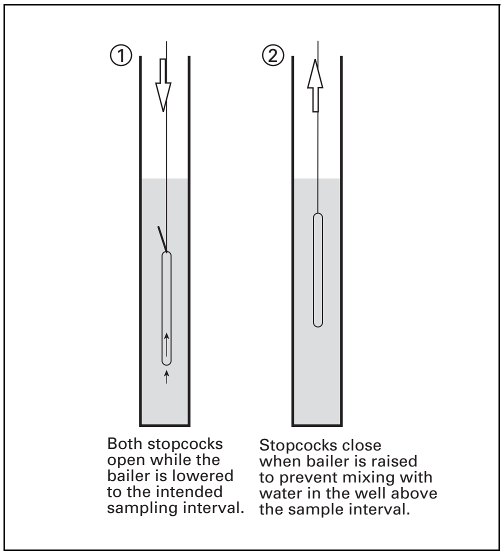

Figure 6.4–3. Use of a dual-valve (double stop-cock) Teflon bailer.

Referring to figure 6.4–2, ground water is pumped directly from the well through tubing and into an airtight flowthrough cell/chamber containing either a calibrated pH electrode and other sensors (typically, dissolved oxygen, specific electrical conductance, and temperature sensors (fig. 6.4–2A), or a multiparameter sonde (fig. 6.4–2B).

After successful calibration of the pH instrument system on site, pH measurement of sample water may proceed either on discrete samples obtained from a bailer, or on pumped ground water circulated through a flowthrough cell/chamber.

- ▶ Use of the bailer to obtain ground-water samples is analogous to the approved use of samplers in a surface-water situation, as described below.
- ▶ Use of a flowthrough cell/chamber has the advantage of concurrent monitoring of ground-water field measurements in addition to pH, as described below.

To make a pH measurement using a flowthrough cell/chamber system instrumented with single-parameter sensors (fig. 6.4–2):

1. Install the chamber system as close to the well as possible and shield the chamber and tubing from direct sunlight.
2. Check that the electrode fill hole is open to the atmosphere and that the reference junction is entirely submerged.
3. Check for and eliminate any backpressure condition.
4. Monitor pH variation during purging:
    a. Keep the flow constant and laminar.
    b. 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.
    c. Record pH values at regularly spaced time intervals throughout purging (consult NFM 6.0 for detailed guidance). Compare the variability of pH values toward the end of purging. The stability of pH values is assumed when three to five readings made at regularly spaced intervals are constant. If readings continue to fluctuate, continue to monitor, or, if site conditions are demonstrably variable (degassing, in-gassing, rapid thermal changes from water at depth), select the median of three or more readings within about 60 seconds as the value recorded for the specific time interval.
5. Determine sample pH toward the end of purging (for example, during removal of the final purge volume) as follows:
    a. Divert flow from the chamber to allow the sample contained within the chamber to become quiescent (after recording the other field measurements). Record the pH value under quiescent conditions to the nearest 0.01 pH unit.
    b. Determine the median of the pH values recorded under quiescent conditions and report this value as sample pH.
    c. If field personnel have reason to suspect an electrode malfunction, a calibration check at the end of sampling is recommended.

To make a pH measurement on a bailed sample (fig. 6.4–3):

1. Withdraw subsamples from the well and transfer each bailed sample to a churn, cone splitter, or other appropriate compositing device (NFM 2).
2. Remove an aliquot from the sample composite for measurement of pH.

TROUBLESHOOTING 6.4.5

Consult the instrument manufacturer for recommended troubleshooting actions for specific single-parameter and multiparameter pH instrument systems.

- ▶ Nearly all problems encountered during pH calibration and measurement can be attributed directly to the condition and responsiveness of the pH electrode (table 6.4–3).
- ▶ For any problem, first test that the instrument batteries are fully charged. Keep spare batteries on hand that are fully charged.

Table 6.4–3. Troubleshooting guide for pH measurement.

[DIW, deionized water]

Symptom	Possible cause—Corrective action
Instrument system will not calibrate to full scale	• Buffers may be contaminated or old—Use fresh buffers. • Faulty electrode—Recondition or replace electrode (see section 6.4.2). • Weak batteries—Replace with new or fully charged batteries.
Slow response	***For liquid-filled electrodes:*** • Weak or incorrect solution—Change filling solution to correct molarity. • No or low filling solution—Add fresh solution of correct molarity. • Dirty tip (for example, visible chemical deposits or organic or biological matter on the electrode)—Rinse tip with DIW; if residue persists, use solution and cleaning method recommended by the manufacturer. **Take care not to scratch the electrode tip.** • Clogged or partially clogged junction—Follow the manufacturer's instructions to unclog the junction). • Water is cold or of low ionic strength—Allow more time for equilibration; consider using a different electrode (section 6.4.3.B). • Sluggish response to pH changes; pH measurement is biased negatively—Refer to table 6.4–2. ***For gel-filled electrodes:*** • Dirty bulb—Rinse bulb carefully with DIW. If organic/inorganic/biological residue persists, consult the manufacturer's recommendations. • Visibly clogged junction—Follow the manufacturer's instructions to unclog the junction • Water is cold or of low ionic strength—Allow more time for equilibration; consider using a different electrode (section 6.4.3.B).
Erratic readings	• 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 electrode gently. • Too much pressure in flowthrough chamber—Release and reduce pressure. • Weak batteries—Replace with new, fully charged batteries.

6.4.6 REPORTING

Due to the rapidity of pH reactions in environmental samples, the effect of temperature on the operation of the pH instrument system, and chemical and microbiological equilibria within the sample, pH measurements must be completed and recorded as soon as possible after removing the sample from the environmental medium. When entering the pH value for the site into the NWIS database, ensure that the method code selected correctly corresponds to the method that was used for the pH measurement.

- ▶ On field forms (electronic or paper) and in the pH-meter/electrode logbook, record pH calibration and environmental measurements to 0.01 standard pH units.
- ▶ In the USGS NWIS database, report pH values to the nearest 0.1 standard pH unit, unless study and data-quality objectives dictate otherwise and equipment of the appropriate precision and accuracy has been used.

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SPECIFIC ELECTRICAL CONDUCTANCE 6.3

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

Tables

SPECIFIC ELECTRICAL CONDUCTANCE 6.3

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

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

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

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

EQUIPMENT AND SUPPLIES 6.3.1

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

Table 6.3–1. Equipment and supplies used for measuring conductivity[1]
[°C, degrees Celsius; ≤ , less than or equal to; >, greater than; μS/cm, microsiemens per centimeter at 25 degrees Celsius; L, liter]

- ✓ Conductivity instrument and conductivity sensor
  - Battery powered Wheatstone bridge
  - Direct readout
  - Temperature range at least –5 to +45°C
  - Temperature compensating (25°C)
  - Accuracy: Conductivity ≤100 μS/cm, within 5 percent of full scale
    Conductivity >100 μS/cm, within 3 percent of full scale
- ✓ Thermistor thermometer sensor (for automatic temperature-compensating models)
- ✓ Thermometer, liquid-in-glass or thermistor
- ✓ Extra sensors (if possible) and batteries, or backup instrument
- ✓ Conductivity standards at conductivities that approximate and bracket field values
- ✓ Compositing and splitting device for surface-water samples
- ✓ Flowthrough chamber or downhole instrument for ground-water measurements
- ✓ Plastic beakers (assorted sizes)
- ✓ Soap solution, nonphosphate (1 L)
- ✓ Hydrochloric acid solution, 5 percent volume-to-volume (1 L)
- ✓ Deionized water, 1 L, maximum conductivity of 1 μS/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

[1] Modify this list to meet the specific needs of the field effort.

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. Quality-controlled conductivity standards ranging from 50 to 50,000 μS/cm at 25°C can be obtained by USGS personnel through "One Stop Shopping." Order standards outside this range from suppliers of chemical reagents. Conductivity standards usually consist of potassium chloride dissolved in reagent-grade water.

CONDUCTIVITY SENSORS 6.3.1.A

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.

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	.01
1 – 200	.1
10 – 2,000	1.0
100 – 20,000	10.0
1,000 – 200,000	50.0

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

6.3.1.B EQUIPMENT MAINTENANCE

Maintenance of conductivity equipment includes periodic office checks of instrument operation. To 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.
- Protect connector ends in a clean plastic bag.

Sensor cleaning and storage

Conductivity sensors must be clean to produce accurate results; residues from previous samples can coat surfaces of sensors and cause erroneous readings. Refer to the manufacturer's instructions regarding long- and short-term storage of the sensor.

- 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 solutions.
- Clean carbon and stainless steel sensors with a soft brush. Never use a brush on platinum-coated sensors.
- 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.

CALIBRATION 6.3.2

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 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 through 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 ± variation).
    - The temperature-correction factor (if necessary).
13. Discard the used standard into a waste container. Thoroughly rinse the sensor, thermometer, and container 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.

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.

MEASUREMENT 6.3.3

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 the conductivity sensor upstream of the pH electrode.

Conductivity must be measured at the field site.

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 ≤ 100 μS/cm or within 3 percent at conductivity > 100 μS/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.

6.3.3.A SURFACE WATER

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 the water.
   - Values should stabilize quickly to within 5 percent at conductivity ≤100 µS/cm and within 3 percent at conductivity >100 µS/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 (NFM 4). 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 ≤100 μS/cm, or ±3 percent for conductivity >100 μS/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.

6.3.3.B GROUND WATER

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.
- ▶ The well should be purged or in the process of purging before sample conductivity is determined and recorded.

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 the sampling point, followed by the 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 ≤100 μS/cm
      ±3 percent for conductivity >100 μS/cm

- When readings fluctuate rapidly, record the median of three or more readings within about 60 seconds as the value for a specific time interval.
- If the criterion is not met, extend the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals. Record this difficulty on the field forms.

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

Subsample measurement

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

1. Calibrate the conductivity instrument system onsite.
   - Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.
     a. Check the temperature of the water flowing into the bucket against that of standards.
     b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.
   - After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.

2. Draw off subsamples for measurement.
   - **Quality control—Collect three subsamples to check precision.**
   - If samples need to be stored for a short time, or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles—fill to the brim, cap tightly, and maintain at ambient ground-water temperature. Measure conductivity as soon as possible.
3. Follow procedures described in steps 4 through 10 for “Subsample measurement” of surface water (6.3.3.A).

TECHNICAL NOTE: If the sample is measured in an open container and readings do not stabilize within several minutes, the cause may be CO_2 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; ºC, degrees Celsius]

Symptom	Possible cause and corrective action
Will not calibrate to standards	• 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	• 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	• Temperature compensator not working—measure conductivity of a solution. Place solution in a water bath and raise solution temperature to about 20ºC. 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.

REPORTING 6.3.5

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 the NWQL Analytical Services Request form using the correct parameter code.

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USE OF MULTIPARAMETER INSTRUMENTS FOR ROUTINE FIELD MEASUREMENTS

6.8

By **Jacob Gibs, Franceska D. Wilde, and Heather A. Heckathorn**

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Appendix

Tables

The citation for this section (6.8) of NFM 6 is as follows:

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USE OF MULTIPARAMETER INSTRUMENTS FOR ROUTINE FIELD MEASUREMENTS

6.8

By **Jacob Gibs, Franceska D. Wilde, and**
Heather A. Heckathorn

The miniaturization of sensors and other technological advances in electronics have resulted in water-quality instruments that house multiple sensors capable of simultaneous readings for various field measurements[1] in environmental waters. With the use of these multiparameter instruments, field measurements can be determined with considerable reduction in the field work that generally is required when using multiple single-parameter instruments (table 6.8–1). This section addresses the short-term or discrete-measurement use of portable multiparameter instruments. Refer to Wagner and others (2006) for long-term or continuous-monitor deployment in surface water.

MULTIPARAMETER INSTRUMENT: An electronic instrument that contains sensors (each specific to the measurement of a given physical, chemical, or biological property) that are bundled in a single housing (a sonde) and deployed in environmental waters.

