

Guidelines for Collection and Field Analysis of Water-Quality Samples from Streams in Texas

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CONVERSION FACTORS

To convert inch pound units in this report to the International System of units (SI), multiply by the following factors:

Multiply inch-pound unit	By	To obtain SI unit
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
foot (ft)	0.3048	meter
foot per second (ft/s)	0.3048	meter per second
gallon	3.785 3,785	liter (L) cubic centimeter (cm ³)
inch (in.)	25.4	millimeter (mm)
inch per second (in/s)	25.4	millimeter per second (mm/s)
ounce (oz)	28.35	gram (g)
pint	0.4732	liter (L)
pound (lb)	453.6	gram (g)
pound per square inch (lb/in ²)	6.895	kilopascal
quart (qt)	0.9464	liter (L)

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by the formula:

$$F = 9/5 (°C) + 32$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

GUIDELINES FOR COLLECTION AND FIELD ANALYSIS OF
WATER-QUALITY SAMPLES FROM STREAMS IN TEXAS

By

Frank C. Wells, Willard J. Gibbons, and Michael E. Dorsey

ABSTRACT

This manual provides standardized guidelines and quality-control procedures for the collection and preservation of water-quality samples and defines procedures for making field analyses of unstable constituents or properties.

Descriptions and procedures are given for several methods of sampling for which a variety of samplers may be used. Sample-processing devices such as sample churns and filtration apparatus are discussed along with methods of cleaning.

Analyses for unstable constituents or properties are by necessity performed in the field. This manual addresses analytical techniques and quality assurance for: (1) Water temperature; (2) specific conductance; (3) pH; (4) alkalinity; (5) dissolved oxygen; and (6) bacteria.

INTRODUCTION

Samples from streams are obtained and analyzed to evaluate the chemical, physical, and biological quality of the water. As part of its mission to assess the availability and utility of water as a natural resource, the U.S. Geological Survey (USGS) is responsible for a large part of the water-quality data collected from streams throughout the nation. These data are used by planners, developers, water-quality managers, and pollution-control agencies. To be reliable, the data must describe accurately the characteristics or the concentrations of constituents in the water.

Some properties or the concentrations of some constituents in water may change substantially within minutes or hours after sample collection. Samples for some constituents may be stabilized by treatment with a preservative. However, immediate analysis for some properties is required for dependable results. Careful attention to standardization and the exercise of quality control for these field procedures are paramount if the resulting data are to be reliable.

The methods presented in this manual for the collection and analysis of time-critical water-quality parameters conform to policies of the Water Resources Division of the USGS. These methods require care and time on the part of the individuals collecting the water samples and making appropriate field measurements. The collection, field measurement, and processing of water-quality samples may take 4 hours or longer. Collection of water samples from even the smallest stream may require a minimum of 30 minutes. During high flows, when collection of water samples must be made from a bridge, the time required to collect an appropriate sample easily may exceed 1 hour.

Field measurements of temperature, specific conductance, pH, and dissolved oxygen require that instruments be calibrated to precise standards to insure the quality of data collected and reported. These instruments must be calibrated prior to every measurement. At most sites, field personnel must filter and preserve a large amount of water. This water may contain a large amount of suspended sediment, which clogs filters and increases filtration time. Field measurements for indicator bacteria require a large number of individual samples be filtered using sterile equipment. All of these processes require time. The minimum time required to process samples at a special periodic or NASQAN station is 1.5 hours, and may take as long as 3 hours.

With the present emphasis on legal action and social pressure to abate pollution, all personnel should be aware of the responsibility to collect a sample that is a reliable description of the water resource and to provide data that are a reliable description of the sample.

This manual is designed to provide standardized guidelines and quality-control procedures for the collection and preservation of samples and field analysis of the common constituents or properties of samples from streams in Texas. As part of the "Quality-Assurance Plan for Water-Quality Activities of the Texas District," a copy of these guidelines are provided to all personnel in the District who are directly involved in the collection and field analysis of samples from streams in Texas.

The Texas District and Subdistrict office water-quality specialists will provide documentation of additional provisional or revised procedures released by the Water Resources Division's Office of Water Quality to field personnel for inclusion in this manual.

ACKNOWLEDGMENTS

The authors wish to acknowledge Jack Rawson who retired from the USGS in March 1989. Much of the material in this manual is taken directly from the original manual he prepared in 1976 and updated in 1982. Other sections of this manual were taken from a similar manual prepared by J. Rodger Knapton (1985) of the Montana District, Water Resources Division, and from unpublished manuals by Joanne Kurklin (1988) and Jerri V. Davis (1985) of the Oklahoma and Missouri Districts, respectively.

SITE SELECTION

Sampling techniques to be used in a given situation will depend not only on the data needs, but also on the nature of the flow and other conditions. The site often must be located at a specific gaging station; but sometimes, there may be some choice as to location. Generally, the site should be at or near a gaging station because of the need to relate water quality to discharge. Ideally, the site should have uniform depths and uniform velocities throughout the cross section that is to be sampled. Cross sections used to make discharge measurements usually are adequate locations for collection of water-quality samples.

Sites immediately downstream from the confluence of two streams or downstream from a point source of pollution should be avoided because the water at this type of cross section may not be well mixed. If this situation cannot be avoided, the field person should take field measurements of temperature, specific conductance, pH, and dissolved oxygen at a minimum of 10 verticals to document lateral variation, and collect water from a sufficient number of verticals in the cross section to insure that a representative sample has been collected.

Selection of a sampling site immediately upstream from the confluence of two streams also should be avoided unless the distance upstream from the confluence is adequate to minimize the effects of backwater.

After a sampling site has been selected, samples should be collected at the same cross section throughout the period of record, if possible. This is not to say that the same section used during the low-flow wading stage must be used during higher stages that require the use of a bridge or cableway. Again, the same cross sections that are used to make discharge measurements generally are adequate for the collection of water-quality samples. The location of these cross sections at varying flow conditions should be documented and maintained in the station folder.

After site selection has been made, but before routine sampling has begun, field measurements of temperature, specific conductance, pH, and dissolved oxygen should be made and documented at a minimum of 10 verticals to determine the uniformity of the water quality. These measurements also are to

be made and documented on an annual basis. Over a period of years, these annual cross-section measurements should be made at varying flow conditions when possible.

SAMPLERS

SAMPLING EQUIPMENT, SELECTION, AND MAINTENANCE

Before departing on a water-quality data-collection trip, field personnel should determine the types of samples to be collected and the field measurements required in order to assemble the proper sampling and support equipment.

The streamflow conditions and sampling structures (bridge, cableway, or other) determine which sampler(s) should be used. Stream depths and velocities determine when hand samplers or cable-suspended samplers should be used.

Stream velocity and depth are factors in determining whether or not a stream can be safely waded. When the product of depth in feet and velocity in feet per second equals 10 or greater, a stream's wadeability is questionable. However, application of this rule will vary considerably among individuals according to their weight and stature and with the condition of the streambed.

The depth-velocity product also affects the action of each sampler. The larger the product, the heavier and more stable the sampler required to collect a representative sample.

Federal Interagency Sedimentation Project Sediment Samplers

Depth-integrating water-sediment samplers designed and built by the Federal Interagency Sedimentation Project in St. Anthony Falls, Minn., and available for use in the Texas District are listed in table 1. The choice of appropriate samplers generally depends on the flow and depth in the stream. Where streams are wadeable, or access can be obtained from a low bridge span or cableway, the "DH" series of samplers should be used. These samplers were designed to be used with a wading rod or handline.

When streams cannot be waded, but are shallower than about 15 ft, the "D" series of samplers should be used. These samplers are designed to be suspended from a bridge crane or cableway by means of a standard hanger bar, cable, and reel system.

At depths greater than about 15 ft, the P-61, P-63, and P-72 point samplers may be used. The heavier P-61 and P-63 samplers may be used to depths as large as 180 ft. The lighter weight P-72 may be used to a maximum depth of 72 ft. The "point" samplers may be used for point samples as well as for depth integration. Each requires the use of an external battery pack which may be obtained from the St. Anthony Falls Sedimentation laboratory or from the USGS Hydrologic Instrumentation Facility (HIF) in Bay St. Louis, Miss.

For a more detailed description of the samplers listed in table 1, the reader is referred to USGS Open-File Report 86-531, "Field Methods for Measurement of Fluvial Sediment" (Edwards and Glysson, 1988).

Table 1.--Sampler designations and characteristics

[Epoxy-coated versions of all samplers are available for collecting trace metal samples. in., inch; lb, pound; ft/s, feet per second; ft, foot; DH-, depth integrations hand held by rod or rope; P, pint sampler; Cd, cadmium; Q, quart sampler; H, one-half gallon; D-, depth integration, suspension by cable and reel; Al, aluminum; P-, point sampler]

Sampler designation	Construction material	Sampler dimensions			Nozzle distance from bottom (in.)	Suspension type	Maximum velocity (ft/s)	Maximum depth (ft)	Sampler container size		Intake size (in.)	Nozzle color
		Length (in.)	Width (in.)	Weight (in.)					Pint	Quart		
DH-48	aluminum	13.0	3.2	4.5	3.5	rod	8.86	8.86	X	--	1/4	yellow
DH-75P	Cd-plated	9.25	4.25	1.5	3.27	rod	6.6	16	X	--	3/16	white
DH-75Q	Cd-plated	9.25	4.25	1.5	4.49	rod	6.6	16	--	X	3/16	white
DH-75H _a	Cd-plated	9.25	4.25	1.5	--	rod	6.6	--	(2 liter)		3/16	white
DH-59	bronze	15	3.5	22	4.49	handline	5.0	19	X	--	1/8	red
DH-59	do.	15	3.5	22	4.49	do.	5.0	16	X	--	3/16	do.
DH-59	do.	15	3.5	22	4.49	do.	5.0	9	X	--	1/4	do.
DH-76	bronze	17	4.5	22	3.15	handline	6.6	16	--	X	1/8	red
DH-76	do.	17	4.5	22	3.15	do.	6.6	16	--	X	3/16	do.
DH-76	do.	17	4.5	22	3.15	do.	6.6	16	--	X	1/4	do.
DH-81	plastic	b/7.5	4.0	0.5	(c)	rod	8.9	(d)	(e)	--	3/16	white
DH-81	do.	b/7.5	4.0	0.5	(c)	do.	8.9	9	(e)	--	1/4	do.
DH-81	do.	b/7.5	4.0	0.5	(c)	do.	8.9	9	(e)	--	5/16	do.
D-49	bronze	24	5.25	62	4.0	cable reel	6.6	19	X	--	1/8	green _f
D-49	do.	24	5.25	62	4.0	do.	6.6	16	X	--	3/16	do. _f
D-49	do.	24	5.25	62	4.0	do.	6.6	9	X	--	1/4	do. _f
D-74	bronze	24	5.25	62	4.06	cable reel	6.6	a/19, g/16	X	X	1/8	green
D-74	do.	24	5.25	62	4.06	do.	6.6	a/19, g/16	X	X	3/16	do.
D-74	do.	24	5.25	62	4.06	do.	6.6	a/19, g/16	X	X	1/4	do.
D-74Al	aluminum	24	5.25	42	4.06	cable reel	5.9	a/19, g/16	X	X	1/8	green
D-74Al	do.	24	5.25	42	4.06	do.	5.9	a/19, g/16	X	X	3/16	do.
D-74Al	do.	24	5.25	42	4.06	do.	5.9	a/19, g/16	X	X	1/4	do.
D-77	bronze	29	9	75	7	cable reel	18.0	15.5	(3 liter)		5/16	white
P-61	bronze	28	7.34	105	4.29	cable reel	16.6	a/180, g/120	h/X	X	3/16	blue
P-63	bronze	37	9	200	5.91	cable reel	6.6	a/180, g/120	h/X	X	3/16	blue
P-72	aluminum	28	7.34	41	4.29	cable reel	5.3	a/72.2, g/50.9	h/X	X	3/16	blue

a/ Depth using pint sample container.

b/ Without sample bottle attached.

c/ Depends on bottle size used.

d/ Refer to transit-rate determination graph construction (in section "Transit Rates for Suspended-Sediment Sampling," USGS Open-File Report 86-531) with specific nozzle and bottle size used.

e/ Any size bottle with standard mason jar threads.

f/ The green nozzles used with the D-74 can be used to replace calibrated brass nozzles no longer available.

g/ Depth using quart sample container.

h/ Pint milk bottle can be used with adapter sleeve.

All samplers purchased from the Federal Interagency Sedimentation Project before January 1980 were supplied with brass nozzles. Samplers purchased thereafter were supplied with color-coded nylon nozzles and screws. A color-coded nylon screw is permanently attached to each sampler equipped with color-coded nozzles to serve as a reminder of the proper nozzles to be used.

Caution should be used when the nylon nozzles are screwed into the samplers. Nozzles screwed into the sampler too tightly will bend (USGS Quality of Water Branch Technical Memorandum 80.18). Nozzles should be tightened by hand only to the point at which the knurled part of the nozzle just touches the body.

Using the proper gasket to seal the bottle is as important as using the correct nozzle in the instrument. Each sampler series uses a different size or shape of gasket. Any of the samplers approved for the collection of pesticides and trace metal samples should be equipped with the appropriate nylon nozzles and silicone rubber gaskets.

Additional Water-Sediment Samplers

Weighted Bottle Sampler

The weighted bottle sampler is made of steel and is designed to accommodate a 1-L narrow-mouth glass bottle. It was designed for sampling streams with relatively slow velocities (less than 1.5 ft/s) and for streams which are not transporting sand particles. Samples collected using this sampler should be depth integrated from multiple verticals and composited in a churn splitter.

Texas Basket Sampler

The Texas basket sampler was designed to accommodate glass or nylon quart-size or smaller bottles. This sampler should not be used for routine water-quality samples. Use of this sampler should be reserved for runoff in small urban watersheds where changes in stage or changes in the quality of the water may occur rapidly. Samples obtained using this sampler should be collected using similar size bottles. For example, do not mix quart bottles and pint bottles in the sampler at the same time because the smaller size bottles will overflow.

Biochemical Oxygen Demand Sampler

The biochemical oxygen demand (BOD) sampler accommodates a 300-mL glass BOD bottle and is designed to provide for a threefold displacement of water in the sample bottle without aeration. This 10- to 15-lb metallic sampler or a nylon modification thereof is used in the Texas District for the collection of an unaerated sample for the measurement of dissolved oxygen during weather conditions which make in situ measurements impractical. If velocity of the flow is too fast for the sampler to be lowered to the streambed, sounding weights should be attached to the rope or cable from which the sampler is suspended.

Bed-Material Samplers

The samplers commonly used in the Texas District and described in this section are physically limited to the collection of bed-material samples consisting of particles finer than about 30 to 40 mm in diameter (finer than medium gravel).

USBMH-60

The USBMH-60 sampler is a 30-lb handline sampler designed to sample streams with moderate depths and velocities and with bed material that is moderately firm but contains minimum gravel. The sampler mechanism consists of a scoop or bucket driven by a spring. The scoop, when activated by release

of tension on the hanger rod, can penetrate into the bed about 1.7 in. and can hold approximately 175 cm³ of material.

