



Standard Guide for Collection of Water Temperature, Dissolved-Oxygen Concentrations, Specific Electrical Conductance, and pH Data from Open Channels¹

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1. Scope

1.1 This guide describes procedures to collect cross-sectional means of temperature, dissolved oxygen, specific electrical conductance, and pH of water flowing in open channels.

1.2 This guide provides guidelines for preparation and calibration of the equipment to collect cross-sectional means of temperature, dissolved oxygen, specific electrical conductance, and pH of water flowing in open channels.

1.3 This guide describes what equipment should be used to collect cross-sectional means of temperature, dissolved oxygen, specific electrical conductance, and pH of water flowing in open channels.

1.4 This guide covers the cross-sectional means of temperature, dissolved oxygen, specific electrical conductance, and pH of fresh water flowing in open channels.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory requirements prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

- D 888 Test Method for Dissolved Oxygen in Water²
- D 1125 Test Method for Electrical Conductivity and Resistivity of Water²
- D 1129 Terminology Relating to Water²
- D 1293 Test Method for pH of Water²
- D 4410 Terminology for Fluvial Sediment²
- D 4411 Guide for Sampling Fluvial Sediment in Motion³
- D 5464 Test Method for pH Measurements of Water of Low Conductivity²

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² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 11.02.

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this guide, refer to Terminology D 1129 and D 4410.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *electronic temperature sensor*—an electrical device that converts changes in resistance to a readout calibrated in temperature units. Thermistors and resistance temperature detectors are examples of electronic temperature sensors.

3.2.2 *thermometer*—any device used to measure temperature, consisting of a temperature sensor and some type of calibrated scale or readout device.

4. Summary of Guide

4.1 This guide establishes criteria and describes procedures for the collection of cross-sectional means of temperature, dissolved oxygen (DO), specific electrical conductance (SC), and pH of water flowing in open channels.

4.2 This guide provides only generic guidelines for equipment use and maintenance. Field personnel must be familiar with the instructions provided by equipment manufacturers. There are a large variety of available field instruments and field instruments are being continuously updated or replaced using newer technology. Field personnel are encouraged to contact equipment manufacturers for answers to technical questions.

5. Significance and Use

5.1 This guide describes stabilization criteria for recording field measurements of Temperature, DO, SC, and pH.

5.2 This guide describes the procedures used to calibrate and check meters to be used in the field to records these measurements and the procedures to be use in the field to obtain these data.

5.3 This guide describes quality assurance procedures to be followed when obtaining cross-sectional means of temperature, dissolved oxygen, specific electrical conductance, and pH of water flowing in open channels.

5.4 Field measurement must accurately represent the water flowing in the open channel being measured. Methods need to be used that will result in an accurate representation of the

TABLE 1 Stabilization Criteria for Recording Field Measurements (1)

NOTE—[±, plus or minus value shown; °C, degrees Celsius; ≤ less than or equal to values shown; μS/cm microsiemens at 25°C, >, greater than value shown; unit, standard pH unit; mg/L milligram per liter].

Standard Direct Field Measurement	Stabilization Criteria for Measurements (Variability Should Be Within the Value Shown)
Temperature:	
Electronic Temperature Sensor	±0.2°C
Liquid-in-glass thermometer	±0.5°C
Specific Electrical Conductance:	
when ≤ 100 mS/cm	±5 %
when > 100 mS/cm	±5 %
pH:	
Meter displays to 0.01	±0.1 unit
Dissolved oxygen:	
Amperometric method	±0.3 mg/L

mean of the parameter of interest. Procedures must be used that will take into consideration the variation in the parameter across the sections and with depth.

5.5 Temperature and DO must be measured directly in the water in the open channel. SC and pH are often measured in situ, but also may be measured in a subsample of a composite sample collected using discharge-weighted methods.

6. Procedure

General Comments

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

6.1.1 To ensure the quality of the data collected (1)⁴:

6.1.1.1 Calibration is required at the field site for most instruments. Make field measurements only with calibrated instruments.

6.1.1.2 Each field instrument must have a permanent log-book for recording calibrations and repairs. Review the log-book before leaving for the field.

6.1.1.3 Test each instrument (meters and sensors) before leaving for the field. Practice your measurement technique if the instrument or measurement is new to you.

6.1.1.4 Have backup instruments readily available and in good working condition.

6.1.2 Before making field measurements, sensors must be allowed to equilibrate to the temperature of the water being monitored. Sensors have equilibrated adequately when instrument readings have “stabilized,” that is, when the variability among measurements does not exceed an established criterion. The criteria for stabilized field readings are defined operationally in Table 1, for a set of three or more sequential measurements. The natural variability inherent in surface water at the

time of sampling generally falls within these stability criteria and reflects the accuracy that should be attainable with a calibrated instrument.

6.1.3 Allow at least 60 s (or follow the manufacturer’s guidelines) for sensors to equilibrate with sample water. Take instrument readings until the stabilization criteria in Table 1 are met. Record the median of the final three or more readings as the value to be reported for that measurement point.

6.2 Locating Points of Measurement in Cross-Section:

6.2.1 The location and the number of field measurements depend on study objectives. Generally, a single set of field-measurement data is used to represent an entire stream cross section at a sampling site and can be useful when calculating chemical loads.

6.2.2 To obtain data representative of the section, the variability of discharge and field measurements across the stream must be known. This information is used to determine if the equal-discharge-increment (EDI) or equal-width-increment (EWI) method of locating field-measurement points should be used. See Terminology D 4410 for definitions of these terms.

6.2.2.1 Check the cross-sectional profile data of the stream site to determine the variability of discharge per unit width of the stream and of field-measurement values across the section.

Make individual measurements at a number of equally-spaced verticals along the cross section and at multiple depths within each vertical; or, consult previous records for the site.

Make in situ (see 6.2.3.3) field measurements for the profile.

Field-measurement profiles of stream variability are needed for low- and high-flow conditions and should be verified at least every 2 years or as study objectives dictate.

6.2.2.2 Select the EDI or EWI method to locate points of measurement (see reference (2) for information on EDI and EWI methods) to select and execute the appropriate method.

If stream depth and velocities along the cross section are relatively uniform, use the EWI method.

If stream depth and velocities along the cross section are highly variable, use the EDI method.

In a small and well-mixed stream, a single point at the centroid of flow may be used to represent the cross section. The centroid of flow is defined as the point in the increment at which discharge in that increment is equal on both sides of the point.

6.2.3 Use the following procedure when making a field measurement using the EDI method.

6.2.3.1 Divide the cross section into equal increments of discharge (see reference (1) for details on how to properly do this.)