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[1] The term "field measurement(s)" is synonymous in this report with the terms field properties and field parameters. USGS field measurements include, for example, water temperature, pH, specific electrical conductance, turbidity, oxidation-reduction potential, barometric pressure, and calculations such as salinity and percent of dissolved oxygen in milligrams per liter. The term "field parameter" commonly is used in the environmental literature.

Table 6.8–1. Advantages and limitations of multiparameter instruments for field use

Advantages	Limitations
Efficiency is increased. Instruments are easy to clean, calibrate, and deploy. The time required to collect discrete samples for determining field properties is minimized. The time needed to measure and record multiple field properties is reduced. In situ measurement is likely to be more accurate and precise than measurements made in samples removed from their source. Instruments can store data, either in a display device or to internal memory. Instruments may be capable of long-term deployment.	Repair of sensors while working onsite often is not possible. Sensor replacement in the field may be unwieldy or not possible. Sensors must be replaced in a clean, dry environment. Backup field instruments (single parameter or multiparameter) are recommended to prevent data loss and extended field time. Purchase, repair, and replacement costs for multiparameter instruments are higher than for single-parameter instruments.

Quality assurance. To ensure the quality of the data collected, this section of NFM 6 describes standard operating procedures and recommendations that have been developed for routine U.S. Geological Survey (USGS) field studies. The instrument manufacturer is, however, the primary source of information about the maintenance and use of a specific instrument. The protocols and recommendations described in this section are meant to complement and enhance the manufacturer's guidelines, providing the level of quality assurance for which USGS data are held accountable.[2]

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[2] USGS personnel should discuss any discrepancies between the protocols and recommendations described in this manual and the instructions provided by the instrument manufacturer with their water-quality specialists or with the USGS Office of Water Quality.

EQUIPMENT AND SUPPLIES 6.8.1

Multiparameter instruments are available for long- or short-term deployment at a stream, lake, reservoir, ground-water well, or other environmental setting, and their sondes[3] are suitable for water that is fresh, brackish, saline, or polluted. Sensor housings (the sonde) of multiparameter instruments generally are available in a range of diameters from about 4 inches (in.) (10 centimeters (cm)) to less than 2 in. (5.1 cm). Small-diameter sondes may be used for downhole measurements in wells and may have more limited sensor capability than the larger diameter sonde. Depending on the manufacturer, some instruments can store instantaneous or continuous measurements to internal or external memory in a format compatible with a hand-held display, personal digital assistant (PDA), or laptop computer.

Advances in technology and design are expanding the sensor[3] capabilities of multiparameter instruments and are improving instrument utility. The configuration and sensors that are available for multiparameter instruments can vary considerably among manufacturers. The procedures required for the maintenance, calibration, and use of these instruments also can change over time as a result of the technological changes being implemented; such information generally is available from the manufacturer, either online or as a manual or other document. **Users must stay current as to how their instrument operates and is maintained.**

- Sensors for the determination of water temperature, specific electrical conductance (SC), pH, dissolved-oxygen concentration (DO)[4], and turbidity commonly are bundled in sondes used for USGS water-quality studies, as these measurements are routine for much USGS work.
- Sensors that determine oxidation-reduction potential (ORP or redox) and barometric pressure, and that calculate salinity, also are commonly included in the sonde.

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[3] The term sensor, which is used in this report, is synonymous with the term "probe" that is common in the environmental literature. For multiparameter measurements, the sensors are bundled in a submersible sonde.

[4] DO is calculated as the percent of dissolved-oxygen concentration at saturation.

- For some instruments, sensors are available to measure fluorescence,[5] water depth, and velocity. In some cases, specific-ion electrodes (for example, nitrate, ammonia, ammonium, and chloride) can be incorporated in a sonde. Use of sensors to measure cholorphyll and concentrations of specific nutrient species are becoming more common in USGS work. Some instruments include global positioning systems.
- When making field measurements in surface water, the sondes commonly are immersed in situ (directly within the water body). As an alternative to in situ deployment, a flowthough cell containing the sonde can be set up above land surface, to which sample water is pumped. The flowthrough cell commonly is used to monitor field measurements for ground-water investigations and for calibration of the sensors.

The types and number of sensors that can be bundled in a given sonde depend on the instrument model and manufacturer. When selecting a sensor, consult the manufacturer's recommendations and specifications for the instrument, taking into consideration the environmental conditions to be encountered, the data-quality objectives of the study, and the specific benefit of a particular sensor technology that might be applicable to the anticipated field conditions. The manufacturer is the most knowledgeable source of information for a given instrument. **Consult the manufacturer's maintenance instructions for each instrument model before using the instrument.**

Table 6.8–2 lists the equipment specifications and calibration solutions required when determining field-measurement values using a multiparameter instrument. The ancillary supplies needed for measuring field properties using multiparameter instruments (table 6.8–3) are the same or similar to those required for the calibration and maintenance of single-parameter instruments, and are discussed in greater detail in the individual field-measurement sections (NFM 6.1 through 6.7) of Chapter 6.

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[5] Fluorescence sensors indicate different algal pigment concentrations; see NFM 7.4 for additional information.

Table 6.8–2. Specifications and calibration solutions for multiparameter instruments

[±, plus or minus; -, minus; +, plus; °C, degrees Celsius; mV, millivolt; >, greater than; SC, specific electrical conductance; µS/cm, microsiemens per centimeter at 25°C; DO, dissolved oxygen; mg/L, milligrams per liter; ORP, oxidation-reduction (redox) potential; NIST, National Institute of Standards and Technology; L, liter; ≤, less than or equal to; µm, micrometer; mL, milliliter; MSDS, Material Safety Data Sheet; SDVB, styrene-divinylbenzene beads; TDS, total dissolved solids; NFM, *National Field Manual for the Collection of Water-Quality Data*; USGS, U.S. Geological Survey.]

Item[1]	Description[2]
Instrument (sensor) specifications:	Visual display - digital readout.
pH and millivolt	pH sensor - range of at least 2 to 12, preferably 0 to 14, pH units. Accuracy, ±0.2 pH units. Millivolt readout - accuracy, ±1.0 mV.
Temperature	Temperature sensor - thermistor range, at least -5 to +45°C. Accuracy, ±0.2°C.
SC	SC sensor - temperature compensating. Accuracy, the greater of 0.5±0.5 percent of reading or ±2 µS/cm.
DO	**DO polarographic sensor** (amperometric method) - range from 0.05 to 20 mg/L. Accuracy, the greater of ±2 percent of reading or ±0.2 mg/L. **DO optical sensor** (luminescent-sensor method) - range from 0.05 to 20 mg/L. Accuracy, the greater of ±1 percent of reading or ±0.1 mg/L.
Turbidity	Turbidity sensor[3] - range and accuracy depend on the instrument type, manufacturer, and field conditions (see NFM 6.7). Choice of instrument will depend on application. Most multiparameter-instrument turbidity sensors use a monochrome light source with a spectral output typically near infrared (780 to 900 nanometers), usually a light-emitting diode. *Note*: Instrument should include a calibration cup specifically designed by the manufacturer, if available.
ORP[3]	ORP sensors - accuracy, ±20 mV. For guidance on Eh measurements using the platinum electrode, refer to NFM 6, section 6.5 and the manufacturer's instructions.
Air pressure	Select instruments that incorporate an **altimeter/barometer** (measures to the nearest 1 millimeter).
Other sensors[3]	Check the text for this section and the manufacturer's instructions for the availability of other sensors.

Table 6.8–2. Specifications and calibration solutions for multiparameter instruments — *continued*

Item[1]	Description[2]
Sensor-calibration solutions:	(Keep the respective **MSDS guidance** on hand in the laboratory and in the field. Dispose of hazardous waste according to regulations, using a licensed disposal company.)
pH buffers	Standard buffers are pH 4, 7, and 10. Temperature-correction chart(s) supplied by the buffer manufacturer or distributor are required.
SC standards	Use the SC standard(s) recommended by the manufacturer for calibration. NOTE: The manufacturer might require a proprietary calibration solution. For field verification of the calibration, select additional standard(s) that bracket the expected or known sample SC. Do not dilute a concentrated standard to prepare a standard of lower conductivity.
DO standard	Zero DO calibration solution. Dissolve 1 gram of sodium sulfite and a few crystals of cobalt chloride[4] in 1 liter of deionized water (prepared during the week of use). **Cobalt chloride is toxic; check the MSDS for safe handling.**
ORP standard	ZoBell's solution[5] - This solution contains cyanide and may be harmful if absorbed through skin, inhaled, or swallowed. Check the MSDS for safe handling. - Use a dedicated hazardous waste disposal container for ZoBell's solution. **Do not pour ZoBell's solution down the sink drain or onto the ground. Do not mix with acids or combustible materials.**
Turbidity standard	Turbidity standard solutions with various ranges are available commercially. Most sensor manufacturers recommend either formazin-based or SDVB-polymer standards for calibrating their turbidity sensors. **Do not use gels or solids for calibrating instruments** (see sections 6.8.2 and NFM 6.7). - Turbidity-free water (deionized water filtered through a ≤0.2-µm membrane filter). - Formazin stock suspension can be obtained commercially or prepared in-house from hydrazine sulfate and hexamethylenetetramine (safety precautions for handling these chemicals are described in NFM 6.7, section 6.7.2)

[1] Modify this list to meet the specific needs of the field effort and the specific requirements for the multiparameter instrument to be used.

[2] The accuracy specification provided in this table has been generalized, based on a survey of three or more manufacturers with instruments in common use among USGS field studies. Consult the manufacturer's operators' manual for the level of accuracy for a specific instrument.

[3] The turbidity sensor commonly is required or recommended for use (section 6.7). ORP sensors are less commonly used for USGS studies; see the description in section 6.5. Follow the manufacturer's guidance for use of the salinity or TDS option, and for other ion-selective sensors (for example, for nitrogen species and chlorophyll).

[4] Prepare fresh zero DO solution for each use. CAUTION: Use of cobalt chloride is recommended in Standard Methods (American Public Health Association, 2005); however, this is a toxic substance that must be handled with care and disposed of in accordance with prevailingregulations. If possible, prepare a zero-DO solution without using cobalt chloride.

[5] Alternatives to Zobell’s are being investigated (January 2008).

EQUIPMENT TRANSPORT 6.8.1.A

Transport the multiparameter instrument in a case that is designed to protect this equipment.

- ▶ To avoid damaging the sensitive and expensive field-measurement sensors, keep either the sensor guard or transportation/calibration cup installed. Some manufacturers specify adding a small amount of water to the transportation/calibration cup for transport between field sites; follow the manufacturer’s recommendations.
- ▶ When packing the instrument for transport, use a case provided by the manufacturer; alternatively, obtain a suitable case, such as a Pelican™ case, Otter® box[6], or a tool box, and modify it as needed.
  - — Cases must be padded to absorb shock, using material that does not absorb water.
  - — Pelican and Otter boxes are airtight; the case needs to be vented if using sensors that have a flexible or semi-permeable membrane.
  - — A white or light-colored case should be used to help deflect solar heating of the sonde.

INSTRUMENT MAINTENANCE AND STORAGE 6.8.1.B

Each instrument requires its own (dedicated) log book that accompanies the instrument, in which permanent records of instrument calibrations, bench checks, sensor replacements, general maintenance, and repairs are logged. The following recommendations pertain to maintenance of the multiparameter instrument that is deployed over discrete or short (attended) time intervals. For maintenance of instruments intended for long-term or unattended instrument deployment, refer to Wagner and others (2006) and the instructions provided by the manufacturer.

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[6] Examples of transport cases can be found at www.otterbox.com or www.pelican.com (accessed 5/22/2007).