To cock the bucket into an open position for sampling, the sampler must first be supported by the handline; then the bucket can be opened with an allen wrench. The hanger rod to which the handline is attached is grooved so that a safety yoke can be placed in position to maintain tension on the hanger rod assembly and to hold the bucket open for cleaning.

CAUTION: AT NO TIME SHOULD THE HAND
OR FINGERS BE PLACED IN THE BUCKET
OPENING. ACCIDENTAL CLOSING OF THE
BUCKET MAY CAUSE PERMANENT INJURY!

The bucket closes when the safety yoke is removed and tension on the handline is released, as will occur when the sampler comes to rest on the streambed.

USBM-54

The USBM-54 is a 100-lb cable-and-reel sampler designed to sample bed material of streams of any reasonable depth, except for streams with extremely fast velocities. Operation of the sampler is similar to the USBMH-60 in that it takes a sample when the tension on the cable is released as the sampler touches the bed.

This sampler should be equipped with a safety bar which can be rotated over the front, or cutting edge, of the bucket when cocked into open position. Again, at no time should the hand or fingers be placed in the bucket opening even though a safety bar is used.

The driving force of the bucket is a coil-type spring. The tension on the spring is adjusted by the nut-and-bolt assembly protruding from the front of the sampler. Maximum tension should be used only when the streambed material is very firm.

Support Equipment

The following is a list of the most commonly used field support equipment. Field persons are encouraged to copy, modify, or adjust the list to their specific needs, and use it as a checklist for field-trip preparation.

1. Field meters
 - A. Thermistor (or thermometer)
 - B. Conductance meter and probe
 1. Conductance standards
 - C. pH meter and probe
 1. Spare probe
 2. Buffers (4, 7, 10)
 3. Electrolyte (potassium chloride (KCl))
 - a. One- or three-mL syringe
 - D. Dissolved oxygen meter and probe
 1. Spare probe

2. Probe repair kit
 - a. Filling solution
 - b. Membranes
 - c. O-rings
3. Air calibration chamber
4. Oxygen solubility table
5. Altimeter/barometer
2. Sampling equipment
 - A. Three- or four-wheel base with crane
 1. Hanger bar
 2. Pins
 - B. Reel
 - C. Rope
 - D. Tagline
 - E. Stopwatch
 - F. Waders/hip boots
 - G. Appropriate sample bottles for low and high flow
 1. Several clean narrow-mouth glass bottles for sampling
 2. Assorted glass and plastic bottles for samples
 - H. Churn splitter(s)
 - I. Peristaltic pump and filter (142 mm or 100 mm)
 1. Pump tubing
 2. 142-mm filter support screens
 3. Filter papers
 4. Stainless steel forceps
 - J. Labels
 - K. Sample preservatives
 1. Nitric acid (HNO_3), mercuric chloride (HgCl_2) ampules, etc.
 2. Ice chest
 - L. Field sheets (TX-72Q) and clipboard
 - M. Field folders
3. Alkalinity supplies
 - A. Buret or Hach $\frac{1}{2}$ digital titrator and delivery tube
 - B. Alkalinity acid (cartridge for Hach)
 - C. Volumetric pipet(s) 25 mL and/or 50 mL
 - D. Magnetic stirrer and stirring bars
 - E. Nylon beakers (100 mL)
4. Coliform supplies
 - A. Media plates
 - B. Buffer water
 - C. Sterilized water
 - D. Incubators
 - E. Setup kit
 1. Sterilized graduated cylinders (100 mL)
 2. Sterilized dilution bottles
 3. Sterile disposable pipets (1.0 to 10.0 mL)
 4. Sterile disposable syringes (1.0 mL)
 5. Alcohol burner
 6. Supply of methanol
 7. Filter apparatus and vacuum pump

1/ Use of brand names in this publication is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

- 8. Sterile 0.47 $\mu\text{S}/\text{cm}$ at 25 °C filters
- 9. Stainless steel forceps
- 10. Grease pencils
- 5. Chlorine test/titration kit
 - A. Anhydrous sodium sulfite
 - B. 1:1 acetic acid
 - C. Potassium iodide (KI)
 - D. Thyodene
 - E. Scoop (1 g)
- 6. Miscellaneous
 - A. Cleaning supplies
 - 1. Soap solution (Alconox)
 - 2. 5 percent hydrochloric acid (HCl) solution (1 L)
 - 3. Tissues, towels, brushes, etc.
 - 4. Deionized water
 - 5. Spray bottle (for soap solution and deionized water)
 - 6. Hexane
 - B. Tool kit
 - C. Pens, pencils, permanent markers
- 7. Safety equipment
 - A. Signs, cones, etc.
 - B. Bright vest
 - C. Flashing red light
 - D. First aid kit
 - E. Eyewash
 - F. Disposable rubber gloves
 - G. Fire extinguishers
 - H. Personal flotation device
 - I. Safety glasses

METHODS OF CLEANING SAMPLERS AND SUPPORT EQUIPMENT

Prior to using any sampler, it must be thoroughly cleaned. The critical parts of the depth-integrating water-sediment sampler are the nozzle, that part of the head underneath the gasket, and the entire center part of the sampler head that may contact the sample.

It is recommended that the sampler be cleaned with a moderate amount of low-phosphate detergent solution and washed with tap water, and then rinsed with deionized water prior to the field trip and in the field after sampling a particularly dirty site. The use of excessive quantities of detergent is discouraged to avoid possible contamination of nutrient samples. If the sampler is to be used for the collection of samples for pesticide analysis, the sampler should be rinsed with hexane before the tap water rinse.

Upon arriving at each field site, and prior to sampling, field personnel should thoroughly rinse the empty sampler in the stream to wash away any contaminant.

The USGS churn splitter used for compositing and splitting water-sediment samples should be cleaned prior to the field trip as follows:

1. Soak the churn for about 4 hours with a 5-percent solution of HCl.
2. Clean with a low-phosphate detergent.

3. Rinse with tap water.
4. Rinse with deionized water.

Cleaning the churn in the field between individual sampling sites normally can be accomplished by rinsing with deionized water immediately after sampling is completed and then rinsing with native water at the next site. Sampling of a particularly dirty site may require that the sampler be thoroughly cleaned in the field. Thus, field vehicles should be equipped with the following materials:

1. Low-phosphate detergent
2. Deionized or distilled water
3. Hexane
4. Stiff long-handle brush.

Prior to the field trip, if the BMH-60 sampler is to be used for the collection of bed material for pesticide analysis, it should be cleaned as follows:

1. With the bucket in a closed position, remove the two large flathead screws and the socket-head capscrew at the downstream edge of the bucket.
2. Insert the allen wrench in the shaft, open the bucket about one-third of the way, and remove the cover-plate gasket assembly.
3. Open the bucket fully and insert the safety yoke.
4. Using a stiff long-handle brush, clean the bucket thoroughly with detergent, hexane, detergent again, and tap or deionized water.
5. Clean the cover-plate gasket assembly with detergent, and hexane and tap or deionized water.
6. Reassemble the sampler and keep the bucket closed until ready for sampling.
7. Upon arriving at each field site and prior to sampling, rinse the sampler with native water.

SAMPLE COLLECTION AND TREATMENT

GENERAL CONSIDERATIONS

Many of the ions or other constituents normally present in a water sample at the time of collection may not remain in the sample until it is analyzed in the laboratory because of such chemical reactions as oxidation, reduction, precipitation, absorption, and ion exchange. Some properties or constituents such as temperature, specific conductance, alkalinity, dissolved oxygen, and bacteria may change substantially within a few minutes or hours after sample collection. Immediate measurement in the field is required for dependable results for these parameters. Samples for other constituents may be stabilized by preservative treatment, such as the addition of mercuric chloride and refrigeration to minimize chemical change resulting from biologic activity, or the addition of nitric acid to prevent the precipitation of cations.

Analysis for "total" or "total recoverable" constituents requires a raw (unfiltered) sample of the water-sediment mixture; analysis for "dissolved" constituents requires a filtered sample (generally, through a 0.45- μm membrane filter). Other analyses may require bottom material, residue of a filtered sample, or biota obtained from the stream. The types of samples,

sample containers, preservative treatments, and the volume of samples required for analysis are documented in a series of reports issued periodically by the National Water Quality Laboratory (NWQL). This information for current NWQL schedules is retrieved annually, or more frequently, by the execution of the computer program "LABSCHED" on the Amdahl computer in Reston, Va., or by the "SPN" program on the NWQL Prime computer (NWQL node is LCOARV). Requirements for the more common schedules included in sampling programs in the Texas District are maintained in the Prime computer file, <QWATER>QA>LABORATORY.SCHEDULES.

METHODS FOR COLLECTING DEPTH-INTEGRATED WATER SAMPLES

Approved sampling methods are (1) the equal-discharge-increment (EDI) method, and (2) the equal-width-increment (EWI) method. If depth-integrating samplers are not adequate because of large depths or large velocities, a series of discharge-weighted samples may be collected by using a point-sediment sampler. If the EDI method is used, four to nine verticals should be sampled. If the EWI method is used, 10 to 20 verticals should be sampled. If a point-sediment sampler is used, and the EDI method is used to determine sampling locations, four to nine verticals are required. If the EWI method is used to determine sampling locations with a point sampler, 10 to 20 verticals are recommended.

NOTE: Regardless of the method used to collect water-quality or suspended-sediment samples, care should be taken not to overfill the sample bottles. A sample bottle is overfilled when the water surface in the bottle is above the nozzle or air exhaust, with the sampler held level. Another guide for sample bottle overfilling is the "three finger" test. To use this test, grasp the bottle with the index finger wrapped around and level with the top of the bottle. If the water surface in the bottle is above the third finger, the sample is overfilled and must be discarded.

Upon arrival at a water-quality sampling station, the field person must determine the sampling method appropriate for that station and flow conditions. The field person must first determine if a weighted narrow-mouth glass-bottle sampler or an approved suspended-sediment sampler should be used (fig. 1). If a discharge measurement has been made immediately prior to sample collection and the largest measured velocity did not exceed 1.5 ft/s, an approved suspended-sediment sampler is not required to collect the depth-integrated sample.

If the largest measured velocity is greater than 1.5 ft/s, or if a discharge measurement has NOT been made immediately prior to sample collection, then the field person must determine if the stream is transporting sand particles. This is done by going to the fastest flowing area of the sampling cross section and obtaining a single vertical depth-integrated suspended-sediment sample using an approved suspended-sediment sampler. If sand is present, it will settle to the bottom of the pint or quart bottle in a few seconds. If sand particles are present, then the water samples collected at this station must be collected using an approved suspended-sediment sampler.

If it is determined that the single vertical depth-integrated suspended-sediment sample contains NO sand, then the water sample may be obtained by depth integrating with a clean, glass 1-L narrow-mouth bottle at multiple ver-

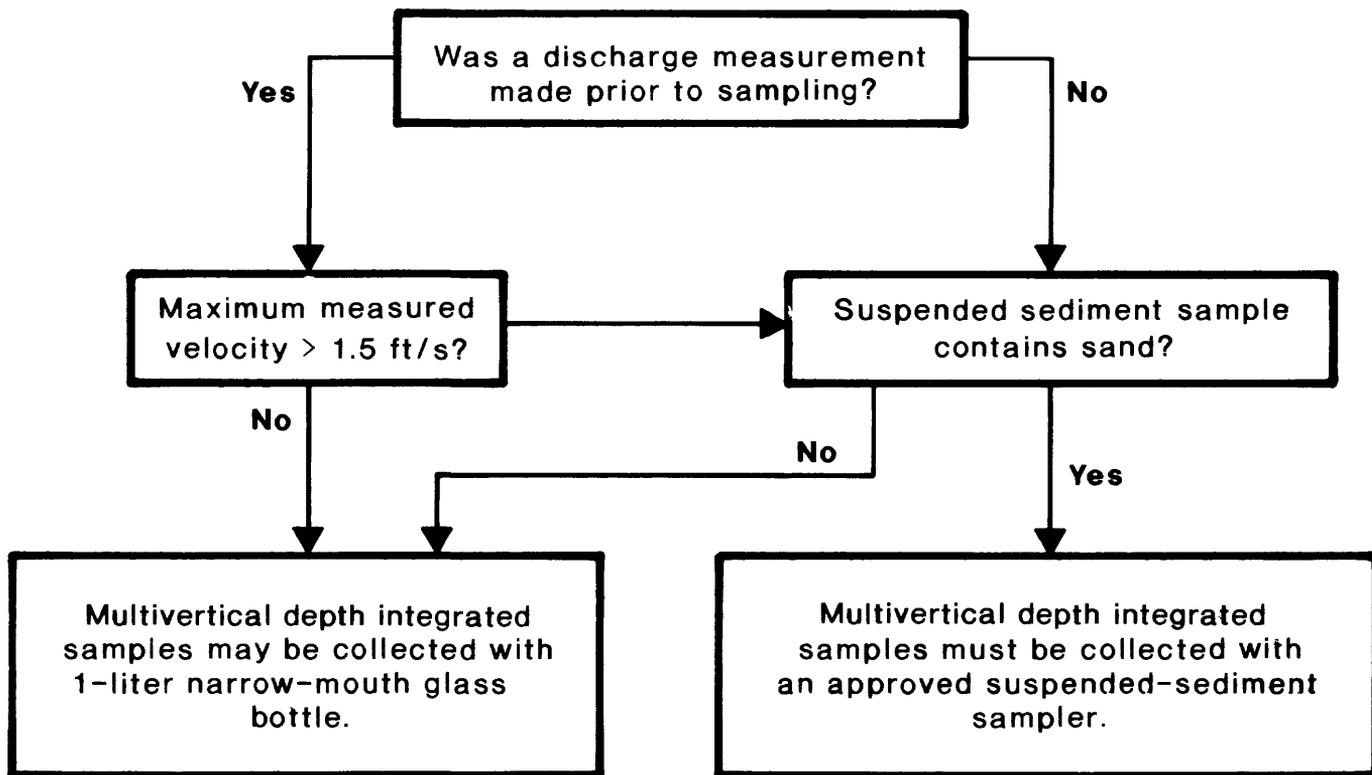


Figure 1.--Decision-making flowchart to determine whether a 1-liter narrow-mouth glass bottle or an approved suspended-sediment sampler should be used to collect water-quality samples.

ticals. If the EDI method is used to determine sampling locations, four to nine verticals will be sampled. If the EWI method is used to determine sampling locations, 10 to 20 verticals will be sampled. Care should be taken not to overfill the 1-L glass bottle. Under normal circumstances it takes approximately 30 to 40 seconds for these bottles to fill. All samples collected using the 1-L narrow-mouth glass bottle will be composited in the churn splitter, and appropriate subsamples will be withdrawn from the churn splitter. Samples for organic and bacteria analysis should not be collected from multiple verticals because these samples cannot be composited in the churn splitter. Samples for organic and bacteria analysis should be collected near the centroid of flow from a single vertical.

All water samples except those for suspended-sediment, bacteria, and organic analysis, will be composited in a churn splitter. If raw water is required for analysis, then the raw water samples will be withdrawn from the churn using appropriate churning techniques. Once all raw water has been withdrawn from the churn, water may then be withdrawn for filtered samples.