6.2.3.2 Select either the in situ or subsample method and follow the instructions in 6.3 or 6.4.

6.2.3.3 *In Situ Method*—Go to the centroid of the first equal-discharge increment. Using submersible sensors, measure at mid-depth (or multiple depths) in the vertical. Repeat at each vertical. The value recorded at each vertical represents the median of values observed within approximately 60 s after sensor(s) have equilibrated with stream water.

⁴ The boldface numbers in parentheses refer to the list of references at the end of this guide.

6.2.3.4 *Subsample Method*—Collect an isokinetic depth-integrated sample at the centroid of each equal-discharge increment, emptying the increment sample into a compositing device. Measure field parameters either in the sample collected at each increment or in a subsample taken from the composite of all the increment samples.

6.2.3.5 The final field-measurement value is the mean of the in situ or individual increment-sample value for all the EDI verticals in the section (the composite subsample yields a single value). Note for pH it is necessary to calculate the mean by (1) converting each pH measurement to its antilogarithm times minus one ($10^{-(\text{pH})}$), (2) using these transformed values to calculate the mean, and (3) converting the mean value to a logarithm multiplied by minus one (refer to 6.8.4.5).

6.2.3.6 Enter data on a field form.

6.2.3.7 *Example*—Table 2 is an example of how mean conductivity measured in situ is calculated using the equal-discharge-increment method.

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

6.2.4 Use the following procedure when making a field measurement using the EWI method.

6.2.4.1 Divide the cross section into equal increments of width (see reference (1) for details on how to properly do this.)

6.2.4.2 In situ field measurements are made at the midpoints of each increment. Area-weighted concentrations can be computed from these measurements (Table 3).

6.2.4.3 Subsample field measurements are made in discrete samples that usually are withdrawn from a composite sample collected using an isokinetic sample and isokinetic depth-integrating method. The volume of the isokinetic sample must be proportional to the amount of discharge in each increment and measurements in subsamples taken from the compositing device result in discharge-weighted values.

6.2.4.4 Select either the in situ or subsample method and follow the instructions in 6.3 or 6.4.

6.2.4.5 *In Situ Method*—Measure at the midpoint of each equal-width increment. Using submersible sensors, measure at mid-depth in the vertical.

6.2.4.6 *Subsample Method*—Collect an isokinetic depth-integrated sample at the midpoint of each equal-width increment, emptying each sample into a compositing device. Use of the correct sampling equipment is critical to execute this method successfully: standard samplers cannot meet isokinetic requirements when stream velocity is less than 1.5 ft/s.

6.2.4.7 Record a value for each field measurement for each vertical. The value recorded represents the stabilized values observed within approximately 60 s after the sensor(s) have equilibrated with the stream or subsample water.

6.2.4.8 *Example*—Table 3 provides an example of an area-weighted median measurement for conductivity measured in situ. In the example, the area-weighted median conductivity equals 130 $\mu\text{S}/\text{cm}$. To calculate an area-weighted median, multiply the area of each increment by its corresponding field measurement, sum the products of all the increments, and divide by total cross-sectional area. Note that if the conductivity reported was selected at mid-depth of the vertical of centroid of flow (Section 10), it would have been reported as 125 $\mu\text{S}/\text{cm}$; if the conductivity reported was near the left edge of water, it would have been reported as 150 $\mu\text{S}/\text{cm}$.

6.2.4.9 The final field-measurement value normally is calculated as the mean of the values recorded at all EWI increments, resulting in an area-weighted mean (for pH it is necessary to calculate the mean by (1) converting each pH measurement to its antilogarithm times minus one ($10^{-(\text{pH})}$), (2) using these transformed values to calculate the mean, and (3) converting the mean value to a logarithm multiplied by minus one.)

6.3 In Situ Measurement Procedures:

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

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

6.3.2.1 In situ measurement is mandatory for determination of temperature and dissolved-oxygen concentration.

6.3.2.2 In situ measurement also can be used for pH and conductivity.

TABLE 2 Example of Field Notes for a Discharge-Weighted Conductivity Measurement

NOTE—[ft/sec, feet per second; ft, feet; ft², square feet; ft³/s, cubic feet per second; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25°C; LEW, left edge of water; —, not available; REW, right edge of water].

Equal Discharge Increment	Percent of Flow in Increment	Mean Velocity, in ft/s	Width of Increment, in ft	Depth of Increment, in ft	Area of Increment, in ft ²	Increment Discharge, in ft ³ /s	Median Conductivity, in $\mu\text{S}/\text{cm}$
LEW	0	—	—	—	—	—	—
1	20	2.0	22	5.7	125	250	185
2	20	2.2	11	10.4	114	250	170
3	20	2.3	9	12.0	109	250	155
4	20	3.9	5	12.8	64	250	155
5	20	3.4	10	7.4	74	250	150
REW	0	—	—	—	—	—	—

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

TABLE 3 Example of Field Notes for an Area-Weighted Conductivity Measurement

NOTE—[ft, feet; LEW, left edge of water; ft², square feet; μS/cm, microsiemens per centimeter at 25°C; —, not available; REW, right edge of water].

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

Calculation of conductivity: sum of values in last column divided by the total cross-sectional area 27 836/214 = 130 μS/cm.

6.4 *Subsample Measurement:*

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

6.4.2 Before using a sample-compositing/splitting device, preclean and field rinse the device in accordance with approved procedures such as described in Horowitz and others, 1994 (3).

6.4.3 When compositing and splitting a sample, follow instructions for the clean hands/dirty hands technique such as those detailed in Horowitz and others (3), as required.

6.5 *Temperature:*

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

6.5.2 *Equipment:*

6.5.2.1 Liquid-in-glass thermometers and electronic temperature sensors are most commonly used to measure water temperature.

6.5.2.2 Recommended liquid-in-glass thermometers are total-immersion thermometers filled with alcohol. Before measuring temperature, check the type of liquid-filled thermometer being used. (Partial-immersion thermometers are not recommended: these have a ring or other mark to indicate the immersion depth required.)

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

Keep thermometers clean (follow manufacturer's recommendations).

Carry thermometers in protective cases; thermometers and cases must be free of sand and debris.

Store liquid-filled thermometers in a bulb-down position and in a cool place away from direct sunlight.

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

6.5.3 *Calibration:*

6.5.3.1 To calibrate a thermometer, instrument readings are checked across a range of temperatures against those of a thermometer of certified accuracy. Calibrate liquid-in-glass and electronic temperature sensors in the office at regularly scheduled intervals. Tag acceptable thermometers with date of calibration.

6.5.3.2 Calibrate a liquid-in-glass thermometer every 3 to 6 months, using a 2-point calibration, and annually, using a 3-point calibration.