- **Sensor and sonde care and maintenance:**
  - Rinse the sensors immediately after each use with deionized water (DIW).
  - If the multiparameter instrument (handheld display and sensors-containing sonde) is particularly dirty or will be stored for longer than one day, clean it with a mild, nonphosphate detergent solution using a small, nonabrasive brush or cotton swab or cloth, followed by a thorough water rinse.
  - Avoid using organic solvents or other corrosive solutions to clean the sensors.
  - O-rings used for some types of dissolved-oxygen sensors are not very robust; inspect such O-rings before each DO measurement and replace if damaged.
  - **Do not coat the sonde or sensors with protective or anti-fouling paint,** except as specifically instructed by the manufacturer.
  - Manufacturers may have instructions specific to their sensors—**check the manufacturer's operating manual for each instrument that will be in use.**
- **Wiper and wiper-brush maintenance**:
  - Inspect the wiper pad and (or) wiper brush for dirt, deterioration, and damage after each use of the sonde. (Not all instruments have a wiper or wiper-brush mechanism.)
  - Check wiper pads for wear, excessive discoloration, and particle accumulation, and change the pads as needed. Check that the wiper arm is parking properly. Follow the manufacturer's guidance for conditions requiring changing the pads and for wiper maintenance.
  - A soft toothbrush can be used to clean wiper-brush bristles. Rinse with fresh tap water or DIW.
  - Wiper-brush bristles should be kept moist at the start of the operation to prevent them from drying. If the bristles have dried, soak them in DIW and manually loosen them before deploying the sonde.

▶ **General care of multiparameter instruments:**

- Do not leave instruments in vehicles for long periods of time during extremes in temperature.
- At least once a year inspect cables for damage, and electronic connectors and sensor ports for corrosion.
- Inspect and clean the bulkhead O-rings and grease them with silicone lubricant annually, at a minimum. Replace any damaged O-rings.
- Store cables in a plastic container only after they are clean, dry, and neatly coiled (no tighter than 6-inch-diameter coils). Use protective plugs when cable connectors are not in use. When in use, protect cables from abrasion or unnecessary tension.
- Make sure that the instrument is running on software and firmware that is up-to-date. Check for updates from the manufacturer every 6 months or more frequently and follow the download or other installation instructions.

▶ **General storage recommendations for multiparameter instruments and instrument cases**:

- For short-term storage, some sensors need a small amount of the storage solution added to the protective (transport) cap or calibration cup; check the manufacturer's instructions.
- For long-term storage (longer than several weeks), remove the internal batteries; however, be sure to check the instrument manual for guidance before removing all of the batteries.
- Store multiparameter instruments in a carrying case or plastic container with foam cushioning (for shock protection). Keep the instrument and case out of direct sunlight and protected against extremely hot or cold temperatures.
- Insert a sensor-port plug into any vacant sensor port to prevent damage to the vacant port during maintenance, operation, or storage.

Table 6.8–3. General supplies related to field-measurement activities

[DO, dissolved oxygen; mL, milliliter; L, liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; ASTM, ASTM International Company; NFM, *National Field Manual for the Collection of Water-Quality Data;* USGS, U.S. Geological Survey]

Item[1]	Information
Flowthrough cell	Standard flowthrough cell, obtained from the manufacturer of the instrument. (Commonly used for ground water or other water pumped from the water source to the airtight cell for measurement of field properties.)
Extra sensors and meters	Single-parameter meters and sensors or a multiparameter sonde (as a field backup). Refer to equipment lists and descriptions and instructions provided in NFM 6, sections 6.1 through 6.7.
Membrane-replacement kit for amperometric DO	Membrane-replacement kit (includes membranes or screw-on membrane caps, O-rings, filling solution).
Calibration (laboratory) thermometer	Liquid-in-glass or electronic-thermistor thermometer, either NIST-certified or manufacturer-certified as NIST-traceable. (See NFM 6, section 6.1 for USGS standard specifications.)
Field thermometer	Non-mercury liquid-in-glass or thermistor thermometer that has been office-laboratory certified against a properly certified calibration thermometer. (See NFM 6, section 6.1 for USGS standard specifications.)
Turbidity container and flasks	Bottle for turbidity-free water, cleaned and rinsed three times with filtered water before starting each field trip. Volumetric flask, Class A, 100 mL or 500 mL, if dilution of stock solutions is necessary (see section 6.8.2).
Carrying case	Protective case, vented, white or other reflective color, to hold the multiparameter instrument during transport and storage.
Holding stand[2]	A stand to support the multiparameter sonde during calibration.
Log book(s)[3]	One log book per instrument (multiparameter and single-parameter), for recording instrument calibrations, maintenance, and repairs. Log book travels with the instrument.
Flasks, beakers, and other measurement vessels	Insulated flask or beaker and additional polyethylene or Teflon® preferable beakers for temperature check or other field needs. Assorted sizes, 50 to 150 mL. Beakers must be clean but not acid rinsed.
Deionized water (DIW)	1 L of DIW with a maximum conductivity of 1 µS/cm (ASTM Type 1) for rinsing sensors.
Paper tissues	Laboratory grades (for example, lint free and (for turbidity) extra lint free Kimwipes®), soft, disposable.

Table 6.8–3. General supplies related to field-measurement activities — *continued*

Item[1]	Information
Dispenser (squeeze) bottles	Polyethylene to contain DIW; for rinsing instruments and instrument sensors.
Disposable gloves	Laboratory gloves, disposable, non-powdered and of a material suitable to contact anticipated chemical solutions and environmental waters or wastewater. Keep a supply on hand in the field vehicle.
Brushes for equipment cleaning	Brushes of various sizes, but generally small and soft to prevent scratching the sensor(s) or other surfaces.
Minnow bucket with tether, mesh bag, or equivalent	Used to contain fresh sample water into which tightly capped calibration solutions are immersed for thermal equilibration with the temperature of the sample water before being used for sensor calibration.
Antistatic spray or polish	Used on the digital display screen of a multiparameter instrument.
Cleaning solution	1 L of nonphosphate laboratory detergent (see NFM 3 for solution-concentration guidelines).
Batteries and/or battery pack(s)	Check that batteries are fully charged; bring spares.
Safety equipment	Select safety equipment appropriate for the field effort conditions, such as gloves, eye protection, face mask, apron, chemical spill kit, first-aid kit.
Waste-disposal containers	Appropriate for safe containment of regulated (hazardous or toxic) substances and dedicated to use for the respective waste material (examples: ZoBell's solution, methanol, and acid and turbidity calibration solutions).

[1] Modify this list to meet the specific needs of the field effort.

[2] USGS personnel may check for the availability of instrument stands (HIF # 6103032 or #6103035) at the USGS Hydrologic Instrumentation Facility.

[3] Bound log books with water-resistant pages are available to USGS personnel through the USGS One Stop Shopping store.

6.8.2 CALIBRATION

Multiparameter instruments must be tested and the sensors calibrated before each field use**.** With some exceptions (for example, turbidity calibration), calibrations are performed in the field in preparation for making measurements.

When visiting more than one site for field measurements, the sensors and sonde housing must be cleaned and then the sensor calibration verified for each site. Field calibration should be completed in an area sheltered from wind, dust, and temperature fluctuations. Consult the manufacturer's guidelines before beginning the calibration process and contact the manufacturer's technical support if problems or questions arise.

Ensure that the sensors are properly installed in the sonde. Before beginning the calibration process, check the power source; only use batteries that indicate a full charge.

- ▶ Most multiparameter instruments perform best if allowed to warm up for at least 10 minutes after being turned on, or according to the manufacturer's recommendation.
- ▶ The following order is recommended for performing calibration or accuracy checks in the field:
    1. **Temperature** (using a thermometer that has been calibrated and office-certified, as described in NFM 6.1)
    2. **Specific electrical conductance (SC)** (note that the value of the SC standard solution changes by more than 3 percent when the temperature is less than (<) 6°C or greater than (>) 40°C; do not calibrate with standards <6°C or >40°C.
    3. **Dissolved oxygen (DO)** (amperometric or luminescent-sensor methods using polarographic or optical sensors, respectively)
    4. **pH** (be sure to check and adjust for the buffer pH value at the buffer temperature)
    5. **Oxidation-reduction potential (ORP)**
    6. **Turbidity** (most manufacturers recommend that the turbidity calibration be performed in a laboratory or other stable environment)
    7. **Ion-selective electrodes, followed by chlorophyll-fluorescence and other sensors**.

- Complete the calibration field form during calibration (Appendix 6.8–A). Accurate calibration records must be maintained and entered into the appropriate instrument log book at the time of calibration.[7]
  - Keep a hard copy of the field form in the field or site folder. These records contain vital information that can be referenced if technical or legal questions arise. Interpretation of data analyses or data quality may depend on the documentation regarding instrument performance and the calibration solutions and the methods used, in addition to the results recorded. This record should be checked and verified by a second or third party.
  - The field form documents that a sensor has met the data-quality objectives of the study and that the calibration was performed according to the required standard operating procedures. Lot numbers and expiration dates of calibration solutions are recorded on the electronic or paper field form (Appendix 6.8–A).
  - The instrument log book is the archival document for recording details chronologically, including calibrations, maintenance specific to the sensors, and general repairs. Log book entries should be recorded using black or blue ballpoint ink, preferably on water-resistant paper with the pages consecutively numbered and bound to deter page removal. To ensure the legal viability of the log-book record, a page never should be removed and a single line should be drawn through any erroneous information or data and initialed. (USGS personnel can obtain log books through One Stop Shopping).
- Clean the instrument onsite after each use to reduce the potential for site and sample cross contamination and loss of calibration.

Reagents used for calibration may be hazardous to health and require special handling. Review the MSDS for the reagent of concern. Keep the safety sheets handy.

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[7] For USGS studies, the worksheet is included in the electronic (PCFF) and paper national surface-water and ground-water water-quality field-notes forms. Meter-calibration log books are available to USGS personnel through One Stop Shopping.

6.8.2.A STANDARD USGS CALIBRATION PROCEDURES FOR MULTIPARAMETER INSTRUMENTS

The results of sensor calibrations are recorded on a field form at the time of calibration (Appendix 6.8–A provides an example of a field form for recording calibrations and field measurements). In addition, a historical record of calibrations for each sensor used in a given multiparameter instrument must be kept in an instrument log book that accompanies the instrument to the field. This log book also is used to document maintenance, repairs, and sensor replacements for the instrument.

When calibrating multiparameter-instrument sensors:

1. **Follow the manufacturer’s instructions** for the instrument model and sensors being used.
    - Become familiar with the operation and setup of the handheld or other display hardware and software. Make sure that the batteries are fully charged, or install fresh batteries.
    - Ensure that the instrument has been set for the appropriate measurement unit, if this option is available.
    - Ensure that the instrument has been warmed up for the amount of time recommended by the manufacturer.
2. **Bring calibration solutions (calibrants) to the temperature of the sample source**, to the degree possible.[8] Note there are exceptions to this protocol for SC and turbidity, as described below. To allow equilibration of the calibration solutions with ambient sample-water temperature, calibrant containers can be partially immersed in the stream being sampled, or in a bucket to which the ground water being sampled is pumped. **Great care must be taken to prevent water from getting close to the top of the calibrant container and contaminating the calibrant.**

Note 3/8/2012: Calibration requirements for field sensors are under review**.**

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[8] For calibration of sensors for turbidity and specific electrical conductance, check with the manufacturer for guidance.

- Calibrate the instrument in a temperature-stable environment, out of the wind and direct sunlight.
- Use the calibration cup that comes with the instrument for calibration, unless otherwise instructed by the manufacturer. If a calibration cup is not available, follow the manufacturer's alternative recommendations.
- Use the recommended volume of calibrant when filling the calibration cup. The calibrant must cover the temperature sensor, as most sensors require temperature compensation.
- Be careful not to overtighten the calibration cup. This is especially important for DO calibration. Many calibration cups have vents that allow their equilibration with ambient pressure.
- For SC, do not equilibrate the temperature of the standards to that of the sample source if source temperature is less than 6°C or greater than 40°C, because the value of the SC calibration standard changes significantly (by more than 3 percent) as a function of temperature at these temperature extremes. In such situations, perform the SC calibration inside a room or vehicle in which the ambient temperature of the standards is maintained at a temperature >6°C and < 40°C.
- For turbidity, calibrations should be performed in an environment that is protected from wind and thermal fluctuations.