For those stations where NO raw water is required for analysis by the NWQL, the field person does not need to use an approved suspended-sediment sampler even if sand is present. These stations usually are the daily stations. A depth-integrated multivertical sample using a clean 1-L narrow-mouth glass bottle is required at these stations. If the EDI method is used to determine sampling locations, four to nine verticals should be sampled. If the EWI method is used to determine sampling locations, 10 to 20 verticals should be sampled. All samples are to be composited in the churn splitter, and filtered and preserved at the station. They are not to be brought back to the field service unit for filtration. Alkalinity at the daily stations should be determined in the field if the field person has the appropriate equipment. If equipment for determining alkalinity is not normally carried in the field vehicle, an 8-oz filtered, chilled sample may be returned to the field service unit for the alkalinity determination.

Samples collected for checking conductivity at the daily stations may be collected from the centroid of flow. Depth integration of these samples is not required because the sample is not used for chemical analysis.

Samples collected for analysis of suspended sediment must be collected using an approved suspended-sediment sampler. Samples collected for suspended sediment should be collected at the same verticals that samples for chemical analysis are collected. More than one vertical may be collected in a single bottle. For example, when using the EWI method of sampling, water from more than one vertical may be collected in a single bottle, provided that the transit rate at each vertical is equal, and that the bottle is not overfilled. If the bottle overfills, the field person should discard the water and resample the verticals that were composited in that bottle.

Deviations from the above prescribed procedures may be allowed, but for most streams, deviations should be kept to a minimum. Any deviations from the above procedures should be noted on the field sheets and the reason for deviation also should be noted. Conditions for deviation from the above procedures would be if the stream was too shallow, or too narrow to obtain a depth-integrated multivertical sample. At times when a multivertical depth-integrated

sample is not practical, samples should be collected from the centroid of flow and composited in a churn splitter.

Safety hazards also may prevent the field person from following these prescribed procedures, but safety may not be a constant factor. If a station is unsafe on a consistent basis, the Subdistrict Chief and the District Safety Officer should be notified so that appropriate actions may be taken to reduce the safety hazards.

Much of the following discussion on proper sampling procedures is taken directly from USGS Open-File Report 86-531. All personnel are encouraged to obtain a copy of this report and become thoroughly familiar with proper sampling procedures.

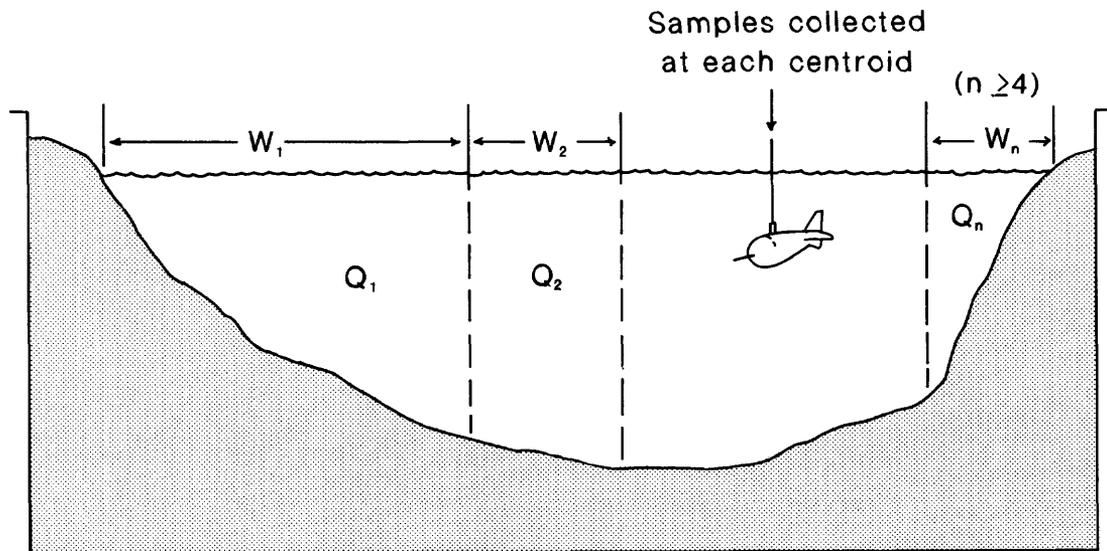
Equal-Discharge-Increment Method

With the EDI method, samples are obtained from the centroids of equal discharge increments (fig. 2). This method requires some knowledge of the distribution of streamflow in the cross section based on a long period of discharge record or based on a discharge measurement made immediately prior to selection of the sampling verticals. If such knowledge can be obtained, the EDI method can save time and labor because fewer verticals are required than when using the EWI method.

A minimum of four and a maximum of nine verticals should be used when using the EDI method. This method assumes that the sample collected at the centroid represents the mean concentration for the subsection. If this assumption is not true, the number of verticals should be increased until it becomes true or the EWI method should be used. For example, if tributary or effluent inflow upstream from the sampling location is causing lateral variation in field measurements of temperature, specific conductance, pH, or dissolved oxygen, then the EWI method would be preferable to the EDI method.

To use the EDI method without the benefit of previous knowledge of the flow distribution in the sampling cross section, first measure the discharge of the stream. Equal-discharge increments and centroids at which samples are to be collected can be determined from the discharge measurement preceding the sample (fig. 3). For example, assume that five verticals would be sampled. Equal increments of discharge are then computed by dividing the total discharge by the number of verticals ($166/5 = 33.2$). The first vertical (A) is located at the centroid of the initial EDI or at a point where the cumulative discharge from the left edge of water (LEW) is half of the EDI, in this case $33.2/2 = 16.6$. Subsequent centroids (B, C, D, and E) are located by adding the increment discharge to the discharge at the previously sampled centroid; in this example $A = 16.6$, $B = 33.2 + 16.6$, $C = B + 33.2$, etc. Samples are therefore collected at locations where cumulative discharge relative to the LEW is 16.6, 49.8, 83.0, 116.2, and 149.4.

To determine the sampling locations of the centroids, the field person must include a midpoint sampling locations column and a cumulative discharge column (ΣQ) to the sheet of discharge-measurement notes by determining the midpoint between the stations and by adding the discharges shown in the "discharge column," and keeping a running total as shown in figure 4. The



EXPLANATION

- W Width between verticals (not equal)
- Q Discharge in each increment (equal, equal-discharge increment)
- n Number of verticals sampled

Figure 2.--Equal-discharge-increment samples collected at the centroid of flow of each increment.

next step is to estimate the station of the above determined centroids. Each centroid is located at the station in the cross section corresponding to the occurrence of its computed cumulative discharge. The previously determined EDI of 16.6 ft³/s is located between the midpoint stations 30 and 38, but closer to midpoint station 38. Interpolation between these midpoint stations would locate the sampling location at station 36. Using the same procedure, estimates of centroid stations for discharges of 49.8, 83.0, 116.2, and 149.4 yields centroid stations of 60, 83, 109, and 144.

If the cross section at the measurement site is stable and the control governing the stage at the measurement cross section is also stable, previous discharge measurements may be used to determine centroids of equal increments of discharge.

By plotting the cumulative discharges versus stations for the example, the stations of the centroids may be read directly from the curve. The values are 36, 60, 83, 109, and 144, which correspond to the previously estimated values.

A number of these measurements may be plotted on the same sheet and carried into the field (fig. 5). If the cumulative percent of the total discharge is plotted against sampling locations as shown in the figure, then the selection of appropriate stations becomes a relatively easy task. For discharges that fall between those plotted, the field person can estimate the locations of the centroids by interpolating between the curves.

Equal volumes of water should be collected at each of the sampling locations using the EDI method. Transit rates between sampling locations may vary to obtain equal volumes of water (fig. 6). For example, in a given cross section, slower transit rates will be needed in slow-flowing water, and faster transit rates will be needed in faster-flowing water to obtain equal volumes of water. Equal sample volumes are of primary importance when using the EDI method. Approximate filling times for pint and quart sample bottles are given in figures 7 and 8. The field person should note that although transit rates may vary, transit rates should not exceed 0.4 times the mean velocity of flow in the vertical.

Equal-Width-Increment Method

A depth-integrated multivertical sample obtained by the EWI method requires a sample volume proportional to the amount of flow at each of several equally-spaced verticals in the cross section. This equal spacing between the verticals across the stream and sampling at an equal transit rate at all verticals yields a gross sample volume proportional to the total streamflow. This method is used most often in shallow, wadeable streams and sand-bed streams where the distribution of discharge in the cross section may vary between sampling trips. It is also useful in streams where tributary flow has not completely mixed with the main-stem flow.

The number of verticals required for an EWI measurement depends on the distribution of sediment and flow in the cross section at the time of sampling as well as on the desired accuracy of the result. In general, a minimum of 10 verticals should be used for streams over 5 ft wide. For all but the very wide and shallow streams, a maximum of 20 verticals usually is ample. For

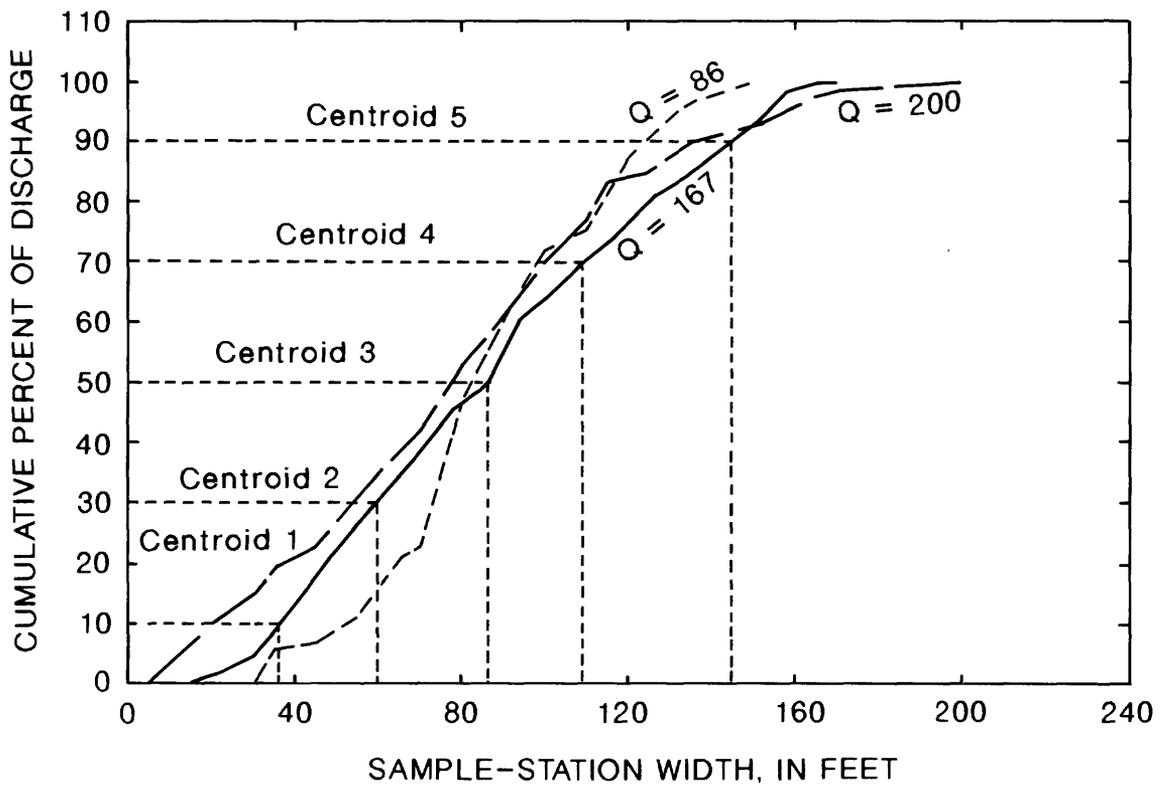
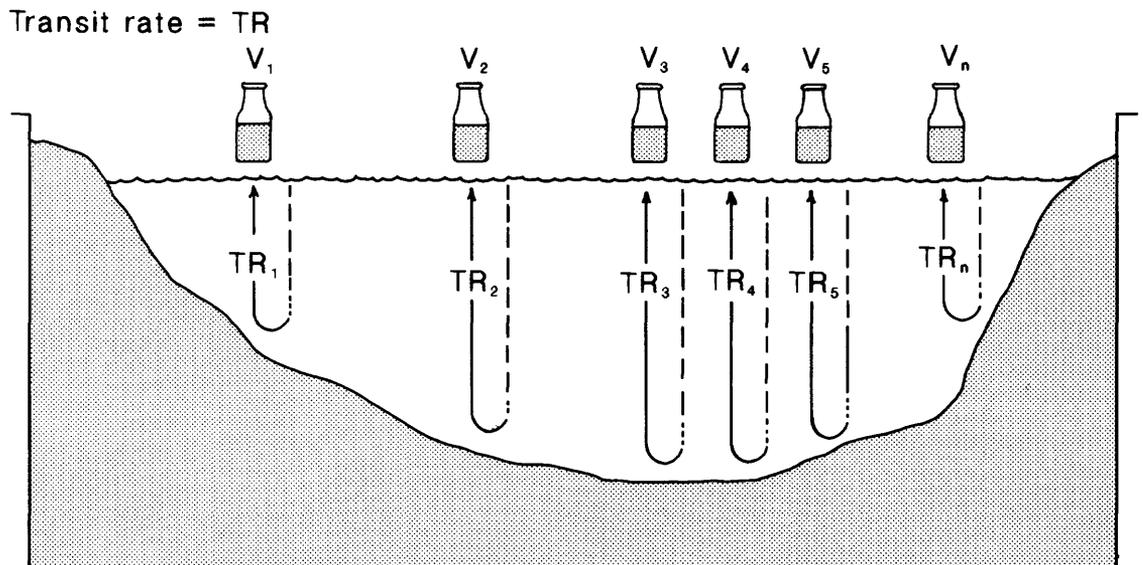


Figure 5.--Three cumulative percents of discharge (Q) relative to equal-discharge-increment centroid-determination stations.



EXPLANATION

- TR Transit rate each centroid (not equal)
- V Volume collected at each centroid (equal)
-  Centroid in each increment (samples collected)

Figure 6.--Vertical transit rate relative to sample volume collected at each equal-discharge-increment centroid.