6.5.3.3 Calibrate an electronic temperature sensor annually using a 5-point calibration check and every 3 to 4 months check several reading against reading from a NIST-certified thermometer.

6.5.3.4 For further information and instructions on calibrations see reference (1).

6.5.4 *Measurement:*

6.5.4.1 Before measuring temperature:

Inspect liquid-in-glass thermometers to be certain liquid columns have not separated.

Inspect bulbs to be sure they are clean.

Inspect protective cases to be sure they are free of sand or debris.

6.5.4.2 The reported surface-water temperature must be measured in situ. Do not measure temperature on subsamples from a sample compositing device.

6.5.4.3 To measure the temperature of surface water:

Make a cross-sectional temperature profile to determine temperature variability; an electronic temperature sensor works best for purpose.

Determine from the cross-sectional profile and from study objectives which sampling method to use (see 6.2).

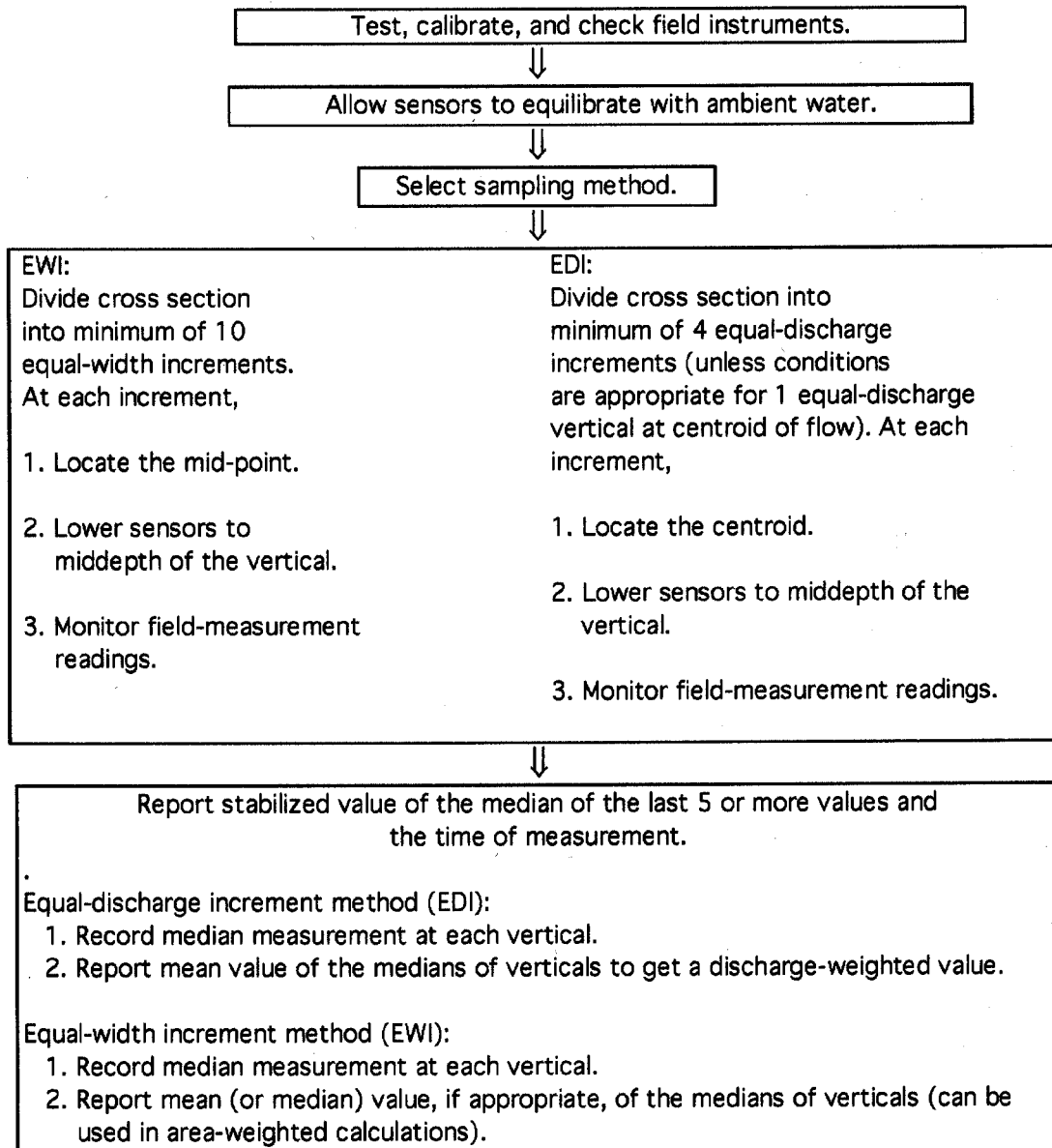


FIG. 1 In Situ Field-Measurement Procedures (1)

Measure temperature in those sections of the stream that represent most of the water flowing in a reach. Do not make temperature measurements in or directly below stream sections with turbulent flow or from the stream bank (unless this represents the condition to be monitored).

6.5.4.4 Use either a liquid-in-glass thermometer tagged as “certified” within the past 12 months, or an electronic temperature sensor tagged “certified” within the past 4 months.

6.5.4.5 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 an electronic temperature sensor attached to a weighted cable. Do not attach a weight to the sensor or sensor cable.

Still-water conditions—measure temperature at multiple depths at several points in the cross section.

6.5.4.6 Immerse the sensor in the water to the correct depth and hold it there for no less than 60 s until the sensor equilibrates thermally. The sensor must be immersed properly while reading the temperature; this might require attaching the thermistor to a weighted cable. (Technical Note: For in situ measurement with liquid-filled thermometers; the water depth must be no greater than twice the length of the liquid column of the thermometer in order to make an accurate measurement.