3. **Rinse sensors thoroughly three times with deionized water after use of each calibrant, followed by three rinses with the next calibrant to be used.**

   - To avoid dilution of calibration solutions, gently shake excess rinse water from sensors.
   - Use a lint-free laboratory tissue (for example, Kimwipes®) to absorb water droplets without touching or wiping the sensor surface; never touch or wipe the transparent surfaces associated with luminescent DO, pH, and turbidity sensors.

4. **Calibrate the SC and DO sensors before calibrating the pH sensor**. This helps prevent contamination of the SC sensor from pH buffer solutions (pH buffers have much higher conductivities than most environmental waters).

5. **Periodic removal and cleaning of sensors** may be needed for any multiparameter sonde that is deployed for long-term monitoring. The time interval between cleanings will depend on site conditions and study requirements.

Bring calibration solutions (standards and buffers) to the ambient temperature of the environmental sample to the degree possible.

6.8.2.B SENSOR-SPECIFIC CALIBRATION TIPS

The following guidelines comprise standard USGS procedures.

- Check sensor ports to be sure that either the ports have a properly installed sensor or that the empty ports are sealed. Sensors from which data are not being collected routinely can be removed from the sonde for safe storage, provided that the sensor is not necessary for the measurements of interest and provided that the empty port is sealed according to the manufacturer's instructions. The temperature sensor should not be removed. All electrical connections must be clean, dry, waterproof, and protected from dust.
- Clean sensors after each use and keep them maintained and stored according to the manufacturer's instructions.
  - Before calibrating and using an instrument in the field, inspect the sensors to be sure that they are clean and are not damaged.
  - Periodic cleaning may be needed for any instrument that is deployed for continuous monitoring (see Wagner and others, 2006).

Temperature (revised, 3/8/2012)

Check to ensure the accuracy of the temperature sensor at least every 3 months if the multiparameter instrument is in frequent use. **The accuracy of pH and other field measurements depends on the accuracy of the temperature measurement.**

1. Verify the accuracy of the temperature sensor against a certified NIST-traceable digital or liquid-in-glass thermometer ~~following the guidelines provided in NFM 6.1 (annual laboratory verification and biannual field checks are mandatory for USGS studies)~~. ***Note, 3/8/2012**: NFM 6.1 calibrations guidelines are under review. For the calibration check, the NIST thermometer and sonde thermistor should be as close together as possible without touching. For field verification, use a non-mercury thermometer that has been certified as accurate within the past 6 months and is tagged as such by the verifier. When making the field check, record the temperature readings of both the multiparameter instrument and the NIST-traceable thermometer in the instrument log book.
   - If the difference between the readings does not fall within the manufacturer-specified accuracy, return the instrument to the manufacturer for repair or replacement.
   - See NFM 6.1 for a description of the annual and biannual calibration protocol for liquid-in-glass and digital thermometers, which also require calibration checks. *See **Note** above.
2. Make sure that the temperature sensor is completely submerged.
3. Allow at least 1 minute for temperature equilibration and stabilization before recording the temperature value and proceeding with the other measurements.

Specific Electrical Conductance (SC) (see NFM 6.3, section 6.3.2)

1. **Most multiparameter instruments use a one-point calibration** to calibrate the SC sensor. Use a standard having the conductivity recommended by the instrument manufacturer; otherwise, select a standard that is close in conductivity to that of the environmental water.
   - Rinse the calibration cup and sonde using a small amount of standard. **Repeat this two more times** and then fill the cup with the recommended volume of standard.
   - The sensor should be completely submerged in the standard (if a hole exists in the side of the sensor, it must be covered by the standard). Low fluid level can cause an erroneous calibration or may result in an error message on the instrument display.

- The presence of air bubbles in SC electrodes will cause erroneous readings and incorrect calibration.
- Although most SC sensors are shielded from effects caused by proximity to transmission lines and to alternating-current (AC) electrical outlets and radio-frequency noise sources, be aware of the possibility of this interference and check with the instrument manufacturer.

2. Wait for readings to stabilize (approximately 30 seconds under normal conditions) before adjusting and saving the calibration point.

   - The USGS reports SC in units of microsiemens per centimeter (µS/cm). The default SC setting on many multiparameter instruments often is in units of millisiemens per centimeter (mS/cm). Either change the setting to µS/cm (if this option is available) or measure in mS/cm and then convert to µS/cm (multiply mS/cm by 1,000). **To fulfill USGS data protocols, record the SC value in µS/cm on paper or electronic (PCFF) field forms.**
   - Do not override a calibration error message without troubleshooting and correcting the cause of the error. For example, check the fluid level and check for air bubbles in the sensor.

3. To verify that the accuracy of the SC sensor is within the range of the conductivities to be measured:

   - Ensure the linearity of response of the SC sensor at low-conductivity values and check the zero response of the dry sensor in air (Wagner and others, 2006).
   - Select two standards (“check standards”) that bracket the expected SC range of your water as closely as possible; a third standard that is at or close to the actual ambient conductivity helps to pinpoint the accuracy of the sensor. Equilibrate the temperature of the standard to that of the water body, unless the water temperature is < 6°C or > 40°C (use of this protocol can depend also on instrument software – consult the manufacturer’s guidance). Follow the same procedure as for an actual calibration, but **do not lock in or adjust these readings—this is an accuracy check, not a calibration point.**

Handle conductivity standards in a manner so as to prevent their dilution or contamination.

- **Do not use expired standards.**
- **Do not reuse standard or pour used standard back into the bottle.**

Dissolved Oxygen (DO) (see also NFM 6.2, section 6.2.1.B)

Two sensor options are available for the DO measurement when using multiparameter instruments: the polarographic (or Clark cell) sensor or the luminescent (optical) sensor. Referring to NFM 6.2 on DO measurement methods, the polarographic-sensor option corresponds to the amperometric method, and the optical-sensor option corresponds to the luminescent-sensor method.

General comments:

- Follow the manufacturer's guidelines for care, proper setup, and calibration of the DO sensor for the instrument in use. **For either sensor type, most manufacturers recommend that the sensor be allowed to equilibrate to the temperature of the air-saturated water or water-vapor-saturated air for at least 15 minutes before calibration.**
- Before calibrating for 100-percent saturation of DO, loosen the calibration cup. (It should contain less than 1/8 in. (~0.32 cm) of water, or as recommended by the manufacturer.)
- Remove any water droplets from the thermistor or the DO membrane without wiping the membrane. Water droplets on these surfaces can cause a temperature compensation error in the DO calibration.
- Store and transport the sonde in a padded, vented, white (or light-colored) case to make DO calibration checks quicker and reduce the chance of DO sensor drift (since the instrument is in a more temperature-stable environment and can be calibrated within the cooler).
- Calibrate the DO sensor on the morning of the field day and check the calibration at each measurement station. Enter the barometric pressure (see NFM 6.2 for an explanation of corrected and uncorrected values).

> **TECHNICAL NOTE**: Check the manufacturer's instructions regarding the need to recalibrate amperometric-instrument sensors with changes in altitude. For some instruments, the DO sensor should be recalibrated at each site at which there is a change of approximately 900 ft (~ 300 m) in altitude. Luminescent sensors tend to keep calibration over extended time periods; however, verification of sensor performance with appreciable altitude change is recommended to quality assure and document sensor performance. To convert inches (in.) of mercury (Hg) to millimeters (mm), multiply inches by 25.4.

- **The calibration procedure depends on the type of DO sensor being used.** Note the type of sensor being used—amperometric or optical (luminescent)—and follow the appropriate instructions provided by the manufacturer and as described below. Allow the sensor to equilibrate to the temperature of the solution for at least 15 minutes or as recommended by the manufacturer.
- Always perform a 100-percent saturation calibration before beginning the zero DO calibration.

Amperometric method for DO measurement (polarographic or Clark-cell sensor):

Instrument makes and models can vary considerably; always refer to the manufacturer's instructions for the instrument that is in use. To prevent water damage to the sonde's internal parts, maintain the O-rings and sealing surfaces on the sonde as directed by the manufacturer. Be aware that extreme temperatures and instrument vibrations may cause the DO sensor to drift out of calibration on a day when a series of measurements is made.

1. Inspect the DO sensor anodes and cathodes—if they are not bright and shiny, recondition them as instructed by the manufacturer.
2. Install a new membrane or membrane cap of the desired membrane thickness. If not using the membrane cap, the membrane should be tightly stretched, and have no bubbles, wrinkles, or tears. Replace any worn or stretched (loose) O-rings.
    - Membrane replacement should take place 24 hours before use (USGS standard procedure). Manufacturer guidance generally specifies membrane replacement at least 3 to 4 hours before use (M. Lizotte, YSI and Bruce Wilcox, Hach Environmental, written communs., May 2007).

- A tight-fitting O-ring is critical to good sensor performance.
- Run or power up the newly membraned sensor for 15 minutes.
- Do not allow electrolyte solution to wet the sensor or sonde connector or other O-ring sealed areas. Electrolyte solution is highly conductive and will short out electrical connections.

3. A wet towel can facilitate the water-saturated air calibration of the DO sensor as follows: **wrap the sensor guard with a white towel wetted in field temperature water**, forming an enclosed moist environment around the instrument sensor guard and sonde body. Allow time for the air inside the sensor guard and wet towel to become saturated with water vapor (10 to 15 minutes).

4. **Rinse the DO sensor thoroughly, at least three times, with DIW or tap water after being calibrated in the zero-percent solution,** to avoid cross contamination and faulty readings. Inadequate rinsing will cause negatively biased readings.

Luminescent-sensor method for DO measurement (optical sensor):

Great care is required when calibrating optical DO sensors in the field. Optical DO sensors (like polarographic sensors) can be calibrated in either water vapor-saturated air or in air-saturated water (see NFM 6.2). The air-saturated water method is recommended for calibrating optical sensors. **Temperature equilibration of the sensor with the calibration solution must be achieved before proceeding with the calibration; follow the manufacturer’s instructions.**

1. To create an air-saturated water bath, one method is to fill a 5-gallon pail with tap water and aerate the water using a mid-sized aquarium air pump with air stone. Check the manufacturer’s recommendations. Some manufacturers have developed their own bath aeration system to help avoid effects from variance of temperature and hydrostatic pressure on the calibration (R. Mooney, In-Situ Inc., written commun., May 2007).
   - The air-saturated water method is faster and guarantees temperature equilibration of the optical DO sensor and calibration medium.
   - If the water bath is kept air-saturated and ready to use, calibration time can be reduced, as there is no need to wait for a calibration cup or wet towel to saturate the air.

2. Aerate the water for at least 1 hour prior to use.
3. When measuring in low DO environments or after replacing a luminescent-sensor membrane, a two-point DO calibration and (or) a zero DO check is needed or required.
   - If the sensor is equipped with a wiper, remove the wiper before starting the calibration (see the warning in step 5 below).
   - Calibrate the saturated and zero DO levels following each manufacturer's specific instructions.
   - To prepare a zero DO calibration solution, dissolve 1 gram of sodium sulfite and a few crystals of cobalt chloride in 1 liter of DIW (prepare this solution during the week of use). Check the Material Safety Data Sheet (MSDS) for handling of cobalt chloride, which is a toxic substance.
4. Observe the readings for DO; when there is no appreciable change for approximately 30 seconds, lock in or adjust the reading.
5. **After calibrating the sensor with the zero-percent solution, take extra care in rinsing the sensor thoroughly** to remove any residue of the solution. Inadequate rinsing will cause negatively biased DO readings and can result in cross contamination, possibly causing faulty SC or pH readings. The three-time tap-water or DIW rinse recommended for the amperometric-instrument sensor may not be sufficient. One manufacturer recommends rinsing the sensor under **running tap water for at least 10 minutes.**

> **WARNING:** On optical sensors equipped with wipers, remove the wiper before beginning the zero-DO calibration to prevent the wiper from soaking up sodium sulfite and thus contaminating the membrane when the wiper is activated.