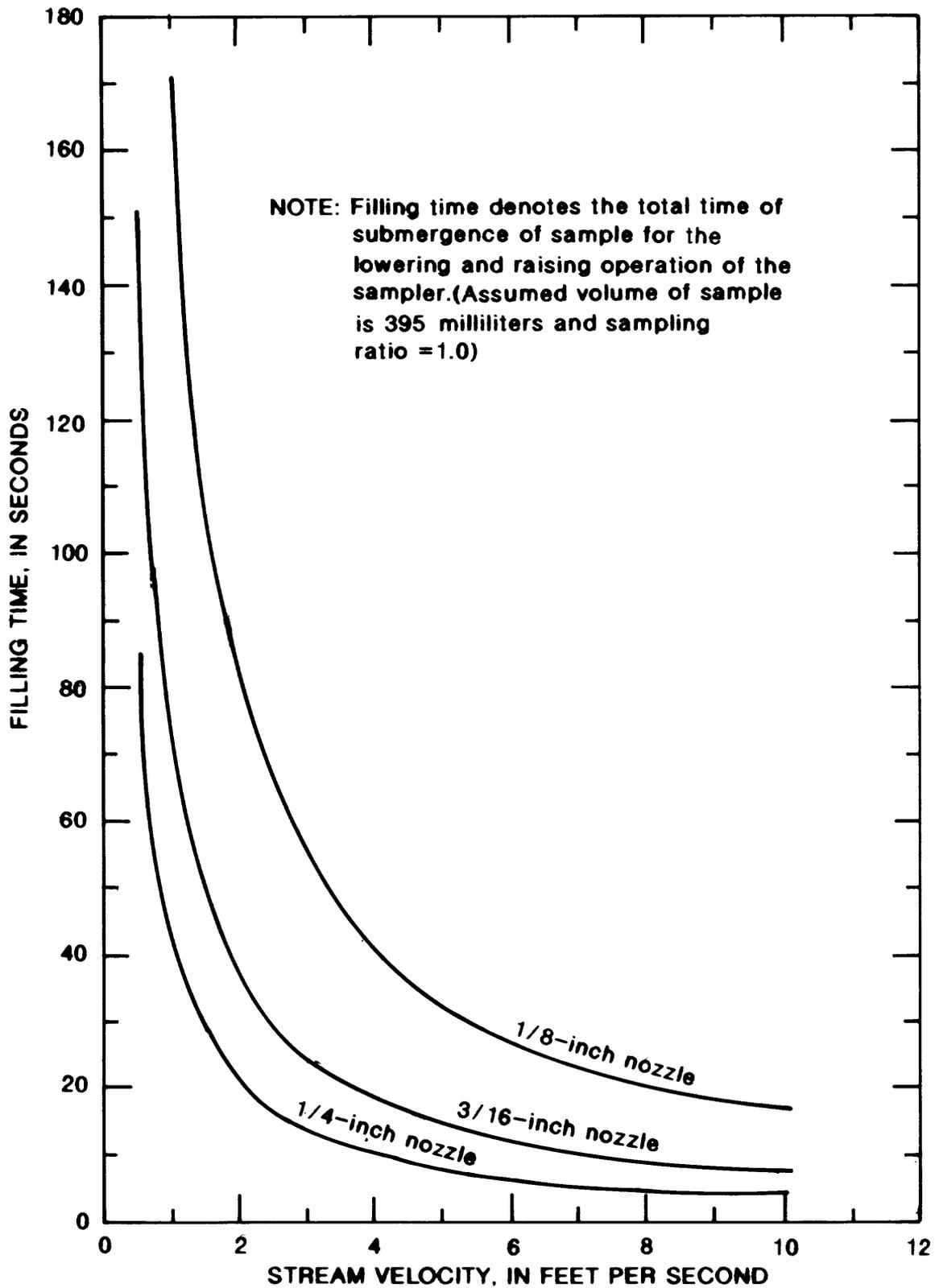


Figure 7.--Filling time for suspended-sediment sample bottle of 1-pint capacity.

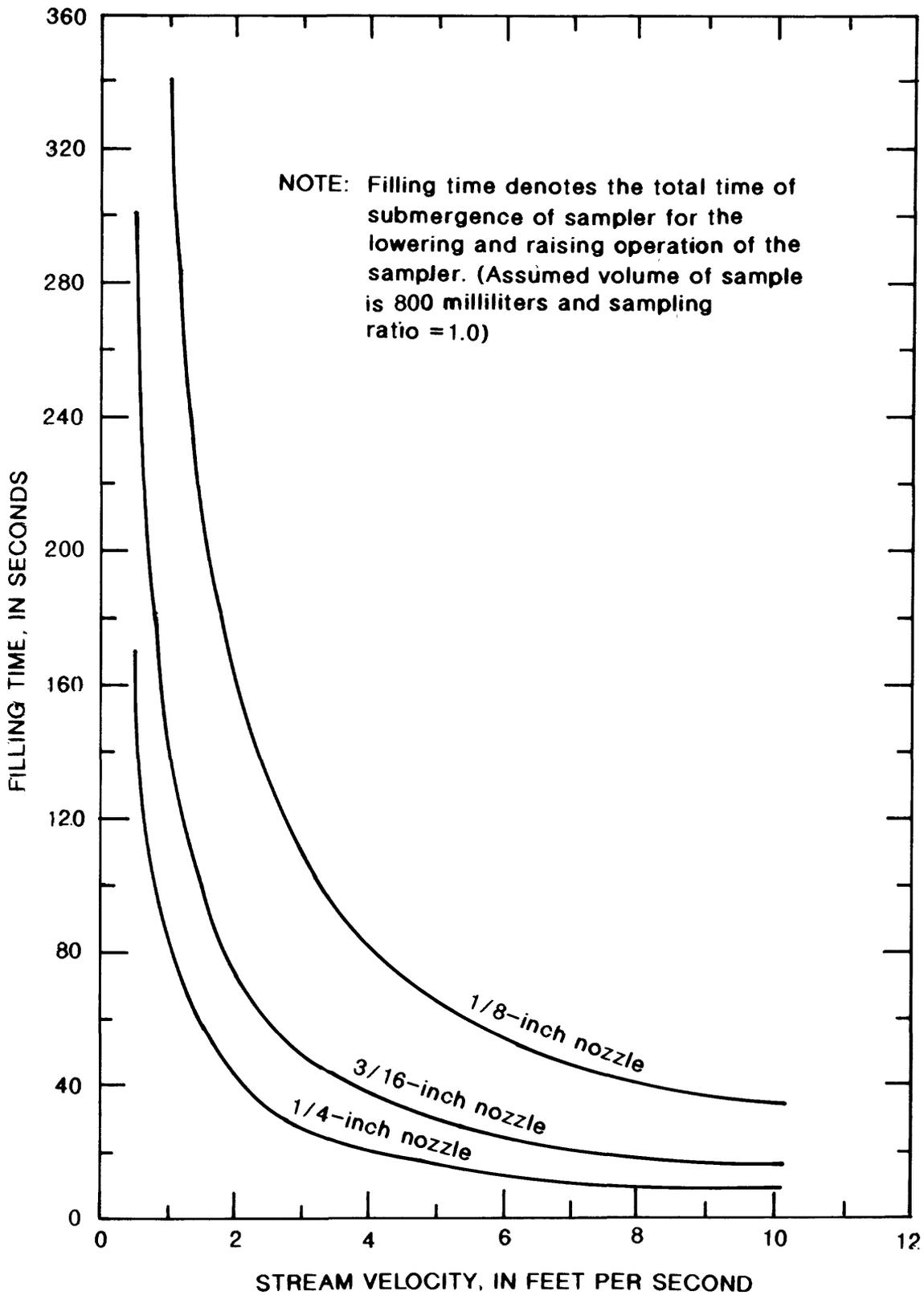


Figure 8.--Filling time for suspended-sediment sample bottle of 1-quart capacity.

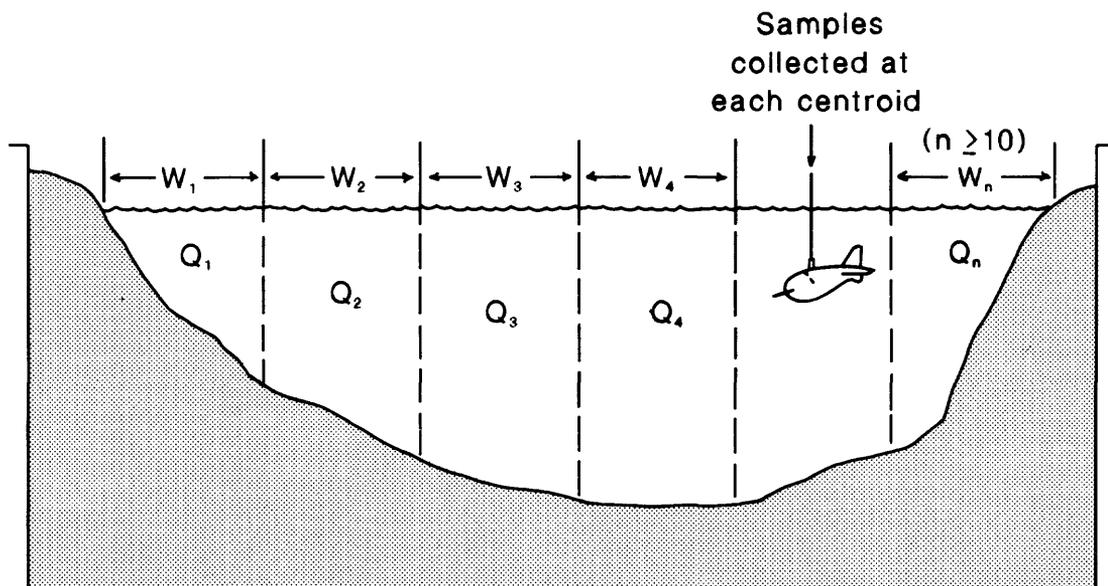
those streams less than 5 ft wide, as many verticals as possible should be used as long as they are spaced a minimum of 3 in. apart to allow for discrete samples of each vertical and to avoid overlaps.

The width of the increments to be sampled, or the distance between verticals is determined by dividing the stream width by the number of verticals necessary to collect a sample that is representative of sediment and flow in the cross section (fig. 9). For example, if the stream width is 160 ft, and the number of verticals necessary to represent the cross section is 10, then the width (W) of each sampled increment would be 16 ft. The sample station within each width increment is located at the center of the increment (W/2), beginning at a location of 8 ft from the bank. Assuming that the edge of water is at station 0, sampling locations would be at 8, 24, 40, 56, 72, 88, 104, 120, 136, and 152 ft.

The EWI sampling method requires that all verticals be traversed using the same transit rate (fig. 9). The descending and ascending transit rates must be equal during the sampling traverse of each vertical, and they must be the same at all verticals. By using this equal-transit technique with a standard depth-integrating sampler, a volume of water proportional to the discharge in the vertical will be collected (fig. 10). Note that by using equal transit rates, equal volumes of water will NOT be collected at each vertical. Larger volumes of water will be collected in fast-flowing water and smaller volumes of water will be collected in slow-flowing water.

It is often difficult to maintain an equal transit rate when collecting samples while wading. The following procedure is useful in alleviating this difficulty. The sampler should be held at a reference point on the body (for example, the hip) at which level the downward and upward integration is started and finished (even though part of the traverse is in the air). The same reference point should be used at each vertical, allowing the same amount of time to elapse during the round trip of the sampler (regardless of the stream depth encountered). It should be remembered that the reference point at which the sampler traverse is started and stopped must be located above the water surface at the deepest vertical sampled and must be the same for each vertical.

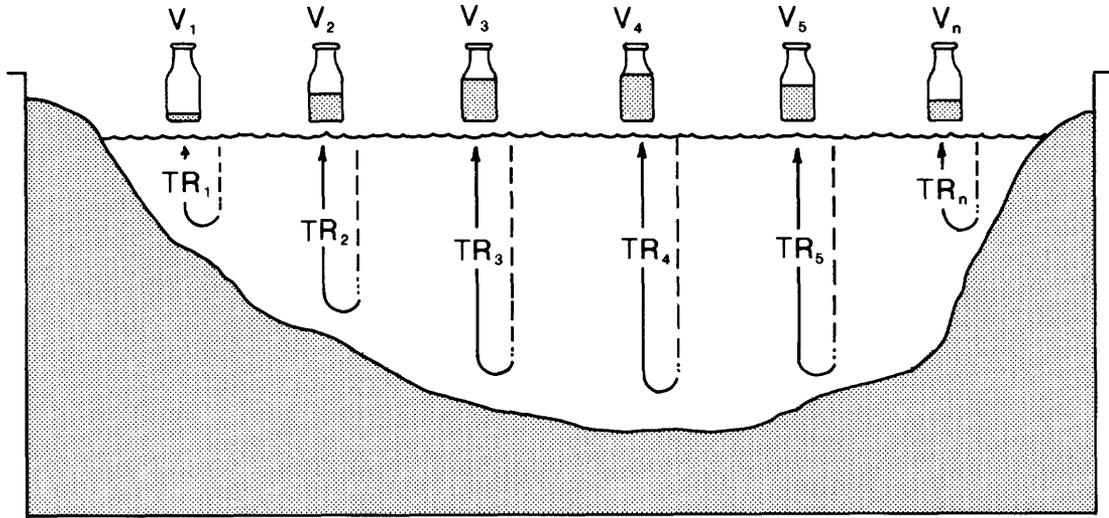
Because the maximum transit rate must not exceed 0.4 times the mean velocity in the vertical, and because the minimum rate must be sufficiently fast to keep from overflowing any of the sample bottles, it is evident that the transit rate to be used for all verticals is limited by conditions at the vertical containing the largest discharge per foot of width (largest product of depth times velocity). A discharge measurement can be made to determine where this vertical is located, but usually it is estimated by sounding for depth and acquiring a "feel" for the relative velocity with an empty sampler or wading rod. The transit rate required at the maximum discharge vertical must then be used at all other verticals in the cross section, and usually is set to fill a bottle to the maximum sample volume in a round trip. It is possible to sample two or more verticals using the same bottle provided the bottle is not overfilled. If a bottle is overfilled, it must be discarded and all verticals previously sampled using that bottle must be resampled.



EXPLANATION

- W Width between verticals (equal, equal-width increment)
- Q Discharge in each increment (not equal)
- n Number of verticals sampled

Figure 9.--Equal-width-increment sampling technique.



EXPLANATION

- TR Transit rate at each centroid (equal)
- V Volume collected at each centroid (not equal, but proportional to the discharge at each increment)
- U Centroid in each increment (samples collected)

Figure 10.--Equal-width-increment vertical transit rate relative to sample volume that is proportional to water discharge at each vertical.

Advantages of the Equal-Discharge-Increment and the Equal-Width-Increment Methods

Some advantages and disadvantages of both the EDI and EWI methods have been mentioned in the previous discussions. It must be remembered, however, that both methods, if properly used, yield the same results.

Advantages of the EDI method are:

1. Fewer verticals are necessary resulting in a shorter collection time.
2. Sampling during rapidly changing stages is facilitated by the shorter sampling time.
3. A variable transit rate can be used among verticals.

Advantages of the EWI method are:

1. Previous knowledge of flow distribution in the cross section is not required.
2. Method is easily learned.
3. Generally, less total time is required if no discharge measurement is deemed necessary and the cross section is stable.

Point Samplers

Depth-integrating samplers cannot be used in streams where the depths exceed about 16 ft (table 1). In those streams, point samplers should be used. Sample vertical locations should be based on the EDI or EWI sampling methods.

Depth Integrating

Point samplers may be used to collect depth-integrated samples in verticals where the depth is greater than about 16 ft. For streams with depths between 15 and 30 ft, the procedure is as follows:

1. Insert a clean bottle in the sampler and close the sampler head.
2. Lower the sampler to the streambed keeping the solenoid closed and note the depth to the bed.
3. Start raising the sampler to the surface using a constant transit rate. Open the solenoid at the same time the sampler begins the upward transit.
4. Keep the solenoid open until after the sampler has cleared the water surface. Close the solenoid.
5. Remove the bottle containing the sample.
6. Insert another clean bottle into the sampler and close the sampler head.
7. Lower the sampler until the lower tail vane is touching the water allowing the sampler to align itself with the flow.
8. Open the solenoid and lower the sampler at a constant transit rate until the sampler touches the bed.
9. Close the solenoid the instant the sampler touches the streambed. (By noting the depth to the streambed in step 2 above, the operator will know when the sampler is approaching the bed.)