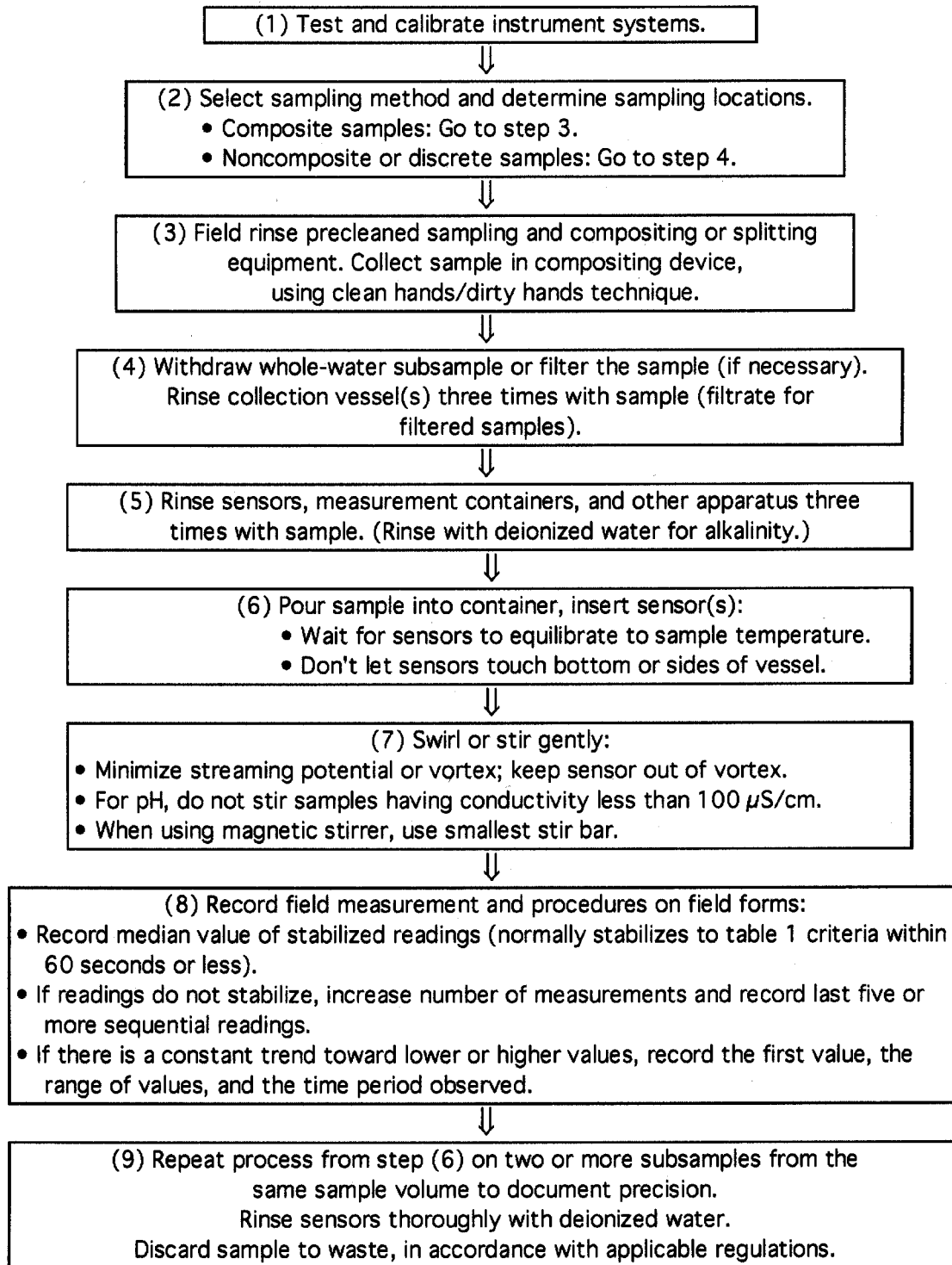


FIG. 2 Subsample Field-Measurement Procedures for Conductivity and pH (1)

6.5.4.7 Read the temperature to the nearest 0.5°C (0.2°C for thermistor readings). Do not remove the sensor from the water.

Using a liquid-in-glass thermometer, check the reading three times and record all values on field forms and note the median of these values.

Using an electronic temperature sensor, wait until the readings stabilize to within 0.2°C, then record the median of approximately the last 5 values.

6.5.4.8 Remove the temperature sensor from the water, rinse it thoroughly with deionized water, and store it.

6.5.5 Record the stream temperature on field forms:

In still water—median of three or more sequential values.

EDI—mean value of subsections measured (use median if measuring one vertical at the centroid of flow).

EWI—mean or median value of subsections measured.

6.6 Dissolved Oxygen:

6.6.1 Accurate data on concentrations of dissolved oxygen (DO) in water are essential for documenting changes to the environment caused by natural phenomena and human activities. Many chemical and biological reactions in surface water depend directly or indirectly on the amount of oxygen present. Dissolved oxygen is necessary in aquatic systems for the survival and growth of many aquatic organisms.

6.6.1.1 There are several field methods for determining concentrations of dissolved oxygen in surface. The more common ones are amperometric method, spectrophotometric method and the iodometric (Winkler) method.

6.6.1.2 The most commonly used field method for measuring DO in water is the amperometric method, in which DO concentration is determined with a temperature-compensating instrument or meter that works with a polarographic membrane-type sensor. Because it is the most commonly used field DO method, the discussion in this guide will assume that it is the method that is being used. (1)

6.6.1.3 The spectrophotometric method such as the one that uses Rhodazine-DTM is recommended for determining concentrations of DO less than 1.0 mg/L.

6.6.1.4 The iodometric (Winkler) method generally is not recommended for field determination of dissolved oxygen because the accuracy and reproducibility achieved depend largely on the experience and technique of the data collector. (1)

6.6.1.5 See Test Method D 888 for more information on the measurement of dissolved oxygen in water.

6.6.2 Equipment:

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

6.6.2.2 Dissolved-oxygen sensors must be temperature compensating; the permeability of the membrane and solubility of oxygen in water change as a function of temperature.

6.6.2.3 All built-in electronic temperature sensors must be calibrated and field checked before use.

6.6.2.4 Equipment and supplies used for amperometric method of dissolved-oxygen determination are listed in Table 4.

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

6.6.2.6 Before each field trip:

TABLE 4 Equipment and Supplies Used for Amperometric Method of Dissolved-Oxygen Determination^A

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

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

^A Modify this list to meet specific needs of the field effort. See (1) Table 6.2-3 for equipment list for iodometric DO determination and Table 6.2-5 for equipment list for Rhodazine-D™ DO determination.

^B Prepare fresh zero DO solution before each field trip.

(1) Check the temperature-display thermistor in the DO sensor against a certified thermometer over the normal operating range of the instrument. If a thermistor reading is incorrect, apply a correction or return the instrument to the manufacturer for adjustment.

(2) Recondition the DO sensor if it fails a performance check.

(3) Check the instrument batteries and all electrical connections.

(4) Test the instrument to ensure that it will read zero in a DO-free solution.

(a) If the instrument reading exceeds 0.2 mg/L, then the sensor membrane and electrolyte (if present) need to be replaced or the sensor needs to be repaired.

(b) Before repairing or replacing the sensor, check zero DO again with a freshly prepared zero DO solution.

(5) On analog instruments:

(a) Check mechanical zero (if applicable) before turning the instrument on; adjust it if necessary.

(b) Check redline and zero readings (if applicable) and adjust as needed.

(c) If the instrument cannot be adjusted, recharge or replace the batteries.