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pH (see also NFM 6.4, section 6.4.2)

1. **The pH measurement requires a two-point calibration.** Select the pH 7 buffer plus a second pH buffer (for example, pH 4 or pH 10) that brackets the expected range of sample pH.
   - Use historical pH data for the sampling site, if available, to select the correct buffers.

- After performing the calibration, a calibration check with a third buffer can be useful if the pH range is unknown or if sites with differing range in pH value will be measured.
- **Do not use expired buffers**. **Discard decanted buffer after one use**—do not reuse buffers or pour decanted buffer back into the original container.

2. Bring the buffers as close as possible to the ambient temperature of the water being sampled.
3. Normally the sensor is calibrated first against the pH 7 buffer; however, this may differ among manufacturers.
4. Rinse the sensors and calibration cup, first with DIW and then with the buffer.
   a. Before using the first buffer, rinse the pH and temperature sensors and the calibration cup three times with the first buffer.
   b. Fill the calibration cup with enough buffer to completely cover the temperature and pH sensors.
5. Allow time for the pH and temperature sensors to equilibrate to the temperature of the buffer.
6. Record the temperature reading after it has stabilized. The pH value is temperature dependent. **Use the chart provided by the buffer manufacturer to determine the true pH value for the buffer at that temperature.** You will need to adjust the calibration reading to that value. **NOTE: Buffers from different manufacturers can yield somewhat different pH values for a given temperature.**
7. Follow the manufacturer's instructions for calibration with the first buffer.
   a. Record the temperature, pH, and millivolt (if available) readings before and after calibration with the first buffer.
   b. If your instrument does not display the percent slope, then calculate and record the slope of the pH sensor.

EXAMPLE: The acceptable tolerance for the pH 4 buffer is 180±50 mV; for the pH 7 buffer, 0±50 mV; and for the pH 10 buffer, -180±50 mV. If a value of +3 mV were recorded for the pH 7 buffer and -177 mV were recorded for the pH 10 buffer, the slope would be 180 mV. The acceptable range for the slope is from 165 to 180 mV.

8. Repeat steps 4, 5, 6, and 7 using the second buffer.
9. If a third buffer will be used to check the calibration range of the sensor, follow the same general procedures described above for the first and second buffers, **but do not lock in a calibration. The instrument reading should be within ±0.2 pH units** of the theoretical pH value at the buffer temperature.

Oxidation-Reduction Potential (ORP or Eh) (see also NFM 6.5, section 6.5.2)

1. **The pH sensor must be calibrated and working properly before calibrating the ORP sensor,** if the instrument uses a combination pH-ORP electrode.
    - For most multiparameter instruments, the ORP electrode usually is combined with pH electrodes in one sensor body in order to utilize a common reference electrode (usually the silver/silver-chloride electrode).
    - Recommended calibration procedures differ among instrument manufacturers. Follow the manufacturer's recommendations for calibration of the specific instrument and electrodes being used.
2. A one-point calibration at a known temperature generally is used to calibrate the ORP sensor. The ORP measurement should stabilize within 1 to 3 minutes.
    - Table 6.8–4 shows the true readings in millivolts for ZoBell's solution as a function of temperature for the platinum/silver-silver chloride paired electrodes. These values must be converted to a standard hydrogen reference electrode when the field measurements are reported in the USGS National Water Information System (NWIS) QWDATA database. See NFM 6.5 for more detailed information about ORP sensors, data conversion to the standard hydrogen reference electrode, and use of ZoBell's solution.
    - The calibration values should be within a tolerance of ±5 millivolts of the values listed in table 6.8–4.
    - **ZoBell's solution is toxic; handle with care.**[9]
3. Calibration can be affected by static electricity. Avoid touching the sensors during calibration and measurement.

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[9] Alternatives to ZoBell's solution are being investigated (January 2008).

4. The ORP sensors of some manufacturers must be oriented near the vertical ±45 degrees for proper operation. Be thoroughly familiar with the manufacturer's instructions before using the instrument.
5. Follow proper procedures for handling and disposal of ZoBell's solution and keep an MSDS for ZoBell's solution with the ORP equipment. Minimize the volume of ZoBell's solution being used and store the spent solution in a separate, dedicated container.

Table 6.8–4. Voltage of ZoBell's solution as a function of temperature for the platinum/silver-silver chloride paired electrodes

[ºC, degrees Celsius; mV, millivolts]

Temperature, in ºC	ZoBell's solution,[1] in mV
-5	270.0
0	263.5
5	257.0
10	250.5
15	244.0
20	237.5
25	231.0
30	224.5
35	218.0
40	211.5
45	205.0
50	198.5

[1] This table is provided as a courtesy by YSI (M. Lizotte, written commun., February 2006). See table 6.5–3 in NFM 6.5 for a chart showing the Eh of ZoBell's solution as a function of temperature.

ZoBell's solution is a toxic solution and considered a hazardous waste. Check with a chemical-substances safety officer and the MSDS for safe handling information and proper and legal disposal of spent ZoBell's solution.

Turbidity (see also NFM 6.7, section 6.7.2)

The methods and standards used for turbidity sensor calibration should be those that are recommended by the instrument manufacturer for the specific instrument type and model, using NFM 6.7 as a guide for USGS work.

Calibration of the turbidity sensor is highly sensitive to environmental fluctuations and should be performed away from wind, sunlight, and temperature fluctuations. (Most manufacturers recommend that the turbidity calibration be performed in a laboratory or other stable environment before departing for the field site. To some extent this is dependent upon the calibrant being used; for example, formazin use is confined to a laboratory environment. USGS protocol stipulates that calibration of the turbidity sensor be verified at each field site. Refer to NFM 6.7 for a detailed explanation.)

- **Calibrants are not necessarily interchangeable**. **Serious calibration errors can result from using the wrong standards.** Three types, or levels, of standard turbidity solutions (calibrants) are used to calibrate and (or) verify the accuracy of turbidity sensors (section 6.7.2). Use only those calibrants that are prescribed for the sensor by the instrument manufacturer. Refer to NFM 6.7 for detailed information on turbidity calibrants and for turbidity units of measurement as operationally assigned according to instrument type by the USGS.[10] The following terminology, taken from ASTM Method D6855, is used by the USGS to distinguish among classes of turbidity standards (C.W. Anderson, U.S. Geological Survey, written commun., December 2006; ASTM International, 2003):
  - — Reference standard: 4000 NTU formazin solution, obtained commercially or prepared in-house (“from scratch”).
  - — Calibration standard: Diluted scratch formazin, StablCal® or styrene-divinylbenzene (SDVB) polymer.
  - — Verification standard: Gels, solids, or diluted SDVB or StablCal.

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[10] The guidelines for reporting turbidity units described in NFM 6.7 were developed jointly by the USGS, ASTM International, and participating instrument manufacturers.

- **Diluting a reference standard for turbidity calibration can result in erroneous data and, in general, is not recommended.**
  - Precise laboratory technique is essential for dilutions and should be performed only by experienced personnel. If not handled carefully, the dilutions can become unstable and particle suspension may be lost.
  - Discard a diluted scratch formazin calibration standard within 24 hours of preparation.
- **The quality of the turbidity measurement is dependent on the type of standard (that is, on the particulate matter contained in the suspension**) that is used to prepare instrument calibration curves.
  - Turbidity-free water, used as a zero-turbidity standard and for the preparation of standard solutions, dilutions, and equipment rinsing, is prepared as described in NFM 6.7.
  - Formazin-based calibration standards are freshly prepared by diluting a 4,000 NTU reference standard, using the dilution formula provided in NFM 6.7. Because the dilution process is subject to preparation errors, document that a calibration standard was used and report it as "calibration standard, prepared by dilution of a 4,000 NTU standard." **A calibration standard must be prepared on the day of use and be discarded on the same day.**
    - Record the source of the 4,000 NTU reference standard. The 4,000 NTU standard has a shelf life not to exceed 1 year.
    - The diluted scratch formazin (calibration standard) has a shelf life of less than 24 hours.
    - Do not use expired standards (American Public Health Association, 2005, Method 2130B, p. 2–9 to 2–11).
  - **Do not dilute SDVB polymer or StablCal standard for use as a calibration standard**. Although a diluted polymer-suspension (less than 10:1) sometimes is used as a verification or calibration check (verification standard), this is not recommended by the USGS and should not be used for USGS studies.
    - Store the verification standards out of sunlight and in PVC bottles.
    - Handle verification standards carefully to maintain the stability of the suspension.

- ▶ Check the turbidity standards for expiration before performing a dilution, calibration, or calibration verification. Note that higher range formazin standards tend to settle and thus are less stable than lower range formazin standards.

The following summary of turbidity sensor calibration does not replace the more detailed information to be found throughout NFM 6.7, and specifically in section 6.7.2.

1. **If the sonde includes a wiper brush and (or) pad for cleaning the DO, pH, and SC sensors, this brush must be removed before calibrating the turbidity sensor**. If the wiper occupies a sensor port, be sure to plug the open port before starting the calibration.
2. **Perform the turbidity-sensor calibration in a protected environment, away from wind and thermal fluctuations**. Standard USGS procedure is to calibrate sensors onsite, but in a location in which stable environmental conditions can be maintained.
   - Prevent disturbance to the standard solutions that might result in forming bubbles, and prevent exposure of these standards to direct sunlight.
   - Verify calibration of the turbidity sensor in an environment in which stable readings can be obtained.
   - If the calibration is performed in a laboratory just before departing for the field site, use a verification standard onsite to check the sensor calibration.
3. **Use only the recommended calibration standards for actual calibration of the sensors.** A verification standard may be used to check the calibration in the field.
4. **Use the manufacturer-supplied calibration (or storage) cup with a non-reflective endcap**.
   - Do not use plastic beakers or containers when working with sensors that use infrared light; clear plastics can reflect the infrared light beam and cause errors.
   - Clear glassware may be used with the sensor guard installed on the sonde.
   - Do not use small-diameter or small-volume containers (for example, 35-mm film-storage containers) for this purpose.

5. **Inspect the instrument carefully**.
    a. Check the instrument—ensure that all submerged parts of the multiparameter instrument are clean before beginning turbidity calibration. Sediment or other particulates from the sonde, wiper, or other parts can contaminate the standard, leading to an incorrect calibration and measurement.
    b. Check the optical ports—the optical surface of the turbidity sensor must be clean and free of bubbles, fingerprints, scratches, or other interferences.
    c. Check the wiper—if your turbidity sensor has a wiper with a pad or brush, inspect the condition of the pad/brush and replace it if necessary. Check that the wiper is parking properly and is operational.
    d. If the sensor is without a mechanical wiper (for example, during discrete sampling), take extra care to maintain a clean, bubble- and solid-material-free optical face. To remove bubbles from the optical face during calibration or field measurement, agitate the sonde by moving it in a vertical or circular motion.
6. Check the manufacturer's instructions for the minimum distance between the sensor face and the bottom of the calibration chamber, before and during the calibration process. Take care to avoid interference from the bottom of the calibration vessel.
7. **Note that if the sensor is equipped with a wiper (or brush), the wiper (or brush) needs to be activated immediately before the calibration data are acquired.**
8. When verifying the turbidity-sensor calibration, a three-point check is recommended before deciding to adjust the calibration.
    - If the sensor readings exceed the established calibration criteria for project data-quality objectives (for example, the greater of ±5 percent of the measured value or 0.5 turbidity units) during the inspection process, the sensor requires calibration.
    - If instrument calibration allows only a two-step process, use two calibration standards that cover the expected turbidity range and check for linearity using a third midpoint standard. If the instrument calibration requires only turbidity-free water and one calibration standard, select a midpoint standard to check for linearity.