The transit rate used when collecting the sample in the upward direction need not be the same as that used in the downward direction. If the stream

depth is greater than 30 ft, the process is similar, except that the upward and downward integrations are broken into segments no greater than 30 ft. The procedure for sampling a stream with a depth of 60 ft is illustrated in figure 11. Note the transit rate used in the downward direction TR_1 and TR_2 is not equal to the transit rate in the upward direction (TR_3 and TR_4) but $TR_1 = TR_2$ and $TR_3 = TR_4$.

Samples must be obtained at a given vertical for both the downward and upward directions.

Point Samples

Point samples also may be obtained from several verticals in a cross section to define the mean concentrations of constituents in the cross section. Between 5 and 10 samples should be collected from each vertical. In Texas, it is recommended that point samples be collected at 0.1, 0.3, 0.5, 0.7, and 0.9 of the total depth at each vertical. The sample time for each sample in the vertical (the time the nozzle is open) must be equal. This will insure that samples collected are proportional to the flow at the point of collection. If the EDI method is used to define the sampling locations of the verticals, the sampling time may be varied among verticals. Equal volumes of water should be collected from each vertical. If the EWI method is used to determine the location of the verticals, a constant sampling time for samples from all verticals must be used.

METHODS OF SAMPLE COLLECTION FOR SPECIFIC CONSTITUENTS

Bacteria, Total Organic Carbon, Suspended Organic Carbon, and Dissolved Organic Carbon

The necessity of utilizing aseptic techniques for the collection of bacteria samples; size of sample bottles provided by the Central Lab for total organic carbon (TOC), suspended organic carbon (SOC), and dissolved organic carbon (DOC); and the possibility of contamination from the USGS churn splitter preclude the use of depth-integrating water-sediment samplers for the collection of these samples. Consequently, bacteria samples are collected by depth-integrating a sterile narrow-mouth 1-L glass bottle at a single vertical near the centroid of flow or by immersing the sample bottle by hand (when the stream is shallow). TOC, SOC, and DOC samples may be collected by depth-integrating a narrow-mouth 1-L glass pesticide bottle at a single vertical near the centroid of flow or by immersing the sample bottle by hand (when the stream is shallow).

Pesticides

The possibility of contamination from the churn splitter precludes its use for compositing and splitting of samples for analysis of pesticides (herbicides and insecticides). The NWQL requires a 1-L sample for herbicides and a 1-L sample for insecticides. Both samples may be collected by depth integration using the weighted-bottle sampler at a single vertical near the centroid of flow or by immersing the sample bottle by hand (when the stream is shallow).

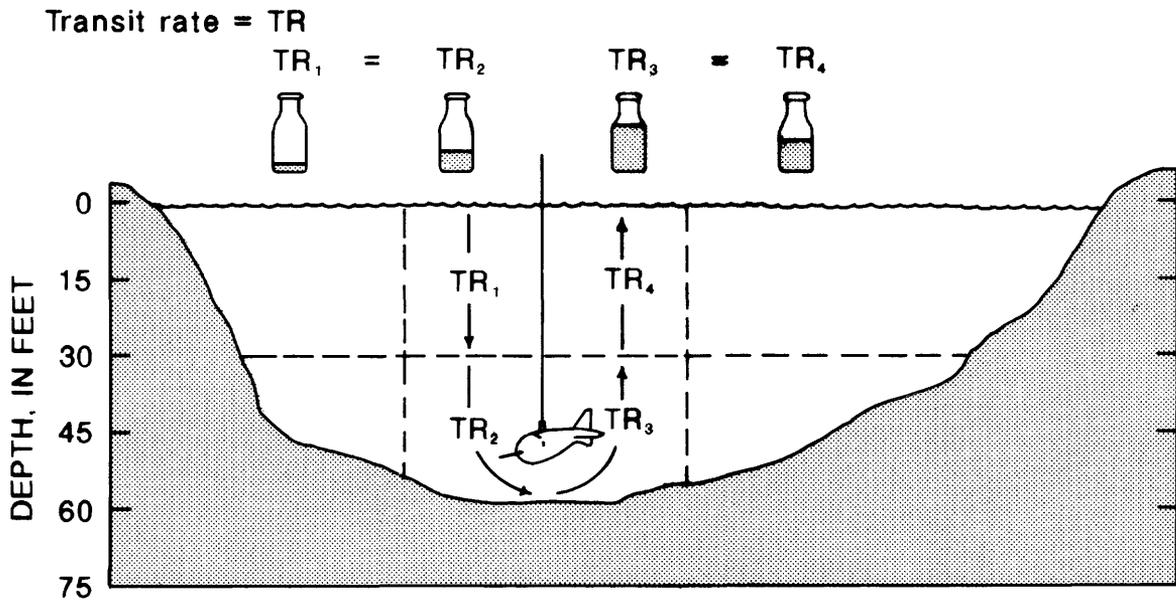


Figure 11.--Use of point-integrating sampler for depth integration of deep streams.

Other Constituents

The necessity of collecting a large number of samples from several sites within a minimum of time during rapidly changing stages may dictate that sampling time at each of these sites be held to a minimum. Under such conditions, samples may be collected using the Texas wire basket or weighted bottle sampler at a reduced number of verticals. The circumstances and number of verticals sampled should be documented in the field notes.

Surface and Dip Sampling

Circumstances are sometimes such that surface or dip sampling is necessary. These circumstances may include: (1) Stream velocity too fast for the sampler to integrate; (2) large floating and moving submerged debris; (3) depth-integrating sampler not available; and (4) very shallow depth.

At some locations, stream velocities are so great that even 100-lb samplers will not reach the bottom. Under such circumstances, all except the largest of sediment particles will usually be thoroughly mixed with the flow, and a surface or dip sample collected with either a depth-integrating or weighted-bottle sampler will be fairly representative (Guy and Norman, 1970, p. 41).

In very shallow water where a depth-integrating sampler cannot be submerged, a representative sample usually can be obtained by immersing a hand-held bottle in the centroid of flow with the mouth of the bottle directed toward the current. Care should be taken to avoid getting the mouth of the bottle too close to the streambed and thereby collecting particles directly from the bed. Because the quality of surface and dip samples is likely to be inferior to those obtained with depth-integrating samplers, they always should be identified appropriately on the field notes.

Bed-Material Sampling

Samples of bed material may be collected with the USBMH-60 or the USBM-54 sampler and placed in an appropriate wide-mouth glass bottle. A sample can be scooped directly into the wide-mouth bottle where depths are too shallow to use one of the bed-material samplers. Bottom material at the selected vertical should consist predominantly of sand, silt, and clay. Where possible, the vertical selected should be one of those sampled for water-sediment mixture.

To use the USBMH-60 or USBM-54:

1. Attach the sampler to the handline or cable and reel.
2. Suspend the entire weight of the sampler by the hanger rod.
3. Cock the bucket in the open position with the allen wrench.

CAUTION: AT NO TIME SHOULD THE HAND
OR FINGERS BE PLACED IN THE BUCKET
OPENING. ACCIDENTAL CLOSING OF THE
BUCKET MAY CAUSE PERMANENT INJURY!

4. Lower the sampler to the surface of the streambed. While lowering the sampler, avoid any jerking motions that would cause the cable to slacken and allow the bucket to close prematurely.
5. After the cocked sampler touches the streambed and tension is released on the line, the sampler should be lifted slowly from the bed so the bucket will scoop a sample.
6. To remove the sample from the bucket, the sampler is positioned above the sample container and the bucket is opened with the allen wrench.
7. Label the sample container.
8. Disassemble and clean the sampler as described in the section "Methods of Cleaning Samplers and Support Equipment."

COMPOSITING AND SPLITTING OF WATER-SEDIMENT SAMPLES

The USGS churn splitter is the best apparatus available for splitting large composite samples of water-sediment mixture into subsamples and is the only acceptable method of splitting samples containing sand-size material in the field (USGS Quality of Water Branch Technical Memorandum 77.01). Samples may be taken from the churn splitter for analysis of all dissolved and suspended inorganic constituents. However, samples for the analysis of suspended sediment, bacteria, and organic parameters should not be taken from the churn.

The laboratory may require many different subsamples for analysis. Appropriate samples collected by the equal-discharge-increment (EDI) method, equal-width-increment (EWI) method, or other methods are composited in either the 8-L churn splitter or the 14-L churn splitter and then split into representative subsamples.

A maximum of 10 L of subsamples of the water-sediment mixture may be withdrawn from the 14-L churn; whereas, 5 L may be withdrawn from the 8-L churn. The 4 L remaining in the 14-L churn and the 3 L remaining in the 8-L churn should not be used for water-sediment subsamples because they will not be representative. However, the water-sediment mixture remaining in either churn may be used for filtered subsamples for the determination of dissolved constituents.

The procedure for use of the churn splitter is as follows:

1. Clean churn as directed in the section, "Methods of Cleaning Samplers and Support Equipment."
2. Before starting to collect samples to be composited in the churn, label all the subsample containers to be used and determine the total sample volume to be composited. To this sample volume add at least 3 L for the 8-L churn splitter and 4 L for the 14-L churn splitter.
3. Thoroughly rinse the churn splitter with native water.
4. Collect representative samples of the streamflow by using one of the methods described previously. Use only one sample bottle when collecting the samples to be composited in order to minimize the amount of sediment lost in transferring from the bottle to the churn.
5. When the predetermined number of verticals in the cross section have been sampled and the required volume has been poured into the churn, place all water-sediment subsample containers within easy reach so that once started, the churning can be continuous.

6. Churn the sample at a uniform rate of about 9 in/s. The disc should touch the bottom of the tank on every stroke and the stroke length should be as long as possible without breaking the water surface. If the churning rate is significantly greater than 9 in/s or if the disc breaks the water surface, excessive air is introduced into the sample and may change the dissolved gases, alkalinity, pH, and other characteristics of the sample. On the other hand, inadequate stirring may result in nonrepresentative subsamples.
7. After churning the sample in the splitter for about 10 strokes to assure uniform dispersion of the suspended material, begin the withdrawal of subsamples. As subsamples are withdrawn and the volume of the sample in the churn decreases, maintain the churning rate of about 9 in/s. If a break in withdrawals is necessary, the stirring rate must be reestablished before withdrawals are continued.
8. After all the required water-sediment subsamples have been withdrawn, the sample remaining in the churn may be filtered for subsamples required for dissolved constituents. Separate subsamples may be withdrawn for the measurement of specific conductance and pH.
9. After all subsamples have been withdrawn, clean the mixing tank and churning disc thoroughly with deionized water. If water will not remove all the residue, clean as directed in section, "Methods of Cleaning Samplers and Support Equipment."

SAMPLE FILTRATION

SAMPLES FOR DISSOLVED INORGANIC CONSTITUENTS

Water-sediment samples collected for the dissolved major inorganic and minor elements should be filtered in the field. The equipment most commonly used in the Texas District for filtration consists of a reversible, variable-speed, battery-operated peristaltic pump that forces the water-sediment sample through flexible silicone or tygon tubing into a plate-type filter. The sediment is retained by a membrane filter while the filtrate passes through to a collecting vessel. Two types of filter plates are available--a 142-mm plate and a 100-mm plate. Two plastic screens for use with the 142-mm plate provide support for the membrane filter (above and below) and permit water flow in either direction without disruption of the membrane. Because of this support, when the membrane on the 142-mm plate becomes clogged with sediment during filtration, some of the sediment cake can be removed by backflushing. The support screens are not provided with the 100-mm plate; therefore, backflushing can not be practiced when this plate is used.

When water-sediment samples contain large quantities of very fine suspended sediment or organic material, the membrane filter on either the 100-mm or 142-mm plate may become clogged after passage of only a few milliliters of sample. The time required to filter these samples can be excessive. Under these circumstances, a pleated capsule filter that has a large effective filtration area, should be used instead of the plate-type filters. However, the pleated capsule filter should not be used routinely because of its greater cost and because it can not be used for more than one site.

Cleanliness is essential in the filtration process. The intent of filtration is to remove particulate matter from the water sample which could interfere with the chemical analysis of the dissolved constituents. If the

filtering environment is not kept clean, there is a good possibility of sample contamination. If care is taken to insure that all sampling, filtration, and support equipment, including the vehicle in which the equipment is transported to the field, are kept clean and in good working condition, these sources of possible contamination can be eliminated. When preparing the filtration equipment for use, care should be taken not to introduce contamination by touching any of the components which will come in direct contact with the water sample. For example, when placing the support screens on the filter plates, grasp the screen on the extreme outer edge using clean stainless steel forceps. When inserting the pump intake tube into the sample to be filtered do not handle the tube near the end that will be inserted in the sample.

Filtration Using the 142-mm Backflushing Filter and the 100-mm Nonbackflushing Filter

1. Place one of the filter support screens on the bottom filter plate. The 100-mm nonbackflushing filter has a porous support disk instead of support screens. (The rough side of the support disk should be down toward the recess in the filter plate.)
2. With a pair of clean stainless steel forceps, place a new 0.45- μ m porosity filter on top of the bottom support screen. Place the second filter support screen on top of the filter. Align the top and bottom filter plates and tighten the plastic nuts or wing nuts firmly by hand.
Caution: Tightening the plates too tightly creates warping and leakage.
3. Place the intake tube into a container of deionized water, set the pump speed control to the midrange, turn the pump on in the forward direction, and flush the new filter with at least 100 mL of deionized water.
4. Remove the intake hose from the deionized water and run the pump until the deionized water has been expelled from the pump tube. Steps 3 and 4 should be repeated each time a new filter is placed in the filter plate.
5. Place the intake tube into the sample to be filtered, turn the pump on and begin filtering. Discard approximately 100 mL of the sample.
6. Continue the filtration process and collect the filtrate in the appropriately labeled sample bottle(s). If clogging reduces the output to an unacceptable flow rate:
 - A. Stop the pump, turn the speed control to near maximum, and turn the pump on in the reverse position until backflushing removes most of the sediment cake from the membrane filter.
 - B. Stop the pump and return the speed control to the midrange position.
 - C. Turn the pump on in the forward position and recommence filtering until the filter is clogged again or until the required volumes of subsamples have been filtered. Step 6.A-C cannot be performed on the 100-mm non-backflushing filter.
7. Immediately after each use, disassemble and clean the filter unit.
 - A. Disassemble the top and bottom filter plates. Turn the pump on in the forward position until all native water is flushed from the pumping system.
 - B. Clean the filter plates and support screens with a small amount of non-phosphate detergent solution (an Alconox solution can be mixed in a spray bottle for this purpose) then rinse with deionized water. If minor elements are being collected, flush the filter plate and tubing with a 5-percent HCl solution, then rinse several times with small amounts of deionized water.

- C. Place the pump intake tube into a container of deionized water and turn the pump on in the forward position. Flush the pump tubing with about 100 mL of deionized water.
 - D. Reassemble the filter unit and place the end of the pump intake tube into a clean whirl-pack.
- NOTE: Always reassemble the filter plate so that the support screens will be in the same position used during the initial filtration.
- 8. At the end of each field trip, remove the filter unit and tubing from the field vehicle. Take it to the field service unit for cleaning and storage until the next field trip.