(6) Calibrate the pocket altimeter-barometer according to manufacturer's specifications.

6.6.3 Calibration:

6.6.3.1 Calibration and operation procedures for the amperometric method differ among instrument types and makes. Refer to manufacturer's instructions. Record all calibration information in instrument logbooks and copy calibration data

onto field forms at the time of calibration. See reference (1) for instructions on calibration.

6.6.3.2 Calibration must be done for atmospheric pressure, salinity, and for the instrument readings. Although the salinity correction can be made either during calibration or after measurement, the preferred USGS method is to apply salinity correction factors after calibration and measurement (recalibration is necessary for each field variation in salinity and temperature if the correction is made during calibration) (1)

6.6.3.3 There are four procedures for calibrating a DO system: (1) air-calibration chamber in water, (2) calibration with air-saturated water, (3) air-calibration chamber in air, and (4) iodometric (Winkler) titration. When using an analog instrument: Do not change scales without either recalibrating or verifying that identical readings are obtained on both scales; Place an analog instrument in its operating position—either vertical, tilted, or on its back—before calibration. More readjustments may be necessary if the operating position is changed, so do not change the position of the meter until DO measurement is complete.

6.6.4 Measurement:

6.6.4.1 Standard DO determination for surface water represents the cross-sectional median or mean concentration of dissolved oxygen at the time of observation. Measuring DO concentration at one distinct spot in a cross section is valid only for flowing water with a cross-sectional DO variation of less than 0.5 mg/L (1). Determining DO in a single vertical at the centroid of flow at the midpoint of the vertical is only representative of the cross section under ideal mixing conditions.

6.6.4.2 Do not measure DO in or directly below sections with turbulent flow, in still water, or from the bank, unless these conditions represent most of the reach or are required by the study objectives.

6.6.4.3 Follow the 7 steps below to measure DO in surface water (1):

(1) Calibrate the DO instrument system at the field site and check that the temperature thermistor has been District-certified within the past 4 months (within 12 months if a liquid-in-glass thermometer is used).

(2) Record the DO variation from the cross-sectional profile and select the sampling method:

(a) Flowing, shallow stream—Wade to the location(s) where DO is to be measured.

(b) Stream too deep or swift to wade—Lower a weighted DO sensor with calibrated temperature sensor from a bridge, cableway, or boat. (Do not attach the weight to the sensors or sensor cables.)

(c) Still-water conditions—Measure DO at multiple depths at several points in the cross section.

(3) Immerse the DO and temperature sensors directly into the water body and allow the sensors to equilibrate to the water temperature (no less than 60 s). If the water velocity at the point of measurement is less than about 1 ft/s, use a stirring device or stir by hand to increase the velocity (to hand stir, raise and lower the sensor at a rate of about 1 ft/s, but do not break the surface of the water). Very high velocities can cause erroneous DO measurements.

(4) Record the temperature without removing the sensors from the water. Turn the operation switch to the range that was used during instrument calibration.

(5) After the instrument reading has stabilized (allow 1 to 2 min and ± 0.3 mg/L), record the median DO concentration.

(6) For EWI or EDI measurements, proceed to the next station in the cross section and repeat steps 3 through 5. When measurements for the stream have been completed, remove the sensor from the water, rinse it with deionized water, and store it according to the manufacturer's instructions.

(7) Record DO concentrations on the field forms:

(a) In still water—median of three or more sequential values.

(b) EDI—mean value of all subsections measured (use the median if measuring one vertical at the centroid of flow).

(c) EWI—mean (or median) of all subsections measured.

6.7 Specific Electrical Conductance (SC):

6.7.1 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.

6.7.1.1 See Test Method D 1125 for more information on the measurement of SC in water.

6.7.2 Equipment and Supplies:

6.7.2.1 The instrument system used to measure conductivity must be tested before each field trip and cleaned soon after use. Every conductivity instrument must have a logbook in which repairs and calibrations are recorded, along with manufacturer make and model description and serial or property number.

6.7.2.2 Table 5 contains a list of equipment and supplies

TABLE 5 Equipment and Supplies Used for Measuring Conductivity^A

NOTE—[°C, degrees Celsius; L, liter; μ S/cm, microsiemens per centimeter at 25°C]

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 μ S/cm, within 5 % of full scale
Conductivity >100 μ S/cm, within 3 % of full scale
Electronic Temperature Sensor 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 % volume-to-volume (1 L)
Deionized water, 1 L, maximum conductivity of 1 mS/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

^A Modify this list to meet the specific needs of the field effort.

used for measuring conductivity.

6.7.2.3 Many conductivity instruments are available; the specifications and instructions provided here are general. Users must be familiar with the instructions provided by the manufacturer.

6.7.2.4 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.

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.

6.7.2.5 Quality-controlled conductivity standards be ordered from suppliers of chemical reagents. Conductivity standards usually consist of potassium chloride dissolved in reagent-grade water. They are readily available from 50 to 50,000 $\mu\text{S}/\text{cm}$ at 25°C. Values outside of this range can be prepared or special ordered. 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.

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

Protect the conductivity system from dust and excessive heat and cold.

Keep all cable connectors dry and free of dirt and extraneous matter.

Protect connector ends in a clean plastic bag when not in use.

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

Clean sensors thoroughly with deionized water (DIW) before and after making a measurement (this is sufficient cleaning in most cases).

Remove oily residue or other chemical residues (salts) with a detergent solution. Sensors can soak in detergent solution for many hours without damage.

If oil or other residues persist, dip the sensor in a dilute hydrochloric acid solution. Never leave the sensor in contact with acid solution for more than a few minutes. Check the manufacturer's recommendations before using acid solution on sensors.

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

6.7.2.8 Refer to the manufacturer's recommendations on sensor storage. 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.

6.7.3 Calibration:

6.7.3.1 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 logbook and on field forms at the time the instrument is calibrated. Remember, the temperature sensor on the conductivity sensor must be calibrated and certified within the past 4 months.

6.7.3.2 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.

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

(1) Inspect the instrument and the conductivity sensor for damage. Check the battery voltage. Make sure that all cables are clean and connected properly.

(2) Turn the instrument on and allow sufficient time for electronic stabilization.

(3) Select the correct instrument calibration scale for expected conductivity.

(4) Select the sensor type and the cell constant that will most accurately measure expected conductivity.

(5) Select two conductivity standards that will bracket the expected sample conductivity. Verify that the date on the standards has not expired.

(6) Equilibrate the standards and the conductivity sensor to the temperature of the sample.

(a) Put bottles of standards in a minnow bucket, cooler, or large water bath that is being filled with ambient water.

(b) Allow 15 to 30 min 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.

(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 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.

(a) If the sensor contains a calibrated thermistor, use this thermistor to measure water temperature.