> **TECHNICAL NOTE:** The range of standards recommended for verification of turbidity-sensor calibration varies, depending on the manufacturer and the linearity of the instrument being used.

9. Perform multipoint calibrations in the order of increasing turbidity.

   a. First rinse the calibration cup, turbidity sensor (and sensor guard) three times, each time using a small amount of zero-turbidity solution.

   b. Using the zero-turbidity solution, carefully fill the calibration cup along the inside surface, so as to avoid aerating the solution. Set the multiparameter instrument on top of the calibration cup (do not engage the threads). Verify that there are no air bubbles on the sensor face; then run the wiper (if present) at least once before accepting the first calibration point. Record the first calibration point. Use 2 Formazin Nephelometric Units (FNU) as the low-end calibration point.

> **TECHNICAL NOTE:** Consult the instrument manufacturer if the accuracy and precision of measurements below 2 FNU are important for the study, as calibration procedures within the 0 to 2 FNU range can differ depending on the instrument. Some manufacturers advise that instruments can be better calibrated to 2 or to 10 FNU than to 0 FNU.

   c. Before using the next standard, re-rinse the calibration cup, sensor guard (if present), and sensor three times with the zero-turbidity solution. Repeat this rinse between each new standard.

   d. To assess the actual performance of the instrument near the detection limit, periodically check using standards in the 1 to 5 turbidity-unit (low-level) range.

   e. Calibrate at the second point, again removing air bubbles and wiping the sonde or sensor at least once before accepting the value.

f. Monitor each output carefully to ensure that turbidity readings are stable before confirming the calibration value. Report the measurements in the proper units, as specified in NFM 6.7, table 6.7–4.

g. **Never override a calibration-error message without fully troubleshooting the cause of the problem.** Calibration-error messages usually indicate that a problem exists that will result in incorrect field readings.

10. While in the field, check instrument performance periodically using either a calibration standard (StablCal, SDVB polymer, or diluted scratch formazin) or a verification standard (gels, solids, or diluted SDVB or StablCal) and turbidity-free water.

TECHNICAL NOTE: Field experience is the best guide as to how often the turbidity sensor will benefit from recalibration. The need for recalibration depends on the condition of the optical windows, which in turn depends on the environment in which the instrument is deployed. Instruments deployed in biologically active environments, for example, require frequent cleaning and calibration checks. Periodic checks of the sensor against calibrants can be beneficial for indicating how well the sensor is holding its calibration.

WARNING: Contamination of the zero turbidity standard (from inadequately cleaned equipment) often is the cause of negative turbidity readings in clear environmental waters. Contact the instrument manufacturer for recommendations if negative turbidity readings cannot be eliminated.

6.8.3 MEASUREMENT

The field-measurement procedures implemented depend on the type of water body for which the chemical and physical properties are being determined, onsite characteristics and conditions at the time of measurement, and on the study objectives and data-quality requirements of the project. Refer to the respective sections of this chapter for detailed information regarding field measurement of temperature, specific electrical conductance, dissolved-oxygen concentration, pH, oxidation-reduction potential, and turbidity.

- Record a description of site conditions and any anomalies at the time of sampling.
- Allow time for the readings on the display to stabilize within the criteria shown on table 6.8–5.
- Record all required and targeted field measurements on the appropriate paper or electronic field forms, laboratory analytical request forms, project log books, chain-of-custody logs, and other documentation that might be required for the study (Appendix 6.8–A). Note on the appropriate forms any onsite conditions that could have affected the quality of the data.

Table 6.8–5. Standard criteria for stabilization of common multiparameter-instrument sensors

[±, plus or minus; ºC, degrees Celsius; %, percent; ≤, less than or equal to; µS/cm, microsiemens per centimeter; >, greater than; mg/L, milligrams per liter; FNU, formazin nephelometric units]

Sensor	**Standard sensor stabilization criteria** (Note that the actual accuracy of the sensor varies, depending on sensor model and manufacturer)
Temperature (thermistor)	± 0.2ºC
Specific electrical conductance (SC)	± 5% for SC ≤100 µS/cm, or ± 3% for SC >100 µS/cm
Dissolved oxygen (polarographic or optical)	± 0.2 mg/L to ± 0.3 mg/L
pH	± 0.1 to 0.2 pH unit; if drifting persists or if measuring low-conductivity waters (≤75 µS/cm), allow ± 0.3 pH units
Turbidity	± 0.5 FNU or 5% of the measured value, whichever is greater, for turbidity 100 FNU; or 10% of the measured value, for turbidity >100 FNU

SURFACE WATER 6.8.3.A

Field measurements commonly are monitored within a cross section of the surface-water body to (a) help determine how well mixed the stream is, and consequently the sampling method to be used (NFM 4.1), and (b) determine the field-property values of the water body at the selected site. In situ use of a multiparameter instrument is the most efficient means of obtaining such data.

- ▶ Many instruments include a pressure transducer that produces a value for water depth or level. For instruments without pressure transducers, the approximate depth of the sonde as it is lowered through a transect can be noted by placing incremental marks along the instrument cable or be connected to a pressure transducer. Depending on site conditions, the sonde might need to be weighted (consult the manufacturer).
- ▶ Wait a minimum of 60 seconds for the sensors to reach thermal equilibrium with the water temperature at each new location. Some instruments require a longer equilibration time; check the manufacturer's recommendations.
- ▶ At each measuring point, allow the field-measurement values on the instrument display to stabilize within an established criterion before recording final field measurements (table 6.8–5).
  - — Field-measurement values generally are considered stable if the variability among three or more consecutive readings, spaced some number of minutes apart, conforms to the designated criteria. See NFM 6.0 for a discussion on sensor-stabilization criteria.
  - — After making multiple measurements across a stream transect, return to the original measurement location within the transect and make a second measurement at that location, to check for measurement stability. Repeat the transect measurements if the original measurement is not replicated within the stabilization criterion shown on table 6.8–5.
  - — When aggregating the data from a cross section, **document the median** of the cross-sectional data for each field measurement.
- ▶ Biological growth or debris in the water can foul sensors, which will adversely affect sensor readings. If field conditions and quality-assurance protocols allow, adjust the spacing of the measurement intervals along the cross section or transect in order to avoid areas that will result in having to stop and clean algae, sediment, or debris from the sensors.

6.8.3.B GROUND WATER (revised 3/8/2012)

The stability of field-measurement values is monitored toward the end of well purging to help indicate when the water being withdrawn represents fresh formation water and when sample collection for other analytes should begin (NFM 4.2). The final field measurement typically is recorded after three or more well volumes have been purged and stability criteria have been met.

If the purpose of sampling is to obtain field measurements only, these data can be obtained in situ by deploying the sensor or multiparameter sonde downhole, followed by a submersible pump to draw water upward. If water-quality samples will be collected, pumping the water from the well to and through a flowthrough cell that contains the sonde or sensors is another efficient method for collecting field-measurement data without having to remove and redeploy sampling instruments. Flowthrough cells are supplied by the manufacturers of the multiparameter instruments.

- ▶ Connect all sampling-pump discharge-tubing fittings securely so that atmospheric oxygen does not enter the flowthrough cell of the multiparameter instrument, as this can affect the accuracy and quality of the measurements.
- ▶ Shield the flowthrough cell from direct sunlight to minimize changes in the temperature of the ground-water sample as it is withdrawn; changes in temperature also can affect the accuracy of the pH, ORP, and DO measurements, with respect to their ambient ground-water values, and incident light can affect turbidity readings.
- ▶ Wait a minimum of 60 seconds for the sensors to equilibrate to ambient ground-water conditions before monitoring field-measurement values. Some instruments require a longer equilibration time; check the manufacturer’s recommendations.
    - — Allow the value(s) on the instrument display to stabilize before recording a final field-measurement value (table 6.8–5).

— Field-measurement values generally are considered stable if, while purging the last of three well volumes of water, the variability among three or more consecutive readings spaced at least 3 to 5 minutes apart conforms to the designated criteria. See NFM 6.0, section 6.0.1 for a discussion on sensor-stabilization criteria and problems. See NFM 4.2.3 for detailed information about well purging.

— Good field judgment and experience are required to make a final determination when readings keep drifting or if what the values represent is in question. Such problems should be documented and advice (if needed) should be sought from a senior technician.

Field-measurement sensors must first be allowed to equilibrate to the ambient temperature of the water body being sampled or monitored. This can take from 60 seconds to more than 30 minutes, depending on the instrument and the start and final temperature range. Ensure that all field-measurement readings have stabilized before recording the final field measurement values.

6.8.3.C MEASUREMENT TIPS

Measurement accuracy depends on the adequacy of the calibration procedures used, and many of the precautions described in section 6.8.2 on calibration also apply when measuring the field properties of environmental waters. The following tips can enhance the quality of the field measurement and address some common onsite practices or issues.

- **Equipment use:** Each instrument must be tested and the sensors calibrated before use.
  - Apply the same precautions for measurement as were recommended for calibration.
  - Avoid faulty readings by cleaning calibration residues and dirt from sensors before use.
  - Instruments may be sensitive to static electricity. Keep the instrument at least 3 ft (about 1 m) away from objects that are not electrically grounded.
- **Sensor-sample equilibration:** Allow a minimum of 60 seconds for an instrument to warm up and the sensors to reach thermal equilibrium with the water temperature before recording field measurements. Some instruments require a longer equilibration time (up to 30 minutes); check the manufacturer's recommendations.
- **Measurement accuracy:** If the water matrix or other condition triggers a concern regarding the accuracy or replication of the measurement, check the sensor calibration and document any changes in the sensor response after sampling or completing a set of field measurements. This record will help to determine deterioration or malfunction of one or more of the sensors. A calibration check of the DO sensor is recommended as a routine practice, especially if the measurement was made in a suboxic environmental water.
- **pH and ORP** (see NFM 6.4, section 6.4.3, and NFM 6.5, section 6.5.3, respectively):
  - Check the slope of the pH electrode before use to verify that the electrode is working properly (the slope is determined as part of the calibration process; see section 6.8.2.B and NFM 6.4 for pH calibration tips).

  - Record changes in ambient air or water temperature while onsite, as temperature affects pH and ORP readings.
  - Depending on the sensor type and manufacture, pH or ORP sensors may or may not be designed for horizontal or near horizontal placement during measurement; check manufacturer's instructions (Hach pH sensors, for example, do allow for horizontal placement).
  - ORP field values that are determined with a silver/silver chloride reference electrode must be converted to standard hydrogen electrode (SHE) values. See NFM 6.5 for calculation instructions.

- **Turbidity** (see NFM 6.7, section 6.7.3):
  - Cover the flowthrough cell with aluminum foil to avoid potential bias to the readings from ambient light.
  - Inspect the sensor body to ensure that no bubbles are on the optical surface before beginning measurement.
  - If using a flowthrough cell, ensure that no bubbles are entrained in the sample water. The presence of bubbles will result in a high bias to readings.
  - For sensors with wipers, follow the manufacturer's instructions for how to verify that the wiper arm is operating correctly.
  - **Instrument precision often decreases at turbidities less than 2 turbidity units—**consult the manufacturer's specification for the expected accuracy of the measurement. Some instruments have the capability of processing low-turbidity data to improve reproducibility. Check whether the instrument has a user-adjustable turbidity data-filter option. If working in low-turbidity water, review the guidance in NFM 6.7 for selection of the appropriate multiparameter (or single-parameter) instrument type.