Filtration Using the Pleated Capsule Filter

1. Remove the capsule filter from the protective bag.
2. Attach the discharge tube from the peristaltic pump to the inlet (male barbed) connection of the capsule so that the flow direction is the same as the indicated flow arrows on the filter. A small hose clamp may be used to secure the discharge hose to the inlet connection.
3. Place the intake tube in a container of deionized water. Flush the new filter with about 100 mL of deionized water.
4. Remove the intake hose from the deionized water and run the pump in a forward direction until all deionized water has been expelled from the filtering system.
5. Place the intake tube into the sample to be filtered, turn the pump on in the forward position with the speed control near midrange and begin filtering. Discard the first 100 mL of the filtrate.
6. Continue the filtration process until clogging reduces the output to an unacceptable flow rate.
7. Stop the pump and turn the pump on briefly in the reverse position until backflushing removes most of the sediment cake from the membrane. Do not use the backflushing option more than once during the filtering operation!
8. Stop the pump and return speed control to midrange position.
9. Turn the pump on in the forward position and recommence filtering until the required volumes of subsamples have been filtered.
10. Disconnect and discard the capsule.

SAMPLES FOR SUSPENDED AND DISSOLVED ORGANIC CARBON

A special filtration unit consisting of a small pressure cylinder of zero-grade (carbon-free) nitrogen gas, a pressure regulator, and a stainless steel filter assembly fitted with flexible silicone or tygon tubing and a 0.45- μ m porosity silver (Ag) membrane filter should be used for filtering dissolved organic carbon (DOC) and suspended organic carbon (SOC) samples. (Do not use plastic membrane filters!)

Samples for DOC and SOC should be collected and filtered into 100-mL organically clean glass bottles supplied by the National Water-Quality Laboratory (NWQL). Do not use subsamples composited in the USGS churn splitter!

The following guidelines should be used for filtration.

Suspended Organic Carbon

1. Remove the filter assembly from the plastic storage bag and disassemble.
2. With a pair of stainless steel forceps, place the Ag membrane filter on the assembly base between the support screen and teflon seal ring.
3. Screw the base on the funnel barrel.
4. Pour about 50 mL of deionized water into the funnel barrel, screw on the top portion of the filter assembly barrel, and attach to the pressure tank.
5. Turn the handle on the pressure regulator counter clockwise for several turns until the pressure regulator valve is closed. Open the valve to the nitrogen cylinder. Open the valve to the pressure regulator by turning the handle clockwise until 12 to 15 lb of pressure are registered on the gage. (Each unit should be equipped with a pop-off valve set to 20-lb pressure.)
6. Filter and discard the filtrate from the deionized water rinse.
7. Close the valve to the nitrogen cylinder. After the pressure gage shows no pressure, close the valve to the pressure regulator.
8. Remove the top cap of the filter assembly. Shake the sample for SOC vigorously to resuspend the settled particles and immediately transfer (by clean pipet or graduated cylinder) the required volume of sample to the filter funnel barrel. Repeat Step 5 and filter the required volume of sample.

The volume of water to be filtered for SOC analysis depends upon the concentration of suspended sediment in the water-sediment sample. The following volumes are recommended:

<u>Approximate suspended-sediment concentration (mg/L)</u>	<u>Volume of water-sediment sample to be filtered (mL)</u>
0 - 500	50
500 - 1,000	25
>1,000	10

For most waters in Texas, 25 to 50 mL of water-sediment sample should be filtered.

9. After completing the filtration, depressurize the filtration apparatus (Step 7) and disassemble. With stainless steel forceps, remove the Ag membrane, fold the membrane in half with the filter cake on the inside, and place the folded filter in a petri dish.
10. Place a gummed label on the outside of the petri dish cover, identify the sample, record the volume filtered, and insert the petri dish in a whirl-pack bag. Immediately chill the sample in the petri dish on crushed ice in an ice chest.
11. Continue with the filtration for DOC.

Dissolved Organic Carbon

1. With a pair of stainless steel forceps, place a new Ag filter on filter base between the support screen and the teflon seal ring.
2. Screw the base on the funnel barrel.

3. If a sample for SOC has been filtered, no additional rinsing of the filter assembly is required. If a sample for SOC has not been filtered, rinse assembly with deionized water as described in Step 4 of the procedure for SOC.
4. Transfer about 100 mL of the water-sediment sample to the filter funnel barrel, screw on the top part of the filter assembly barrel, and attach to the pressure tank. Place the discharge tube into the receiving vessel.
5. Pressurize the filtration apparatus as described in Step 5 of the procedure for SOC. (Discard the first 10 to 15 mL of filtrate if a SOC sample has not been filtered.)
6. Continue the filtration process until 100 mL of sample is filtered and collect the filtrate in the appropriately labeled 100-mL DOC bottle. Place the sample bottle on crushed ice.
7. After completing the filtration, depressurize the filtration apparatus and disassemble.
8. Rinse the filter assembly several times with small amounts of deionized water and store in a clean plastic bag.

SAMPLE PRESERVATION

The need for preservation of some of the samples collected by the Texas District is discussed briefly in other sections of this manual. The types, volumes (or weights), and methods of sample preservation for most of the laboratory schedules used by the Texas District are shown in table 2. If additional information concerning the types, volumes, and preservation of samples is required, personnel should refer to the latest NWQL "Services Catalog" or contact the Subdistrict water-quality specialist or the District Water-Quality Unit.

REAGENTS FOR FIELD DETERMINATIONS

Preparation of some of the reagents for field determinations are outlined in various sections in this manual. These and other reagents utilized for field determinations and methods of preparation are listed in the following tabulations.

When the chemicals to be used for the preparation of these reagents are received they need to be dated and stored in dust-free cabinets or desiccators, or refrigerated as appropriate. When the reagents are prepared, label with the date they were prepared and the initial(s) of the analyst(s).

These reagents can be prepared by District water-quality personnel, or prepared in field service units in Subdistrict offices, provided appropriate equipment is available in the field service units.

Specific Conductance

Potassium chloride solution, 0.00702N = 1,000 μ S/cm (microsiemens per centimeter)--Dissolve 0.5232 g KCl, dried at 180 °C for 1 hour, in deionized water and dilute to 1,000 mL.

Table 2.--Types, volumes (or weights), and methods of preservation of samples for analysis

[mL, milliliter; RC, raw chilled; HgCl₂, mercuric chloride; FC, filtered chilled; pt, pint; FU, filtered untreated; L, liter; FAA, filtered acidified acid rinsed; HNO₃, nitric acid; FAM, filtered acidified mercury; K₂Cr₂O₄, potassium dichromate; RUT, raw untreated turbidity; RCB, raw chilled color; RU, raw untreated; g, gram; CU, carton untreated; FA, filtered acidified; RA, raw acidified; RAH, raw acidified hydride; ICP, inductively coupled plasma; BGC, baked glass chilled; GCC, baked glass chilled water; GCI, baked glass chilled insecticide; GCV, glass chilled vial; CHY, chlorophyll; RUR, raw untreated radiochemical]

Schedule number	General type	Bottle requirements	Treatment and/or preservative
0009	Nutrients	250 mL RC	Raw chilled + HgCl ₂ ampule
0059	Lake Houston nutrients	250 mL FC 250 mL RC	Filtered chilled + HgCl ₂ ampule Raw chilled + HgCl ₂ ampule
0086	NASQAN nutrients	250 mL FC 250 mL RC	Filtered chilled + HgCl ₂ ampule Raw chilled + HgCl ₂ ampule
0176	Inorganics and minor elements, low specific	1 pt FU 1 L FAA 250 mL glass FAM 125 mL RUT	Filtered untreated Filtered acidified (4 mL HNO ₃) Filtered acidified (HNO ₃ /K ₂ Cr ₂ O ₄) Raw untreated
0177	Inorganics and minor elements, high specific conductance	1 pt FU 1 L FAA 250 mL glass FAM 125 mL RUT	Filtered untreated Filtered acidified (4 mL HNO ₃) Filtered acidified (HNO ₃ /K ₂ Cr ₂ O ₄) Raw untreated
0329	Physical properties	125 mL RCB 500 mL RU	Raw chilled Raw untreated
LC0114	Total organic carbon	100 mL glass	Raw chilled
0555	Minor elements, bed	100 g CU	Untreated
0583	Dissolved minor elements, lake	500 mL FA	Filtered acidified (2 mL HNO ₃)
0585	Total minor elements, lake	500 mL RA 250 mL RAH	Raw acidified (2 mL HNO ₃)
0586	Anions, minor elements, and potassium	250 mL FA 250 mL FU 250 mL FAM	Filtered acidified (1 mL HNO ₃) Filtered untreated Filtered acidified (HNO ₃ /K ₂ Cr ₂ O ₄)
1003	Major inorganic cations	250 mL FA	Filtered acidified (1 mL HNO ₃)
1005	Major inorganic cations+Mn+Fe	250 mL FA	Filtered acidified (1 mL HNO ₃)
1009	Major inorganic anions	50 mL FU	Filtered untreated
1022	Major dissolved inorganic	250 mL FU 250 mL FA	Filtered untreated Filtered acidified (1 mL HNO ₃)
1043	ICP analysis	100 mL RU 250 mL FA	Raw untreated Filtered acidified (1 mL HNO ₃)
1044	Iron + manganese	250 mL FA	Filtered acidified (1 mL HNO ₃)
1074	District minor elements	500 mL FA 200 mL glass FAM	Filtered acidified (2 mL HNO ₃) Filtered acidified (HNO ₃ /K ₂ Cr ₂ O ₄)
1134	District nutrients total	250 mL RC	Raw chilled + HgCl ₂ ampule
1135	District nutrients + ortho-P	250 mL RC	Raw chilled + HgCl ₂ ampule
1305	Chlorophenoxy acid herbicides, bed material	200 g BGC	Chilled

Table 2.--Types, volumes (or weights), and methods of preservation of samples for analysis--Continued

Schedule number	General type	Bottle requirements	Treatment and/or preservative
1324	Organochlorine insecticide	800 mL GCC	Raw chilled
1325	Organochlorine insecticides, bed	200 g BGC	Chilled
1335	Pesticide organochlorine - phosphorus bed	200 g BGC	Chilled
1359	Insecticide carbamate (total recoverable)	800 mL GCI	Raw chilled
1389	Herbicide-triazine (total recoverable)	800 mL GCI	Raw chilled
1390, 1391	Volatile organics	40 mL GCV (triplicate)	Raw chilled
1474	Pesticide organochlorine - phosphorus - phenoxy (total recoverable)	1,600 mL GCC	Raw chilled
1508	Chlorophyll	1-CHY	Chilled, collect on glass filter (volume)
1703	Radiochemical	4 L RUR	Raw untreated radiochemical
1706	Phytoplankton	1 L	Raw + 40 mL formalin solution
1904	NASQAN inorganic	250 mL FA 500 mL FU 250 mL RUT	Filtered acidified (1 mL HNO ₃) Filtered untreated Raw untreated

Alkalinity

Sodium carbonate standard solution, 1.00 mL = 1.00 mg HCO₃--Dry 1.0 g primary standard Na₂CO₃ at 150 to 160 °C for 2 hours. Cool in a desiccator and dissolve exactly 0.8686 g in a carbon dioxide free deionized water. Dilute to 1 L.

Sulfuric acid standard solution 0.01639N--Add 0.5 mL concentrated H₂SO₄ (specific gravity 1.84) to 950 mL deionized water. After the solution has been thoroughly mixed, standardize it by titrating 25.0 mL Na₂CO₃ to pH 4.5. Adjust the concentration of the sulfuric acid to exactly 0.01639 N by dilution with deionized water or by addition of dilute acid as indicated by the first titration. Confirm the exact normality by restandardization. Although the sulfuric acid solution is reasonably stable, its normality needs to be verified at least monthly or prior to each field trip.

Carbon dioxide free deionized water--Prepare fresh as needed by boiling deionized water for 15 minutes and cooling to room temperature. Cover the beaker in which the water has been boiled with a slightly oversized inverted beaker or other suitable cover to minimize entry of carbon dioxide from the atmosphere during the cooling process.

Dissolved Oxygen

Sodium sulfite solution--Dissolve 4 g of sodium sulfite (Na_2SO_3) and a few crystals (about 1 mg) of cobalt chloride (CoCl_2) in 1 L of deionized water. Note--This solution is intended to be free of any oxygen. During storage of this solution, it is possible for oxygen to enter the solution. This solution should be relatively fresh for testing for an oxygen free solution.

FIELD MEASUREMENTS

INSTRUMENT SELECTION AND MAINTENANCE

Before departing on the field trip, personnel should check the operation and calibration of all field instruments to insure that they are in good working order. All instruments with temperature compensators should be checked for at least three temperature ranges. If the temperature compensator is not working properly, the instrument will not function according to specifications, and it should be returned to the District instrumentation unit for repair. If field meters will not calibrate against standard solutions with known values or if readings are sluggish or erratic, try to determine whether the problem is with the probe or the meter. If a spare probe is available, switch probes. If the switch solves the problem, inspect the defective probe and try to determine the problem. Try remedial procedures suggested by the manufacturer, the District instrumentation unit, or the District Water-Quality Unit.

If the problem is with the instrument rather than the probe, return the instrument with a documentation of the problem to the District instrumentation unit. Even if no problem is encountered, each instrument should be returned to the District instrumentation unit at 6- to 12-month intervals for changing batteries, calibration of electronics, cleaning, and other preventive maintenance.

Extreme care should be taken with water-quality field instruments and probes. These are sensitive electronic devices which are capable of making accurate and precise measurements if properly maintained.

Extreme care should also be used when calibrating the instruments. All field instruments should be calibrated in the field service unit prior to departing for the field. Calibration should be done at every sampling location for each instrument immediately prior to the appropriate field measurement. Again, it must be emphasized that these are sensitive electronic instruments, and transportation between sites may easily alter a previous calibration.

The standards used to calibrate field instruments should be at approximately the same temperature as the water to be measured. This may be done by immersing standards in the stream or by obtaining a bucket of water from the stream and placing the standards in the bucket.

Instruments must be given ample time to "warm up" before they can be calibrated. It is good practice to turn conductivity and dissolved oxygen instruments on at the beginning of the day and to leave them on. pH meters

should be placed on "standby" or left on with the probe(s) connected to the meter and the tip of the probe(s) immersed in a 50 mL solution of pH 4 buffer and four or five drops of saturated potassium chloride.

Ample time should be given for the probe sensors to reach the temperature of the solution to be measured. Generally this should only take a few minutes, but do not simply put the probes in the water and expect an accurate reading.

If analog instruments (those with needles) are calibrated in an upright position, then the field measurements should be made in an upright position. Do not calibrate in an upright position and then take field readings with the instrument on its back and vice versa.

Remember, the data collected in the field is to be published by the USGS and also may be used in legal proceedings. With the increased awareness of a clean environment, USGS data are being used by the Texas Water Commission, the Texas Water Development Board, and the U.S. Environmental Protection Agency, numerous river authorities in the State, and by private environmental groups. Adequate time and care in calibration of field instruments is necessary to obtain accurate and precise data. The data must be reported accurately and to the proper number of significant figures. A list of significant figures for reporting frequently collected water-quality field data is presented in table 3.