(b) 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 an electronic temperature sensor.

(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.

(a) For nontemperature-compensating conductivity instruments, apply a temperature-correction factor to convert the instrument reading to conductivity at 25°C.

(b) 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 (1) or Table 3 in Test Method D 1125.

(c) 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 %, refer to the manufacturer's guide or troubleshooting guide (section 6.3.4) (1).

(12) Record in the instrument logbook and on field forms:

(a) The temperature of the standard solution.

(b) The known and the measured conductivity of the standard solution (including \pm variation).

(c) The temperature-correction factor (if necessary).

(13) Discard the used standard into a waste container. Rinse the sensor, thermometer, and container thoroughly with deionized water.

(14) Repeat steps 7 through 13 with the second conductivity standard.

(a) The purpose for measuring a second standard is to check instrument calibration over the range of the two standards.

(b) The difference from the standard value should not exceed 5 %.

(c) If the difference is greater than 5 %, repeat the entire calibration procedure. If the second reading still does not come within 5 % of standard value, refer to the troubleshooting guide in section 6.3.4 (1) or calibrate a backup instrument.

(d) Switching instrument calibration scales could require recalibration.

(15) Record in the instrument logbook and on field forms the calibration data for the second standard.

6.7.4 Measurement—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. 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 water temperature.

Avoid contamination from the pH electrode filling solution. Measure conductivity on a separate discrete sample from the one used for measuring pH.

6.7.4.1 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 should 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 6.1 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.

(a) Flowing, shallow stream—wade to the location(s) where conductivity is to be measured.

(b) 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.

(c) 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 s) until the sensors equilibrate to water conditions.

(4) Record the conductivity and corresponding temperature readings without removing the sensors from water.

(a) Values should stabilize quickly to within 5 % at conductivity 100 μ S/cm and within 3 % at conductivity >100 μ S/cm.

(b) Record the median of the stabilized values on field forms.

(c) 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:

(a) In still water—median of three or more sequential values.

(b) EDI—mean value of all subsections measured (use the median if measuring one vertical at the centroid of flow).

(c) EWI—mean or median of all subsections measured (see 6.2.4.3).

6.7.4.2 *Subsample 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. Follow the following 10 steps:

(1) Calibrate the conductivity instrument system at the field site.

(2) Select the sampling method (see 6.1) and collect a representative sample.

(3) Withdraw a homogenized subsample using a sample splitter or from a compositing device. Rinse the sample bottles three times with the sample. 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.

(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.

(a) If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.

(b) If the instrument is not temperature compensating, use a calibrated thermistor or a liquid-in-glass thermometer.

(c) 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.

(a) 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.

(b) Report the median of the readings to three significant figures on the field forms.

(c) Discard the sample into a waste container and dispose according to regulations.

(9) Quality control.

(a) Repeat steps 3 through 8 with at least two fresh subsamples, rinsing the instruments once only with sample water.

(b) Subsample values should be within $\pm 5\%$ for conductivity 100 $\mu\text{S}/\text{cm}$, or $\pm 3\%$ for conductivity $>100\ \mu\text{S}/\text{cm}$.

(c) 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.

6.8 *pH Measurement:*

6.8.1 The pH of an aqueous solution is controlled by interrelated chemical reactions that produce or consume hydrogen ions. Water pH is a useful index of the status of equilibrium reactions in which water participates (4). The pH of water directly affects physiological functions of plants and animals, and it is, therefore, an important indicator of the health of a water system.

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

6.8.1.2 pH can be measured either electrometrically or colorimetrically.

The electrometric measurement method uses a hydrogen ion electrode. (Note: This is the only technique that is approved for measuring pH values that are to be reported or entered into the USGS data base (1)).

The colorimetric method uses pH “litmus” indicators that change color with a change in pH. The colorimetric method is suitable only when rough estimates of pH are needed; for example, when assessing the volume of acid or base needed to preserve samples; or, when checking that equipment-cleaning solutions have been adequately neutralized prior to disposal. This method is not used when report the pH of surface water.

6.8.2 *Equipment and Supplies:*

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

6.8.2.2 Table 6 list equipment and supplies used for measurement of pH in open channel flow.

6.8.2.3 pH measurements are only as accurate as the buffers used for calibration. Use buffers that have been certified traceable to the NIST Standard Reference Material; buffers with a pH of 4, 7, and 10 are commonly used in measurement of pH in open channel flow. Note that the routine buffers obtained for measurement of pH from 4 to 10 have a high ionic strength. For pH measurements of dilute waters, obtain low

TABLE 6 Equipment and Supplies Used for Measuring pH^A

NOTE—[mL, milliliters; °C, degrees Celsius; mV, millivolt; μS/cm, micro-siemens per centimeter at 25°C].

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

^A Modify this list to meet the specific needs of the field effort.

ionic-strength buffers. Label buffer and reagent containers with the date when they are received.

6.8.2.4 Label every buffer with its expiration date. Copy this date onto any container into which the buffer is transferred.

6.8.2.5 Discard buffers on their expiration dates. The pH of the buffers may have changed substantially because of carbon dioxide absorption, mold growth, or evaporation.

6.8.2.6 Take the following precautions to maximize the accuracy of pH measurement (5):

(1) Always cap buffer bottles to prevent evaporation and contamination from atmospheric carbon dioxide. (In order of greatest to least sensitivity to CO₂ contamination, pH buffer 10 > 7 > 4. Buffers are stable for the short exposure time during electrode calibration.)

(2) Never pour used buffer back into stock solution bottles. Never insert an electrode or other material into stock solution bottles containing buffers. Always pour the buffer into a separate container.

(3) Be very careful not to contaminate the buffer with another buffer or with other fluids (pH 4 buffer is least resistant to contamination).

(4) Do not dilute buffer, for example, with water dripping from sensors (more important for pH 7 buffer).

(5) Before using buffers, bring them to the temperature of the sample solution, and check with the buffer manufacturer for

temperature-correction factors. (In order of greatest to least pH variation with temperature, buffer of pH 10 > 7 > 4.)

(6) Because of the differences between different manufacturers of pH electrodes, see manufacturer's instruction for maintenance, reconditioning, cleaning, and storage of the electrodes. For generic instructions see 6.4.1.B of reference (1).

6.8.3 Calibration:

6.8.3.1 Calibrate and check the operation of a pH instrument system at the field site.

6.8.3.2 Two pH buffers are needed to properly calibrate the pH instrument system (pH 7 buffer and either the pH 4 or 10 buffer, depending on the anticipated sample pH). A third buffer can be used to check instrument system performance over a larger range.