- **Dissolved oxygen** (see NFM 6.2, section 6.2.1):
  - Table 6.8–6 provides general guidelines for use of the amperometric (polarographic or Clark cell) and luminescent (optical) sensors. Use of the luminescent-sensor method may be more practical for dissolved-oxygen measurement in the field, depending on site conditions.

- For surface-water measurements, selection of the DO amperometric or luminescent sensor should be based on flow regime and stratification of the water body.
- **For an amperometric (polarographic sensor or Clark cell) measurement**, some manufacturers recommend transporting the sonde with the sensor guard (instead of the storage/calibration cup) installed, keeping the sonde wrapped in the wet light-colored towel used for calibration. To reduce evaporation in hot weather, place the entire sonde and wet towel into a perforated plastic bag (that is kept unsealed). The wrapped sonde can be transported in a bucket or cooler.
    - Allow the amperometric instrument to warm up after turning on the display. The DO output should read saturation for the barometric pressure determined for the site.
    - Allow the polarographic sensor to equilibrate to the temperature of the stream, lake, or ground water.
    - **For low-velocity water**, follow the manufacturer's instructions when using an amperometric instrument.
        - Use the stirrer for the DO sensor that is provided or recommended by the manufacturer. **Alternatively, use the luminescent-sensor method, which is not flow dependent.**
        - If the instrument has no stirrer, move the sonde up and down (or side to side in shallow water) at the rate recommended by the manufacturer. (A stirrer is preferable to manually induced flow, especially under stratified conditions at the thermocline of a surface-water body).
        - Flow dependence is diminished when using a "rapid-pulse sensor;" however, some flow over the membrane is needed. Check the manufacturer's instructions.
- To verify the accuracy of the amperometric measurement, rinse the sensors and check the DO calibration by rewrapping it in the wet white towel. The instrument display should return to its saturation set point (±2 percent) within a few minutes. Record any post-measurement calibration check in the field notes.

Table 6.8–6. General guidelines for use of amperometric and luminescent dissolved-oxygen sensors on multiparameter instruments

Amperometric sensor (polarographic or Clark cell) [1]	Luminescent sensor (optical) [1]
Inspect the sonde and sensor for damage, improper installation, or excessive buildup of biofouling matter. Follow the manufacturer's recommendations for cleaning and calibration. Inspect the membrane for damage or improper installation (the average replacement interval is 2 to 4 weeks). Inspect the membrane for biofouling. Replace the membrane if biofouling is evident. Avoid contact of the membrane and sensor with acids, bases, and organic solvents. Replace the potassium chloride (KCl) solution once a month or sooner if performance degrades, and when replacing the sensor. Inspect O-rings periodically and replace as needed or per the manufacturer's recommendation.	Inspect the sonde and sensor for damage, improper installation, or excessive buildup of biofouling matter. Follow the manufacturer's recommendations for cleaning and calibration. The maintenance and use of optical dissolved-oxygen sensors are highly dependent on the technology used by the specific manufacturer. Follow the instructions specified by the manufacturer. *Example A – YSI "ROX" optical sensor*. This sensor should not be left exposed to air for 2 hours or more or otherwise allowed to dry out. Store the sensor wet to avoid drift or having to rehydrate the sensor. *Example B – Hydrolab "LDO" optical sensor*: This sensor should not be left exposed to air and allowed to dry out. The sensor needs to be stored in liquid with its cap on. If the sensor is in a dry environment for several hours it may need to be soaked for up to 5 days before use. The sensor drifts slightly during hydration and must be fully hydrated before being calibrated. *Example C – In-Situ "RDO" optical sensor*. This sensor can be exposed to ambient air for extended periods, can be stored dry, and does not require a hydration period before deployment.
For short-term storage, keep the DO sensor immersed in a calibration cup with enough water to keep electrolyte from evaporating.	Check the manufacturer's instructions for short-term and long-term sensor storage, as requirements can differ substantially among manufacturers.
Anode and cathode maintenance: • The silver anode can be contaminated and might be the cause of poor sensor performance: clean according to the manufacturer's recommendation. • The gold cathode must be bright. Follow the manufacturer's recommendations for cleaning.	Sensors with wipers require manufacturer-specific maintenance procedures: • Use only the wiper recommended by the manufacturer for the sensor in use. • Inspect the wiper pad periodically for wear and tear, and biofouling. • Change the wiper before each long-term deployment, or as recommended by the manufacturer.

[1] Refer to Section 6.2.1 for detailed information on amperometric and luminescent-sensor methods for measuring dissolved-oxygen concentrations.

6.8.4 TROUBLESHOOTING

Multiparameter instruments that perform poorly can be tested and the cause can be identified. The complexity of the series of tests increases with the number of sensors in the sonde. The troubleshooting tests should be performed in a prescribed order that depends on the type of sensors in use and potential for sensor contamination. General troubleshooting tips are provided below in table 6.8–7. More detailed guidance is available from the manufacturer. **Consult the manufacturer's user manual for the specific instrument being used.**

- **If the display shows a warning message, do not use the sensor** until the error has been identified and corrected.
- **Sensor ports on the instrument body should be dry before replacing sensors.** Use compressed air, methanol, or isopropyl alcohol to dry the ports. When using methanol or isopropyl alcohol, gently shake off the excess liquid from the port and allow sufficient time for the liquid to evaporate.

  WARNING: Alcohol or other solvents can damage certain types of plastics and can destroy the sensing surface of the optical DO sensor.

CAUTION: Avoid skin contact with, and fume inhalation of, potentially hazardous equipment-cleaning solutions such as methanol and isopropyl alcohol. If such substances will be used, wear a face mask and protective clothing. If possible, replace sensors under a fume hood.

Table 6.8–7. Troubleshooting tips for use of multiparameter instruments

[DO, dissolved oxygen; NIST, National Institute of Standards and Technology; SC, specific electrical conductance; ORP, oxidation-reduction (redox) potential; Cl, chloride; NH_4, ammonium; NO_3, nitrate; NTU, nephelometric turbidity unit]

Symptom	Possible cause(s), corrective actions, and tips
Erratic or jumpy readings	• May be caused by loose connections or sensitivity to the electrical capacitance of your body and to static electricity**:** avoid touching the sonde housing and try to keep a distance of about 1 meter from the sonde.
Display does not turn on	• Check that the batteries are installed properly and are fully charged. • Battery performance decreases with deceasing temperature. Batteries that charge at room temperature may not perform well when the temperature approaches freezing. Carry spare batteries.
The display does not show readings; the readings seem to be wrong	• Check that the readings are displayed in the appropriate units. Inspect all connectors for moisture, dirt, damage, or a loose connection. Clean as recommended by the manufacturer. • Disconnect and reconnect and recalibrate the sensors. When replacing sensors, the waterproof and dustproof properties of the instrument must be maintained or instrument performance will degrade.
Data on the display appear scrambled	• Check for computer speed and software and hardware compatibility. • Check for a damaged cable. • Check that the correct units are displayed. • If data remain scrambled, consult the manufacturer or authorized service center.
Initial drifting of the readings	• Increase the time for sensors to equilibrate to the water temperature. • Check that the sensors are appropriately submerged and (if necessary for the instrument) that they are at the appropriate inclination from the horizontal.
Dissolved-oxygen reading is unstable or inaccurate	• Check that the sensor has been calibrated to the true onsite barometric pressure or altitude; recalibrate the sensor at the proper barometric pressure and, to the extent possible, with calibrants brought to sample temperature. • Amperometric DO method: Inspect the membrane for a puncture, bubbles, or improper installation. Verify the integrity of the membrane, electrolyte solution, and O-ring by checking the reading against a zero-DO solution. Rinse the sonde thoroughly.
Temperature reading is unstable or inaccurate	• Check for water in the connector; dry the connector and reinstall the sensor. • Check the accuracy of the reading with an NIST-traceable thermometer and have it replaced if necessary. Usually, only the manufacturer can replace a faulty thermistor.
Reading is unstable or inaccurate for SC, pH, ORP, turbidity, Cl, NH_4, or NO_3	• Examine the sensor for dirt or damage. Clean dirty sensors according to the manufacturer's instructions. Replace damaged sensors and recalibrate. • Ensure that the temperature reading is accurate by allowing sufficient time for the temperature sensor to equilibrate to the water temperature. • Check that the calibration solutions used for SC, pH, and ORP were not expired or subject to contamination. • Recalibrate the sensor(s), first bringing the calibration solutions as close to the ambient temperature of the sample as is practical, given ambient field conditions. • Check pH reference junction: if dry, follow manufacturer's instructions for soaking the sensor in tap water or buffer solution until readings stabilize. Alternatively, replace the junction. • Check the sensor connector for water; dry the connector and reinstall the sensor. • If the ZoBell check fails, was temperature dependence of the ZoBell solution accounted for? • The SC sensor must be fully immersed for proper calibration and sample measurement. There must be no bubbles in the cell. • The turbidity sensor wiper must be clean, activated, and rotating properly. Check that expired turbidity calibrants were not used, including any diluted 4000-NTU formazin standard (which must be used within 24 hours of preparation).

6.8.5 REPORTING

USGS personnel are instructed to record all field-measurement values on electronic or paper field forms, and to complete the field-measurement fields on Analytical Services Request forms of the USGS National Water Quality Laboratory or other laboratory at which samples will be analyzed. Field-measurement entries should be checked by a second party and compared for accuracy and consistency with those entered into NWIS.

Table 6.8–8. USGS guidelines for reporting field-measurement values

[±, plus or minus; °C, degrees Celsius; µS/cm, microsiemens per centimeter; >, greater than; mg/L, milligrams per liter; mV, millivolt; SHE, standard hydrogen electrode; FNU, formazin nephelometric units; ppt, parts per trillion; psu, practical salinity units calculated from specific electrical conductance at 25 degrees Celsius]

Field measurement[1]	USGS reporting convention for the National Water Information System (NWIS)[2]	Unit
Temperature	±0.1°C, depending on instrument accuracy and precision	°C
Specific conductance	Three significant figures to the nearest whole number	µS/cm at 25°C
Dissolved oxygen (DO)	Nearest 0.1 mg/L (for the amperometric or luminescent-sensor method) Nearest 0.01 mg/L (for the spectrophotometric/Rhodazine-D™ method) Report ">20 mg/L" for a DO measurement that exceeds 20 mg/L	mg/L
pH	Nearest 0.1 unit for most applications. Can be reported at 0.05 pH unit, depending on accuracy and precision of the calibrated sensor	pH, in standard units
Oxidation-reduction potential	Nearest 1 mV, calculated relative to the SHE (do not report raw data) and the temperature of the sample at the time of measurement	mV
Turbidity	Range: 0 to 10 to the nearest 0.1 FNU 10 to 100 to the nearest 1 FNU >100 to the nearest 10 FNU	FNU[3]
Salinity	<1 to 10, to the nearest 0.1 ppt or psu 10 to 100, to the nearest 1 ppt or psu	ppt or psu

[1] Information is based on manufacturers' specifications for the following multiparameter systems: Hydrolab Quanta and DataSonde 5 and 5X, DS5; YSI 6600; In-Situ Troll 9500; and Eureka Manta.

[2] It is USGS practice to enter values into NWIS that have more significant figures than are the standard for data publication. The NWIS databases produce the values that are rounded correctly, which are then reported in publications. This practice eliminates investigator mistakes when reporting rounded values. NWIS data must be input with the correct parameter and method codes, which can be found by accessing QWDATA.

[3] Most multiparameter instruments used for USGS turbidity measurement contain single-beam infrared wavelength turbidity sensors and are reported in FNU. Check the Excel spreadsheet at http://water.usgs.gov/owq/turbidity_codes.xls to determine the appropriate turbidity unit of measure and NFM 6.7 for detailed information on turbidity measurement and instrumentation.

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6.8.7 ACKNOWLEDGMENTS

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APPENDIX 6.8–A

Example of a USGS field form for recording sensor calibrations and field measurements

NOTE: USGS personnel are advised to use the latest available version of this and other field forms.