PROCEDURES FOR INDIVIDUAL PROPERTIES OR CONSTITUENTS

Temperature

Accurate water-temperature data are essential to document thermal alterations to the environment caused by natural phenomena and by activities of man. This section provides guidelines for recommended procedures for the measurement of stream temperatures. For a thorough discussion concerning influential factors, selection of equipment and measuring sites, and suggested procedures for collecting and reporting water-temperature data, personnel are referred to USGS Techniques of Water-Resources Investigations, Book 1, Chapter D1, "Water Temperature--Influential Factors, Field Measurements, and Data Presentation."

The thermometer is the most widely used device for temperature measurements. It consists of a thin-walled glass bulb joined to a glass capillary stem closed at the opposite end. The bulb and part of the stem are filled with an expansive fluid, either mercury or alcohol. The fluid in the bulb expands or contracts in volume as its temperature rises or falls. The volume change is transmitted to the capillary tube, causing a change in the liquid column length. Graduations on the stem denote change in column length as a function of temperature.

A thermistor is an electrical device made of a solid semiconductor with a large temperature coefficient of resistivity, which would exhibit a linear voltage characteristic if its temperature were held constant. It changes electrical resistance markedly with temperature change; the relation is usually exponential. An electrical signal processor converts the resistance changes to a readout calibrated in temperature units. Resistance-type thermistors are incorporated in several of the combination field instruments

Table 3.--Significant figures for common field constituents

Parameter code and constituent	0 to <.1	0.1 to <1	1 to <10	10 to <100	100 to <1,000	1,000 to <10,000	10,000 to <100,000	>100,000
00010 Temperature	--	0.5	X.5	XX.5	XXX	XXX0	XXX00	XXX000
00095 Specific conductance	--	--	X	XX	XXX	XXX0	XXX00	XXX000
00400 pH	--	.X	X.X	XX.X	XXX	XXX0	XXX00	XXX000
00300 Dissolved oxygen	--	.X	X.X	XX.X	XXX	XXX0	XXX00	XXX000
39036 Dissolved alkalinity as CaCO ₃ to pH 4.5	--	--	X	XX	XXX	XXX0	XXX00	XXX000
00452 Dissolved carbonate	--	--	X	XX	XXX	XXX0	XXX00	XXX000
00453 Dissolved bicarbonate	--	--	X	XX	XXX	XXX0	XXX00	XXX000
39086 Dissolved alkalinity, field incremental titration, as CaCO ₃	--	--	X	XX	XXX	XXX0	XXX00	XXX000
31625 Fecal coliforms	--	--	X	XX	XX0	XX00	XX000	XX0000
31673 Fecal streptococci	--	--	X	XX	XX0	XX00	XX000	XX0000
00025 Barometric pressure	--	--	X	XX	XXX	XXX0	XXX00	XXX000
00310 Biochemical oxygen demand	--	.X	X.X	XX	XX0	XX00	XX000	XX0000
80082 Carbonaceous bio- chemical oxygen demand	--	.X	X.X	XX	XX0	XX00	XX000	XX0000
00061 Instantaneous discharge	0.0X	.X	X.X	XX	XXX	XXX0	XXX00	XXX000

utilized by the Texas District. These include YSI dissolved oxygen meter, Beckman pH meter, and Hydrolab multiparameter instruments. Use of thermistors is encouraged, rather than hand thermometers, provided they can be calibrated. Both hand thermometers and thermistors must be capable of measuring temperatures ranging from -5 to 45 °C and accurate within 0.5 °C.

Calibration

1. Immerse field thermometer and ASTM standard or good grade laboratory thermometer in a water bath with a temperature at approximately 0 °C.
2. Position both thermometers so that the scales can be read. Stir the water bath and hold the thermometers in the water until the liquid columns in the thermometers stabilize (no less than 60 seconds).
3. Without removing the thermometers from the water, read both thermometers to the nearest 0.5 °C.
4. Repeat steps 1-3 in a water bath with a temperature of approximately 40 °C.
5. If the readings of the thermometers do not agree within 0.5 °C, the field thermometers should be replaced. Those found acceptable should be marked for field use.

Thermistor temperature recorders can be calibrated in the same manner described above. In addition to the high and low temperature calibration checks, an intermediate standard of approximately 20 °C should be checked. If the temperature readings are not within acceptable limits consult the District instrumentation unit.

Field Measurements

1. Select a vertical in the stream near the centroid of flow.
2. If the temperature is to be measured in situ in a shallow stream, wade to the site where the temperature is to be measured. Stand so that a shadow is cast upon the site for temperature measurement.
3. Immerse the thermometer or temperature probe in the water and hold it in the water until the liquid column in the thermometer or the meter reading stabilizes (no less than 60 seconds).
4. Without removing the thermometer or temperature probe from the water, read the thermometer to the nearest 0.5 °C, and record the reading on the field notes.

Trouble-Shooting Guide

<u>Symptom</u>	<u>Possible problems and solutions</u>
Thermometer does not read accurately	1. Check the thermometer to see that the mercury has not separated.
Thermistor does not read accurately	1. Dirty probe--remove dirt and oily film. 2. Weak batteries--replace with new batteries.

- Erratic meter readings
1. Break in the cables--replace cables.
 2. Bad connection at meter or probe--tighten connections.
- Meter slow to stabilize
1. Dirty probe--clean probe to remove dirt and oily film.

Specific Conductance

Specific conductance is a measure of the ability of a water to carry an electrical current. Specific conductance is defined as the reciprocal or opposite of the resistance in ohms of a 1 cm cube of water at a specified temperature. The units of specific conductance are the reciprocal of ohm/cm or mho/cm, and 1 millionth of this is the $\mu\text{mho/cm}$ that had traditionally been used to report specific conductance. In 1984 the USGS began reporting specific conductance in $\mu\text{S/cm}$ (WRD Memo 85.28).

The conductivity cell, which houses the electrodes that measure the resistance of the water, is simple in basic structure and consists of two metal plates or electrodes firmly spaced within a chamber that serves to isolate a portion of the sample to be measured. When an electrical current is placed at the two electrodes, the water acts as a resistance to the flow of the current, and this resistance is measured and converted into $\mu\text{S/cm}$. Generally, the more ions present in the water, the lower the resistance between the electrodes and thus larger specific conductance values are obtained for more mineralized water.

Because solution conductivity varies with the temperature as well as with the concentration of ions, it is desirable to relate conductivity measurements to a reference temperature. In the USGS, this reference temperature is 25 °C. A practical means of providing temperature compensation is to introduce into the circuit a resistive element which will change with temperature at the same rate as the solution being tested. The temperature compensation may require manual adjustment on some of the older instruments, or it may adjust automatically as is done with more recently manufactured equipment. In either case, the temperature compensator should be checked prior to each field trip to insure that it is working properly.

The accuracy and reproducibility of field conductivity meters usually are within about 5 percent of values measured under laboratory conditions. Occasionally, errors in field measurements are larger for a number of reasons, and it is good practice for field personnel to collect an unfiltered check sample to be run in the laboratory or field service unit. If field and laboratory values of specific conductance differ by less than 5 percent, field service units will report the field values. If the field and laboratory values differ by more than 5 percent, field service units should check the sample for the possibility of precipitation. If a precipitate is found in the check sample, the field value should be reported. If no precipitate is found, field personnel should confer with the Subdistrict water-quality specialist to determine the best value to report and to try to determine the discrepancy between the field and laboratory values.

Calibration

Prior to every water-quality field trip and immediately before field measurements, conductance meters must be calibrated using at least two standards.

1. For lab calibration checks, check the calibration for each scale that will be used during field measurements.
 - A. Calibrate the meter using the standard for greatest conductance available for the selected scale.
 - B. Measure the conductance of a midrange standard (about one-half the value of the standard for greatest conductance) that will depict the linearity of the selected scale.
If after calibration the observed reading of a midrange standard differs from the standard value by ± 5 percent, take appropriate steps to remedy the problem or replace the meter/probe.
2. For field calibrations where the meter scale cannot be determined prior to calibration, collect a sample and measure the conductance to identify the meter scale. Calibrate the meter using two FRESH standards that will bracket the expected field reading.
 - A. Calibrate the meter using a standard with a value that is greater than the expected field conductance reading.
 - B. Measure the conductance of a standard with a value that is less than the expected field conductance reading.
 - C. Record the calibration results on the field sheet (TX-72Q).
If after calibration the observed reading of the lesser standard differs from the standard value by ± 5 percent, take appropriate steps to remedy the problem or prepare calibration curves to correct the observed reading.
3. Refer to the manufacturer's instructions for meter operation, proper probe usage, and any precalibration instrument adjustments.
4. For field calibrations, adjust the temperature of the conductance standards to the temperature of the sample by immersing the standards in the stream or in a large water bath filled with water from the stream.
5. Turn the meter on and allow sufficient time for the electronic components to stabilize (5 to 10 minutes).
6. Flush the probe and probe chamber(s) with a small amount of deionized water, then flush with a small amount of the appropriate standard.
7. Place the conductance probe in the standard. Allow sufficient time for the temperature of the probe to equilibrate to the temperature of the standard solution (5 to 10 minutes or until the meter reading stabilizes).
8. Vigorously thrust the probe up and down under the water surface to expel air trapped in the cell.
9. Support the probe at a distance of 2 to 3 in. from insulating or conducting bodies (sides and bottom of the standard container).
10. Note the meter reading then thrust the probe up and down under the water surface and read the meter again. Repeat this procedure until consecutive readings are the same.
11. Repeat steps 6 through 10 until calibration instructions in steps 1 or 2 are satisfied.

Field Measurements

Prior to field measurements, conductance meters must be calibrated (see section on conductance calibration).

1. Refer to the manufacturer's instructions for meter operation and proper probe usage.
2. If the conductance is not measured in situ, flush the probe and probe chamber(s) with a small amount of sample water.
3. Place the conductance probe in the water sample. Allow sufficient time for the temperature of the probe to equilibrate to the temperature of the water sample (5 to 10 minutes).
4. Select the scale that will produce the highest on-scale meter reading.
5. Vigorously thrust the probe up and down under the water surface to expel air trapped in the cell.
6. Support the probe at a distance of 2 to 3 in. from insulating or conducting bodies (sides and bottom of sample container).
7. Note the meter reading, then thrust the probe up and down under the water surface and read the meter again. Repeat this procedure until consecutive readings are the same.
8. Record the conductance reading on the field sheet (TX-72Q).
9. Flush the probe and probe chamber(s) with deionized water.

Trouble-Shooting Guide

<u>Symptom</u>	<u>Possible problems and solutions</u>
Will not calibrate to standards	<ol style="list-style-type: none">1. Standards may be old or contaminated --use fresh standards.2. Electrodes dirty--clean with a soap solution, then 5-percent HCl.3. Air trapped in cell--vigorously thrust probe up and down to expel trapped air.4. Weak batteries--replace.
Erratic meter readings	<ol style="list-style-type: none">1. Loose or defective connections--tighten or replace.2. Broken cables--repair or replace.3. Air trapped in cell--expel air.
Meter requires frequent calibration changes	<ol style="list-style-type: none">1. Temperature compensator not working--measure the conductance of a solution. Place the solution in a hot pot of water and raise the solution temperature about 20 °C. Measure the conductance again allowing sufficient time for the probe to equilibrate to the temperature of the solution. If the two values differ by 10 percent or more, the compensator probably is bad. Replace the conductance probe.

pH

pH is without a doubt the most sensitive measurement determined in the field. pH is defined as the negative logarithm (base 10) of the hydrogen ion concentration in the water. For example, pure water has a pH that is equivalent to a hydrogen concentration of 0.0000001 M (molar) or 1×10^{-7} M. Since the atomic weight of hydrogen is 1, this represents 0.0000001 g of hydrogen per liter of water, or 0.1 μg of hydrogen ions per liter of water. It is helpful to remember that a 1-unit change in pH represents a tenfold change in the hydrogen ion concentration. Thus a solution with a pH of 6.0 contains 10 times as many hydrogen ions as a pH 7.0 solution.

How are such small concentrations of hydrogen ions measured? Certain electrodes, when immersed in a solution, develop voltages which are dependent upon the pH of the solution. Thus properly designed voltmeters become direct-reading pH meters. The glass bulb electrode is the key to making a pH measurement. The special composition glass used is very selective and sensitive to hydrogen ions. The potential which is developed at the glass membrane can be related to the pH of the solution. In order to complete the circuit and provide a stable and reproducible referencing potential, another electrode is required. This electrode is known appropriately as a "reference electrode." The reference electrode makes contact with the solution through a "junction" which allows for a slow leakage of the filling solution inside the reference electrode. When the glass (pH) electrode and reference electrode are paired, or built together as in a combination electrode, and connected to a pH meter, the voltage developed at the electrode pair is amplified and displayed on the pH meter.

Temperature has two effects on the measurement of pH (table 4). It can affect the electrode potential, and it can change the hydrogen ion activity within a sample. The electrode potential problem can be solved if the electrodes are allowed to come to the same temperature as the solution, and the meter is compensated for temperature. The meter may be compensated manually by using a temperature adjustment control, or on some of the newer meters, the temperature is automatically compensated.

Temperature also affects the pH of the sample as well as the buffers used to calibrate the pH meter. As the temperature of the buffer changes, the pH of the buffer also changes (table 4). This is especially true for pH 10 buffers. pH 10 buffers change more per unit change in temperature than do pH 4 buffers. In the calibration of pH meters, the temperature of the buffer solution must be known before any calibration adjustments are made.

Extreme care should be taken with the pH probes. The glass bulb should be protected at all times. It is very sensitive, and any oily film or scratches on the glass bulb will interfere with the pH measurement. The reference electrode and the combination electrode should also be checked to insure that ample filling solution is present. Filling solutions vary, and if it becomes necessary to add filling solution to the electrode, always check to determine which type filling solution is required for that particular electrode.

Proper storage of electrodes is important for accurate response when making pH measurements. Proper storage varies for various types of

Table 4.--Effects of temperature on pH buffer solutions

[°C, degrees Celsius]

Temperature (°C)	pH (units)	Temperature (°C)	pH (units)	Temperature (°C)	pH (units)
Beckman phthalate pH 4 buffer (color code--red)					
0	4.00	30	4.02	70	4.13
10	4.00	40	4.04	80	4.16
20	4.00	50	4.06	90	4.21
25	4.01	60	4.09	95	4.23
Beckman phosphate pH 7 buffer (color code--yellow)					
0	7.10	30	6.99	70	6.99
10	7.06	40	6.98	80	7.00
20	7.02	50	6.97	90	7.02
25	7.00	60	6.98	95	7.03
Beckman carbonate pH 10 buffer (color code--blue)					
0	10.32	20	10.06	40	9.90
5	10.25	25	10.01	45	9.86
10	10.18	30	9.97	50	9.83
15	10.12	35	9.93		

A copy of this tabulation for the appropriate buffer should be attached to the bottle containing that buffer and should be used for standardization of field instruments.

electrodes. Perhaps the best overall storage solution, especially for combination electrodes, is a 50-mL solution of pH 4 buffer and about 4 to 5 drops of saturated potassium chloride.

In aqueous solutions, pH is controlled primarily by the hydrolysis of salts of strong bases and weak acids or of weak bases and strong acids. Dissolved gases such as carbon dioxide, hydrogen sulfide, and ammonia also affect the pH measurement. Degasification, such as loss of carbon dioxide, precipitation, and other chemical and physical reactions, may cause the pH of a water sample to change substantially within several hours or even minutes after the sample is collected. Immediate analysis of pH of a sample is required for dependable results. Consequently, laboratory values of pH should not be reported or stored in the water-quality data base.