6.8.3.3 The pH of the buffer solution is temperature dependent: pH 10 buffers change more per unit change in temperature than do pH 4 buffers. The temperature of buffer solutions must be known, and temperature-correction factors must be applied before calibration adjustments are made. Calibration and operating procedures differ with instrument systems. Check the manufacturer's instructions.

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

6.8.3.5 Follow the 10 steps listed below to calibrate the pH meter:

(1) Temperature equilibration of equipment (this is not needed if using an automatic compensating meter).

(a) Bring the pH buffers, thermometer (if necessary), container, and electrode to the temperature of the sample.

(b) Allow 15 to 30 min for the buffers to adjust to the sample temperature. When making temperature corrections, use the correction factors provided by the buffer manufacturer (temperature coefficients can vary with buffer manufacturer). To equilibrate to stream temperature, place the buffer bottles in a minnow bucket or mesh bag and suspend them in the stream.

(2) Inspect the pH electrode.

(a) Check for damage to the electrode bulb, body, or cables.

(b) Rinse any precipitate off of the electrode with deionized water (the measurement can be affected if precipitate falls into the buffer or sample).

(c) If there is one, slide the protective sleeve up or down to uncover the filling hole.

(d) Gently shake or tap the electrode to dislodge and remove air bubbles trapped in the sensing tip of the electrode and to remove excess deionized water. Do not wipe the electrode.

(e) Look for oily coating and scratches on the pH bulb and check the frit (reference) for darkening.

(3) Calibration rinse.

(a) Rinse (with pH 7 buffer) the electrode, thermometer or automatic temperature compensating (ATC) sensor, and a container large enough to hold the sensors and buffer. Discard the used pH buffer into a waste container.

(b) Pour fresh pH 7 buffer into the buffer-rinsed container that holds the electrode and thermometer. Allow the instruments to equilibrate for 1 min (if necessary), then discard the buffer into a waste container.

(4) Calibration. Only the first two and last steps are needed for autocompensating meters.

(a) Pour fresh pH 7 buffer into the container that holds the electrode and thermometer or ATC sensor. The bulb of the pH electrode must not touch the bottom or side of the container. Add enough pH buffer to cover the reference junction.

(b) Swirl the sample gently or stir carefully with the electrode. If using a magnetic stirrer, stir slowly enough so that a vortex is not created. Place a thin piece of insulating material (styrofoam or cardboard) between the magnetic stirrer and beaker to prevent transfer of heat to the buffer solution.

(c) Measure the temperature of the buffer solution; remove the thermometer (it is not necessary to remove the ATC sensor).

(d) Determine the theoretical pH of the buffer from the temperature-correction tables.

(e) Note and record the pH temperature readings. Adjust the meter reading to the pH value using the “standardize” function on the meter (usually a knob or pressure pad). Record the adjusted pH value for the 7.0 buffer and associated millivolt reading.

(f) Remove the electrode and ATC sensor (some instruments require that the meter be switched to the standby or off position before removing the electrode from the solution).

Repeat the calibration steps using fresh portions of reference buffer solution until two successive readings are obtained at the adjusted pH value for pH 7 buffer without further adjustment to the system.

Discard the used pH 7 buffer into a waste container.

(5) Slope adjustment rinse.

(a) Rinse the electrode and thermometer or ATC sensor thoroughly with deionized water.

(b) Rinse a clean container, electrode, and thermometer with a second buffer (usually pH 4 or 10) that brackets the expected pH value of the sample; discard the used buffer into a waste container.

(c) Pour the second buffer into a container holding the electrode and thermometer or ATC sensor. Allow the temperature to equilibrate for 1 min, then discard the used buffer into a waste container.

(6) Slope adjustment. This step is automated in modern meters.

(a) Pour a fresh portion of the second pH buffer into a container holding the electrode and thermometer or ATC sensor.

(b) Stir slowly (no vortex) or swirl manually. Follow the directions in 4, above.

(c) Measure the temperature and pH of the buffer solution and check the pH value of the buffer on temperature coefficient tables. Record the pH and temperature readings.

(d) Adjust the slope to the value of the second pH buffer at known temperature. (Some meters have separate slope-adjustment knobs, pressure pads, or other devices, whereas

others have to be adjusted by use of a temperature knob.) Record the adjusted pH value and associated millivolt reading.

(e) Discard the used buffer into a waste container.

(f) Repeat above steps using successive portions of the buffer solution until two successive readings are obtained without further adjustment.

(7) Rinse the electrode and thermometer or ATC sensor thoroughly with deionized water.

(8) If using a noncompensating or nonautomated meter, repeat the calibration rinse (step 3) and calibration procedures (step 4) to ensure that the slope adjustments did not affect the calibration adjustment.

(a) This step is a check only; no adjustment should be needed, but the result should be recorded. If adjustment is needed, repeat the entire calibration procedure.

(b) If adjustment is still needed, a systematic problem is likely. Inspect the instrument system, clean the electrode or add filling solution, or use a spare electrode or meter.

(9) Calibration check rinse.

(a) Rinse the electrode and thermometer or ATC sensor with deionized water.

(b) Rinse another clean container, electrode, and thermometer with a third buffer (pH 4 or 10) and discard the used buffer into a waste container.

(c) Pour the third buffer into a container holding the electrode and thermometer or ATC sensor. Allow the temperature to equilibrate for 1 min (if necessary), then discard the used buffer into a waste container.

(10) Calibration range check.

(a) Pour a fresh portion of third pH buffer into a container holding the electrode and thermometer or ATC sensor.

(b) Stir without forming a vortex or swirl slowly.

(c) Measure the temperature of the buffer solution (remove the liquid-filled thermometer and check the temperature-adjusted pH value), if necessary for the meter being used.

(d) The pH instrument system should read the value of the third buffer at a known temperature within ± 0.1 pH units.

Meters reading to three or more places to the right of the decimal will not provide better accuracy than ± 0.05 units, and their accuracy must be verified.

If it checks, the instrument system is calibrated over a range of pH 4 to 10 and is ready for ANC or alkalinity titrations as well as pH measurement.

If the instrument system does not check over the entire range, recalibrate before measuring the sample pH. Recalibrate before an alkalinity/ANC titration if the sample has a pH greater than 7.0.

(e) Discard the used buffer into a waste container.

(f) Rinse the electrode and thermometer (or ATC sensor) with deionized water.

6.8.3.6 Proper calibration of pH instrument systems with standard buffers does not guarantee accurate pH measurement in water with conductivity less than 100 $\mu\text{S}/\text{cm}$. The following steps are recommended for pH measurement in low-conductivity water (5).