November 2006 **METER CALIBRATIONS/FIELD MEASUREMENTS** STN NO____________________

Calibrated by:____________________ Location:____________________
Date:______________ Time:____________

TEMPERATURE Meter MAKE/MODEL ______________ S/N ____________ Thermister S/N ____________ Thermometer ID ____________

Calibration criteria: ± 1 percent or ± 0.5 °C for liquid-filled thermometers ± 0.2 °C for thermisters

Lab Tested against NIST Thermometer/Thermister? N Y Date: ________________ ±__________ °C

Measurement Location: SINGLE POINT AT ______ ft DEEP STREAMSIDE ______ FT FROM LEFT RIGHT BANK VERTICAL AVG/MEDIAN OF _______ POINTS

Field Readings #1 _______ #2 ______ #3 _______ #4 _______ #5 _______ **MEDIAN:**_______ **°C** Method code ______ Remark __ __ Qualifier __ __

pH Meter MAKE/MODEL __________________ S/N ______________ Electrode No. ______________ Type: GEL LIQUID OTHER __________

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

pH BUFFER	BUFFER TEMP	THEO-RETICAL pH FROM TABLE	pH BEFORE ADJ.	pH AFTER ADJ.	SLOPE	MILLI-VOLTS
pH 7						
pH 7						
pH 7						
pH ___						
pH ___						
pH ___						
CHECK pH ___						

TEMPERATURE CORRECTION FACTORS FOR BUFFERS APPLIED? Y N

BUFFER LOT NUMBERS :
pH 7: ________________________
pH ____: ________________________
CHECK pH ____: ________________________

BUFFER EXPIRATION DATES:
pH 7: ________________________
pH ____ : ________________________
CHECK pH ____: ________________________

Calibration Criteria: ± 0.1 pH units

Field Readings #1______ #2______ #3______ #4______ #5______ **MEDIAN:** ______ **Units** Method code _______ Remark __ __ Qualifier __ __

SPECIFIC CONDUCTANCE Meter MAKE/MODEL __________________ S/N ______________ Sensor Type: DIP FLOW-THRU OTHER__________

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

Std Value µS/cm	**Std Temp**	**SC Before Adj.**	**SC After Adj.**	**Std Lot No.**	**Std type (KCl; NaCl)**	**Std Exp. Date**

AUTO TEMP COMPENSATED METER ___
MANUAL TEMP COMPENSATED METER ___
CORRECTION FACTOR APPLIED? Y N
CORRECTION FACTOR= __________

Calibration Criteria: ± 5 % for SC ≤100 µS/cm or 3% for SC >100 µS/cm

Field readings #1_____ #2_____ #3_____ #4_____ #5_____ **MEDIAN:** ______ **mS/cm** Method code _______ Remark __ __ Qualifier __ __

DISSOLVED OXYGEN Meter MAKE/MODEL _________________________ S/N __________________

Sensor Type: Polarographic Luminescent Sensor ID ____________________

Water-Saturated Air Air-Saturated Water Air Calibration Chamber in Water Air Calibration Chamber in Air Winkler Titration Other____________________

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

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

Calibration Criteria: ± 0.2 mg/L

Zero DO Check ________mg/L Adj. to ________ mg/L Date: ____________
Zero DO Solution Date__________ Thermister Check? Y N Date__________
Membrane Changed? N Y Date: ____________ Time: __________
Barometer Calibrated? N Y Date: ____________ Time: __________
Battery Check: REDLINE ______ RANGE ______________

Field readings #1______ #2______ #3______ #4______ #5______ **MEDIAN:** _______ **mg/L** Method code ______ Remark __ __ Qualifier __ __

Calibration form ver. 4.0

Appendix 6.8–A. Example of a USGS field form for recording sensor calibrations and field measurements. (USGS personnel should use the latest available version of this and other field forms.)

Attachment C.2: Example Chain of Custody Forms (blank)

Weck Laboratories, Inc.
Analytical Laboratory Services - Since 1964

14859 East Clark Avenue : Industry : CA 91745
Tel 626-336-2139 ♦ Fax 626-336-2634 ♦ www.wecklabs.com

CHAIN OF CUSTODY RECORD

STANDARD

Page___1___Of___1_____

CLIENT NAME:

PROJECT:

ADDRESS:

PHONE:

FAX:

EMAIL:

PROJECT MANAGER

SAMPLER

SPECIAL HANDLING

- ☐ Same Day Rush 150%
- ☐ 24 Hour Rush 100%
- ☐ 48-72 Hour Rush 75%
- ☐ 4 - 5 Day Rush 30%
- ☐ Rush Extractions 50%
- ☐ 10 - 15 Business Days
- ☐ QA/QC Data Package

Charges will apply for weekends/holidays

Method of Shipment:

ID# (For lab Use Only)	DATE SAMPLED	TIME SAMPLED	SMPL TYPE	SAMPLE IDENTIFICATION/SITE LOCATION	# OF CONT.	ANALYSES REQUESTED										COMMENTS

RELINQUISHED BY	DATE / TIME	RECEIVED BY
RELINQUISHED BY	DATE / TIME	RECEIVED BY
RELINQUISHED BY	DATE / TIME	RECEIVED BY

SAMPLE CONDITION:

Actual Temperature:

Received On Ice	Y / N
Preserved	Y / N
Evidence Seals Present	Y / N
Container Attacked	Y / N
Preserved at Lab	Y / N

SAMPLE TYPE CODE:

AQ=Aqueous
NA= Non Aqueous
SL = Sludge
DW = Drinking Water
WW = Waste Water
RW = Rain Water
GW = Ground Water
SO = Soil
SW = Solid Waste
OL = Oil
OT = Other Matrix

PRESCHEDULED RUSH ANALYSES WILL TAKE PRIORITY
OVER UNSCHEDULED RUSH REQUESTS
Client agrees to Terms & Conditions at: www.wecklabs.com

SPECIAL REQUIREMENTS / BILLING INFORMATION

COC version 042707

CHAIN OF CUSTODY RECORD

Client:

Project Name/Number:

Address

Project Mgr.

P.O. #

Phone Number:

Sampled By ***(signature)***

Date	**Time**	**Comp.**	**Grab**	**Matrix**	**Sample ID**	**Volume/ Number**	**Analysis**										**Comments**

Relinquised By:*(signature)* Date: Time:

Received By:*(signature)* Date: Time:

Relinquised By:*(signature)* Date: Time:

Received By:*(signature)* Date: Time:

temperature upon sample receipt: ºC

Aquatic Bioassay and Consulting Laboratories
29 N. Olive Street Ventura, CA 93001 Phone: (805) 643-5621 Fax: (805) 643-5621

Attachment C.3: Dry Weather Outfall Screening Field Data Sheet (Example)

OUTFALL RECONNAISSANCE INVENTORY/ SAMPLE COLLECTION FIELD SHEET

Section 1: Background Data

Subwatershed:		Outfall ID:	
Today's date:		Time (Military):	
Investigators:		Form completed by:	
Temperature (°F):	Rainfall (in.): Last 24 hours: Last 48 hours:		
Latitutde:	Longitude:	GPS Unit:	GPS LMK #:
Camera:		Photo #s:	
Land Use in Drainage Area (Check all that apply): ☐ Industrial ☐ Ultra-Urban Residential ☐ Suburban Residential ☐ Commercial		☐ Open Space ☐ Institutional Other: ____ Known Industries: ____________________________________	
Notes (e.g.., origin of outfall, if known):			

Section 2: Outfall Description

LOCATION	MATERIAL	SHAPE		DIMENSIONS (IN.)	SUBMERGED
☐ **Closed Pipe**	☐ RCP ☐ CMP ☐ PVC ☐ HDPE ☐ Steel ☐ Other: __________	☐ Circular ☐ Eliptical ☐ Box ☐ Other: _____	☐ Single ☐ Double ☐ Triple ☐ Other: _____	Diameter/Dimensions: ______________________	In Water: ☐ No ☐ Partially ☐ Fully With Sediment: ☐ No ☐ Partially ☐ Fully
☐ **Open drainage**	☐ Concrete ☐ Earthen ☐ rip-rap ☐ Other: _____	☐ Trapezoid ☐ Parabolic ☐ Other: _____		Depth: _____ Top Width: _____ Bottom Width: _____	▨
☐ **In-Stream**	**(applicable when collecting samples)**				
Flow Present?	☐ Yes ☐ No ***If No, Skip to Section 5***				
Flow Description (If present)	☐ Trickle ☐ Moderate ☐ Substantial				

Section 3: Quantitative Characterization

FIELD DATA FOR FLOWING OUTFALLS				
PARAMETER		RESULT	UNIT	EQUIPMENT
☐Flow #1	Volume		Liter	Bottle
	Time to fill		Sec	
☐Flow #2	Flow depth		In	Tape measure
	Flow width	_____' _____"	Ft, In	Tape measure
	Measured length	_____' _____"	Ft, In	Tape measure
	Time of travel		S	Stop watch
Temperature			°F	Thermometer
pH			pH Units	Test strip/Probe
Ammonia			mg/L	Test strip

Outfall Reconnaissance Inventory Field Sheet

Section 4: Physical Indicators for Flowing Outfalls Only

Are Any Physical Indicators Present in the flow? ☐ Yes ☐ No *(If No, Skip to Section 5)*

INDICATOR	CHECK if Present	DESCRIPTION	RELATIVE SEVERITY INDEX (1-3)		
Odor	☐	☐ Sewage ☐ Rancid/sour ☐ Petroleum/gas ☐ Sulfide ☐ Other:	☐ 1 – Faint	☐ 2 – Easily detected	☐ 3 – Noticeable from a distance
Color	☐	☐ Clear ☐ Brown ☐ Gray ☐ Yellow ☐ Green ☐ Orange ☐ Red ☐ Other:	☐ 1 – Faint colors in sample bottle	☐ 2 – Clearly visible in sample bottle	☐ 3 – Clearly visible in outfall flow
Turbidity	☐	See severity	☐ 1 – Slight cloudiness	☐ 2 – Cloudy	☐ 3 – Opaque
Floatables -Does Not Include Trash!!	☐	☐ Sewage (Toilet Paper, etc.) ☐ Suds ☐ Petroleum (oil sheen) ☐ Other:	☐ 1 – Few/slight; origin not obvious	☐ 2 – Some; indications of origin (e.g., possible suds or oil sheen)	☐ 3 - Some; origin clear (e.g., obvious oil sheen, suds, or floating sanitary materials)

Section 5: Physical Indicators for Both Flowing and Non-Flowing Outfalls

Are physical indicators that are not related to flow present? ☐ Yes ☐ No *(If No, Skip to Section 6)*

INDICATOR	CHECK if Present	DESCRIPTION	COMMENTS
Outfall Damage	☐	☐ Spalling, Cracking or Chipping ☐ Peeling Paint ☐ Corrosion	
Deposits/Stains	☐	☐ Oily ☐ Flow Line ☐ Paint ☐ Other:	
Abnormal Vegetation	☐	☐ Excessive ☐ Inhibited	
Poor pool quality	☐	☐ Odors ☐ Colors ☐ Floatables ☐ Oil Sheen ☐ Suds ☐ Excessive Algae ☐ Other:	
Pipe benthic growth	☐	☐ Brown ☐ Orange ☐ Green ☐ Other:	

Section 6: Overall Outfall Characterization

☐ Unlikely ☐ Potential (presence of two or more indicators) ☐ Suspect (one or more indicators with a severity of 3) ☐ Obvious

Section 7: Data Collection

1.	Sample for the lab?	☐ Yes	☐ No	
2.	If yes, collected from:	☐ Flow	☐ Pool	
3.	Intermittent flow trap set?	☐ Yes	☐ No	If Yes, type: ☐ OBM ☐ Caulk dam

Section 8: Any Non-Illicit Discharge Concerns (e.g., trash or needed infrastructure repairs)?