(1) After calibration with pH 4, 7, and 10 buffers, check electrode performance daily in appropriate sulfuric acid standard solution with conductivity less than 20 $\mu\text{S}/\text{cm}$ and with a

pH similar to the stream values that are anticipated to be measured that day. (For solution preparation and handling, refer to reference (5).) Before using the sulfuric acid standard solution, check for contamination by measuring conductivity.

(2) Check electrode performance with deionized water saturated with an analyzed nitrogen-carbon dioxide gas mixture having a carbon dioxide mole fraction of less than 0.5 %. Addition of KCl is not recommended because of the potential for contamination and other complications.

(3) Rinse the electrode at least three times, preferably with a portion of the sample to be measured.

(4) Calibrate and measure pH in quiescent (unstirred) solutions after the sample has been homogenized by stirring.

(5) Check the electrode performance (slope) before using the percent Nernst slope and (or) millivolt readings at pH 7 and pH 4. Keep a record of the electrode slope and millivolt readings; they can signal electrode deterioration.

6.8.4 Measurement:

6.8.4.1 The pH of a water sample can change significantly within hours or even within a few minutes after sample collection as a result of degassing (such as loss of carbon dioxide, hydrogen sulfide, and ammonia); mineral precipitation (such as formation of calcium carbonate); temperature change; and other chemical, physical, and biological reactions.

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

6.8.4.3 *In Situ Measurement*—Follow the 7 steps listed below for in situ pH measurement:

(1) Calibrate a pH system on site (after equilibrating the buffers with the stream temperature, if necessary). Check the electrode performance and the calibration date of the thermometer being used (see the instrument manufacturer's instructions).

(2) Record the pH variation from a cross-sectional profile, if possible, to determine if pH is uniform at any given discharge, and select the sampling method appropriate for study objectives.

(a) Flowing, shallow stream—Wade to the location(s) where pH is to be measured.

(b) Stream too deep to wade—Lower a weighted pH sensor with a calibrated temperature sensor from a bridge, cableway, or boat. Do not attach the weight to sensor or sensor cables.

(c) Still-water conditions—Measure pH at multiple depths at several points in the cross section.

(3) Immerse the pH electrode and temperature sensor in the water to the correct depth and hold them there for at least 60 s to equilibrate them to water temperature.

(4) Measure the temperature.

(a) If the pH instrument system contains an automatic temperature compensator (ATC), use the ATC to measure water temperature.

(b) If the instrument system does not contain an ATC, use a separate calibrated thermometer, adjust the meter to the sample temperature (if necessary), and remove the thermometer.

(5) Record the all pH and temperature values without removing the sensor from the water.

(a) Values generally stabilize quickly within ± 0.05 to 0.1 standard pH unit, depending on the instrument system.

(b) Note the median of the observed values.

(c) If readings do not stabilize after extending the measurement period, check electrode according with Step 2, section 6.8.3.5. Note this difficulty on the field forms along with the pH readings, and note the median value of the last five or more recorded readings.

(6) EWI or EDI measurements—Proceed to the next station in the cross section. Repeat steps 3 through 5. After all stations in the cross section have been measured, rinse the sensors with deionized water and store them.

(7) Record all values of the stream pH on the field forms (Note that for pH it is necessary to calculate the mean by (1) converting each pH measurement to its antilogarithm times minus one ($10^{-(\text{pH})}$), (2) using these transformed values to calculate the mean, and (3) converting the mean value to a logarithm multiplied by minus one:)

(a) In still water—median of three or more sequential values.

(b) EDI—calculate and record the mean value of all subsection measured (use the median if measuring one vertical at the centroid of flow).

(c) EWI—calculate and record the mean of all subsections measured.

6.8.4.4 *Subsample Measurement*—When streams are fast-flowing or the water contains much sediment or algae, pH measurement of a discretely collected subsample might be preferable to in situ measurement. Follow the 12 steps listed below for subsample pH measurement:

(1) Calibrate the pH system on site (after equilibrating buffer temperature with stream temperature, if necessary). Check the electrode performance.

(2) Select the appropriate sampling method and collect a representative sample.

(3) Withdraw properly homogenized sample(s) from the compositing device.

(a) Rinse the collection bottles three times with the sample.

(b) If the samples need to be stored for a short time or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles, fill them to the brim, cap them tightly, maintain them at ambient stream temperature, and measure pH in the field immediately following the collection of the last subsample.

(4) Rinse thoroughly with deionized water—the pH electrode, thermometer or ATC sensor, stir bar, and a measurement container.

(5) Immerse electrode and temperature sensor in sample water for at least 60 s to equilibrate to sample temperature.

(6) Pour fresh aliquot of the sample water into a container holding the electrode and thermometer. Do not let the electrode touch the bottom or sides of container during measurement.

(7) Measure and record the initial temperature. Use the ATC, if it is available and calibrated, or use a separate calibrated thermometer and adjust the meter manually to the sample temperature (if necessary).

(8) Establish equilibrium between the electrode(s) and sample by stirring slowly (no vortex) or by manual swirling.

(a) Do not stir if a vortex is formed that affects the electrode performance.

(b) Do not use a magnetic stirrer for samples with low conductivity (less than 100 $\mu\text{S}/\text{cm}$).

(c) Before recording a pH value, allow the sample to reach quiescence.

(9) Record the pH and temperature measurements on the field forms, along with the sampling, processing, and measurement methods used and any observed anomalies.

(10) Quality control—Repeat steps 6 through 9 with at least two fresh subsamples to check measurement precision. Subsample values should agree within ± 0.1 pH unit (or study-determined criterion). Report the median of the values measured.

(11) Rinse the electrode and temperature sensor thoroughly with deionized water. Replace the plug on the fill hole of refillable electrodes and follow the recommended storage procedure.

(12) Discard the used sample into a waste container and dispose of it according to regulations.

6.8.4.5 *Reporting*—Standard pH measurement in flowing surface water represents the cross-sectional mean hydrogen ion activity or median pH at the time of observation. Compute a mean pH for the stream: (1) Sum the products of each subsection area, using the negative antilogarithm of the median pH determined for each subsection; (2) divide the sum by the total area of the cross section; and (3) express the mean value in terms of pH by converting it to a logarithm multiplied by minus one.

7. Precision and Bias

7.1 The precision is a function of the conditions encountered and the measurement techniques used for each measurement.

7.2 The precision and bias of the field determination of temperature, DO, SC, and pH can not be determined but it is safe to assume that the precision and bias are at least equal to and probably greater than those for these determinations when performed in a controlled laboratory environment.

7.2.1 For information on the precision and bias for laboratory measurements see: SC—Test Methods D 1125 and D 5464, DO—Test Method D 888, and pH—Test Method D 1293.

8. Keywords

8.1 dissolved oxygen; pH; sampling; specific conductance; surface-water; temperature

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