Probe Preparation

A large percentage of all the problems encountered during pH calibration and measurement can be attributed directly to the pH probe. Even new probes are susceptible to some of these problems and may need reconditioning before they can be used. If you are unsure of a probe's condition or are having problems during calibration, it is best to recondition the probe before starting on a field trip. The following are some general guidelines for pH probe preparation and reconditioning.

1. Inspect the probe and probe cable for physical damage.
 - A. Scratched or broken bulb.
 - B. Cut or broken cable.
 - C. Bent or broken connector.
2. Replace the probe filling solution.
 - A. Remove the old filling solution from the probe.
 1. Place the needle of a 1- or 3-mL syringe into the probe filling hole.
 2. Tilt the pH probe until the filling solution is near the filling hole and the needle tip is covered with the filling solution.
 3. Pull back on the syringe plunger until the syringe is full.
 4. Discharge the syringe and repeat steps 2.A.1-4 until all filling solution has been removed from the pH probe chamber.
 - B. Flush the pH probe chamber with deionized water.
 1. Use the syringe to partially fill the pH probe chamber with deionized water.
 2. Use the syringe to remove the deionized water from the pH probe chamber.
 3. As a result of changes in pressure, temperature, and evaporation, crystals may form in the pH probe chamber. Repeat steps 2.B.1-2 until all crystals have been dissolved and removed from the pH probe chamber.
 - C. Fill the probe chamber with new filling solution.
 1. Flush the probe chamber with fresh filling solution.
 - a. Use the syringe to partially fill the pH probe chamber with filling solution.
 - b. Tilt the pH probe so the filling solution will contact all internal probe surfaces.
 - c. Use the syringe to remove the filling solution and discard.

2. Use the syringe to fill the probe chamber with fresh filling solution. Add until the filling solution level is just below the filling hole. Filling solutions for different brands of pH probes are not interchangeable. Refer to the manufacturer's instructions for the recommended filling solution.

Calibration

Prior to every water-quality field trip and immediately before field measurements, pH meters must be calibrated using at least two buffers.

1. Refer to the manufacturer's instructions for meter operation, proper probe usage, and any precalibration instrument adjustments.
2. Adjust temperature of buffer solutions to temperature of sample by immersing buffers in stream or in a large water bath filled with water from the stream.
3. If the probe has a filling hole, slide the sleeve up or down to uncover the filling hole.
4. Rinse the probe with deionized water, then rinse with the appropriate pH buffer (always start calibration with the pH 7 buffer).
5. Immerse the probe tip (about 1 in.) in the buffer solution. Allow sufficient time for the temperature of the probe to equilibrate to the temperature of the standard solution.
6. Measure the temperature of the buffer solution and adjust temperature compensator to the corresponding temperature. If using an automatic temperature-compensated pH meter, immerse the temperature probe with the pH probe in the buffer solution.
7. From table 4, p. 46, showing the effects of temperature on pH buffers, determine the theoretical pH of the buffer.
8. Adjust the meter readout to the theoretical pH value determined in step 7 using the standardize knob. If the meter is automatically calibrated, the meter reading should agree with the theoretical pH value.
9. Repeat steps 4 to 7 with a second buffer solution, either pH 4 or pH 10 depending on the pH values expected in the field. Adjust the meter readout to the theoretical pH value determined in step 7 using the slope adjustment screw or knob. If the meter is automatically calibrated, the meter reading should agree with the theoretical pH value.
NOTE: The pH of most surface waters in Texas usually is above 7. For these sites, the pH meter should be calibrated using the pH 7 and pH 10 buffers.
10. If the meter is calibrated using the pH 7 and pH 10 buffers, repeat steps 4-7 using the pH 4 buffer. If the pH 4 reading differs by ± 0.05 from the theoretical pH value, the probe probably needs reconditioning. If the probe cannot be regenerated, do not make any slope or calibration adjustments at this time.
11. Record the field calibration values on the field sheet (TX-72Q).
12. If alkalinity has to be determined, and the pH 4 buffer did not read within ± 0.05 of the theoretical pH 4 value, recalibrate the pH meter using pH 7 and pH 4 buffers after the field measurement but before the alkalinity titration.
13. After recording the pH measurement make sure the instrument is set back to standby before the probe is removed from a solution.

Field Measurements

Prior to field measurements and alkalinity titrations, pH meters must be calibrated using at least two pH standards. (See section on pH meter calibration.)

1. After the instrument has been calibrated, rinse the probe with deionized water and a small amount of the water sample. Immerse the probe tip in the water sample.
2. After the probe has equilibrated with the sample, read the pH of the sample and record the value to the nearest 0.1 pH unit.

NOTE: If the meter reading does not stabilize within several minutes, outgassing of carbon dioxide or settling of charged particles (clay) may be occurring. Outgassing may be reduced by placing the probe into the sample container through a tightly fitting stopper.

Normally, pH should be measured on an unfiltered sample. However, if the sample contains appreciable sediment, slow settling of the clay particles may cause a continuous "drift" of the observed pH value. Such samples should be filtered before the pH is determined.

In dry windy climates, such as the climate in some parts of Texas, a static charge can build up on the face of a pH meter, which causes erratic readings on the display. Polishing the face of the display with a soft absorbent tissue containing several drops of antistatic solution, such as Novus plastic polish, will minimize this interference.

Trouble-Shooting Guide

<u>Symptom</u>	<u>Possible problems and solutions</u>
Meter will not calibrate full scale	<ol style="list-style-type: none">1. Buffers may be contaminated or old. Use fresh buffers.2. Faulty probe--recondition probe (see section on probe preparation).
Slow response time	<ol style="list-style-type: none">1. Weak filling solution--change filling solution (see section on probe preparation).2. No filling solution--add fresh solution (see section on probe preparation).3. Dirty tip--clean with soap solution. Do not scratch probe tip. If you suspect chemical deposits, place probe in a 5-percent HCl solution for about 20 seconds.4. Clogged or partially clogged junction. Unclog by placing probe in boiling water for about 10 minutes. For some probes it is possible to replace the clogged junctions.5. Water is cold or of low ionic strength --be patient!

Erratic readings

1. Loose or defective connections--tighten or replace connections.
2. Broken or defective cable--repair or replace cable.
3. Static charge--polish face of meter with antistatic solution (Novus plastic polish).
4. Loose battery connection--tighten.

Alkalinity

Alkalinity is a measure of the buffering capacity of water against acid. Degasification, precipitation, and other chemical and physical reactions may cause the concentrations of carbonate and bicarbonate to change substantially within several hours or even minutes after sample collection. Consequently, field values for carbonate and bicarbonate or alkalinity usually are more reliable than values obtained in the laboratory.

Alkalinity is determined by titrating a filtered water sample with a standard solution of sulfuric acid to a pH of 4.5. Selection of this end point is arbitrary and corresponds to the true end point only under ideal conditions. However, the error is not serious for most surface-water samples.

For a discussion of the factors involved in these and in more precise measurements of carbonate, bicarbonate, and carbonate alkalinity, personnel are referred to USGS Techniques of Water-Resources Investigations, Book 1, Chapter D2, "Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents," and Quality of Water Branch Technical Memorandum 82.05.

Calibration

pH meter

Use a pH meter that has been calibrated previously for pH measurements. (See section on pH.) If the pH meter has been calibrated with pH 10 and 7 buffers, a calibration check for the pH 4 buffer should be made before the analysis for alkalinity. If the observed and theoretical values differ by more than 0.05 unit, the meter should be recalibrated with pH 7 and 4 buffers.

Alkalinity acid

The acid you use to determine alkalinity using the buret method listed below has to be checked prior to each field trip. The acid maintained in the field service unit should be checked on a monthly basis to insure its normality. Care should be taken to insure that the alkalinity acid does not become contaminated. The normality of the alkalinity acid supplied by the Water-Quality Unit is 0.01639 N. The normality of the acid in the Hach cartridges is 0.16 N. The normality of the acid in the Hach cartridges is checked by "Lot Number" by the Ocala Water-Quality Service Unit. Because they check the normality of this acid, and because this acid is in a relatively closed system, it is not necessary to check the normality in the Hach cartridges prior to each field trip. Generally the 1.6 N acid is too strong

for alkalinity titrations and should not be used without approval of the Subdistrict or District water-quality specialist. To check the normality of the acid, perform the following steps.

1. Prepare a sodium carbonate standard as outlined in the section "Reagents for Field Determinations."
2. Pipet 25 mL of the sodium carbonate standard into a 100-mL beaker.
3. Titrate with acid to be tested to pH 4.5
4. Record the volume of acid used
5. Determine the normality of the titrant acid by the following:

$$\begin{aligned}\text{Normality} &= (\text{sample size in mL/mL acid}) \times 0.01639 \\ &= \frac{25 \text{ mL}}{\text{mL acid}} \times 0.01639\end{aligned}$$

Field Measurements

Fixed-endpoint titration

Standard buret.--

1. Fill a 25-mL buret with 0.01639 N H₂SO₄ solution.
2. Pipet 50 mL of filtered sample into a clean dry 100-mL beaker. The sample volume may be increased for low ionic strength solution or decreased for solutions of high ionic strength.
3. Rinse pH electrode with an aliquot of the sample.
4. Insert pH electrode and a clean dry stirring bar into the sample.
5. Place the beaker containing the sample on the titration assembly and record the pH.
6. Adjust the stirrer speed to slow, and titrate immediately to pH 4.5. Record the volume of acid used in the titration on the field note sheet.
7. The calculations for alkalinity as CaCO₃ in mg/L using 0.01639 normality acid is:

$$\begin{aligned}\text{Alkalinity as CaCO}_3 \text{ in mg/L} &= 1,000/\text{mL sample} \times 0.8202 \times \text{mL acid} \\ &= \frac{1,000}{50} \times 0.8202 \times \text{mL acid}.\end{aligned}$$

For those who have access to the Prime, use program FIELD CALC to compute alkalinity. Report alkalinity concentrations as follows: Less than 10 mg/L, whole numbers; 10 to 99 mg/L, two significant figures; more than 99 mg/L, three significant figures.

CAUTION: If the volume of titrant used in the determination exceeds 25 mL (size of buret from step 1), DO NOT continue the titration. Select a smaller sample and repeat the procedure from step 3. Be sure to substitute the proper sample volume in the calculation of alkalinity shown above.

Hach digital titrator.--

Apparatus:

1. pH meter with combination pH probe or equivalent.
2. Hach digital titrator with mounting assembly.
3. Titrant acid cartridges with straight- or bent-stem delivery tubes.
4. Magnetic stirrer.
5. Deionized water, Kimwipes.
6. 25-mL, 50-mL, and 100-mL volumetric pipets.

This method uses a digital titrator in place of a buret. The titrant cartridge is inserted into the digital titrator and a delivery tube is attached to the cartridge. The pH electrode is inserted into the electrode assembly. Check to see that the magnetic stirrer has an appropriate power source and is working properly. The assembly is now ready for use. Before going into the field, the field person needs to study the digital-titrator methods manual and perform several "dry runs" in the office.

BECOME THOROUGHLY FAMILIAR WITH THE OPERATION OF THE EQUIPMENT BEFORE ATTEMPTING TO USE IN THE FIELD:

A plunger in the digital titrator forces acid in the titrant cartridge into and out of the delivery tube. The plunger is controlled by a main-drive screw, which in turn, is controlled by rotation of the delivery knob. Thus, the delivery knob controls the titrant volume delivered and the digital counter. A digital-counter value of 800 is equal to 1 mL. A direct relation exists between the digital-counter number for the equivalence point and the milligrams per liter of alkalinity as calcium carbonate. Each digital-counter number is equal to 0.2 mg/L alkalinity as calcium carbonate for the 0.1600 N H_2SO_4 titrant cartridge and 50-mL sample size.

Use a pH meter that has been calibrated previously for pH measurement or calibrate the pH meter as prescribed in the section of this report related to the calibration of pH meters (p. 48). Once the pH meter has been calibrated, precede with the following instructions.

1. If performing a hand-held titration, attach a clean, straight-stem delivery tube to a 0.1600 N H_2SO_4 titration cartridge. If the digital titrator is to be attached to the laboratory stand, use a clean, 90-degree delivery tube. Do not insert the tube past the cartridge extension. Twist the cartridge into the titrator body.
2. Press the plunger release, then manually position the plunger against the cartridge seal. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant and then dry with a soft absorbent tissue. Reset the counter to zero using the counter reset knob.
3. Pipet 50 mL of filtered sample into a clean dry 100-mL beaker. (A 25-mL or 100-mL sample size may be used for extremely large or small alkalinity concentrations.)
4. Rinse the pH electrode with an aliquot of the sample.
5. Insert the pH electrode and a clean, dry stirring bar into the sample.
6. Place the beaker containing the sample on a portable magnetic stirrer and adjust stirrer speed to low.

7. Measure and record pH value and counter number. (Counter should read 0000.)
8. Immerse the end of the delivery tube in the sample. (The delivery tube must be immersed during all acid additions.)
9. Titrate rapidly to a pH of 5.0, then add acid in counts of 1 or 2 to a pH of 4.5.
10. Record the sample size and counter number at pH 4.5 on the field sheet.

Calculate alkalinity in mg/L as calcium carbonate:

1. For those that have access to the Prime, use the Prime program (FIELD CALC). Users of this program can create an abbreviation that will run this program. Create an abbreviation as follows:

AB -AC FIELD CALC PROGRAMS>RUN>FIELD CALC

- A. Type FIELD CALC and a carriage return.
- B. Enter 2 for Hach Alkalinity Calculation.
- C. Enter the sample size and Hach counter number.
- D. Record alkalinity as calcium carbonate on the field sheet.
2. For those that don't have access to the Prime, use one of the following equations:

25-mL sample size
 mg/L alkalinity as CaCO₃ = digital count x 0.40
 50-mL sample size
 mg/L alkalinity as CaCO₃ = digital count x 0.20
 100-mL sample size
 mg/L alkalinity as CaCO₃ = digital count x 0.10

Report alkalinity concentrations: Less than 10 mg/L, whole numbers; 10 to 99 mg/L, two significant figures; more than 99 mg/L, three significant figures.

Incremental titration for carbonate and bicarbonate

Although a fixed-endpoint (pH 4.5) titration often is used to determine alkalinity as calcium carbonate, accurate determination of alkalinity as calcium carbonate as well as the determination of individual components of carbonate alkalinity (HCO₃⁻, CO₃²⁻) must be measured using the incremental titration procedure. The end points for titration of successive proton absorbing species are taken as the inflection points of the titration curve, or as the maximum rates of change of pH per volume of titrant added (fig. 12). Simple computer programs have been developed for constructing the curve to determine inflection points; it is only necessary to input the paired values of pH and volume of titrant in milliliters throughout a given range.

Use a pH meter that has been previously calibrated for pH measurement or calibrate the pH meter as prescribed in the section of this report related to the calibration of pH meters (p. 48). Once the pH meter has been calibrated, proceed with the following instructions.

1. If performing a hand-held titration, attach a clean, straight-stem delivery tube to a 0.1600 N H₂SO₄ titration cartridge. If the digital

FIGURE 12

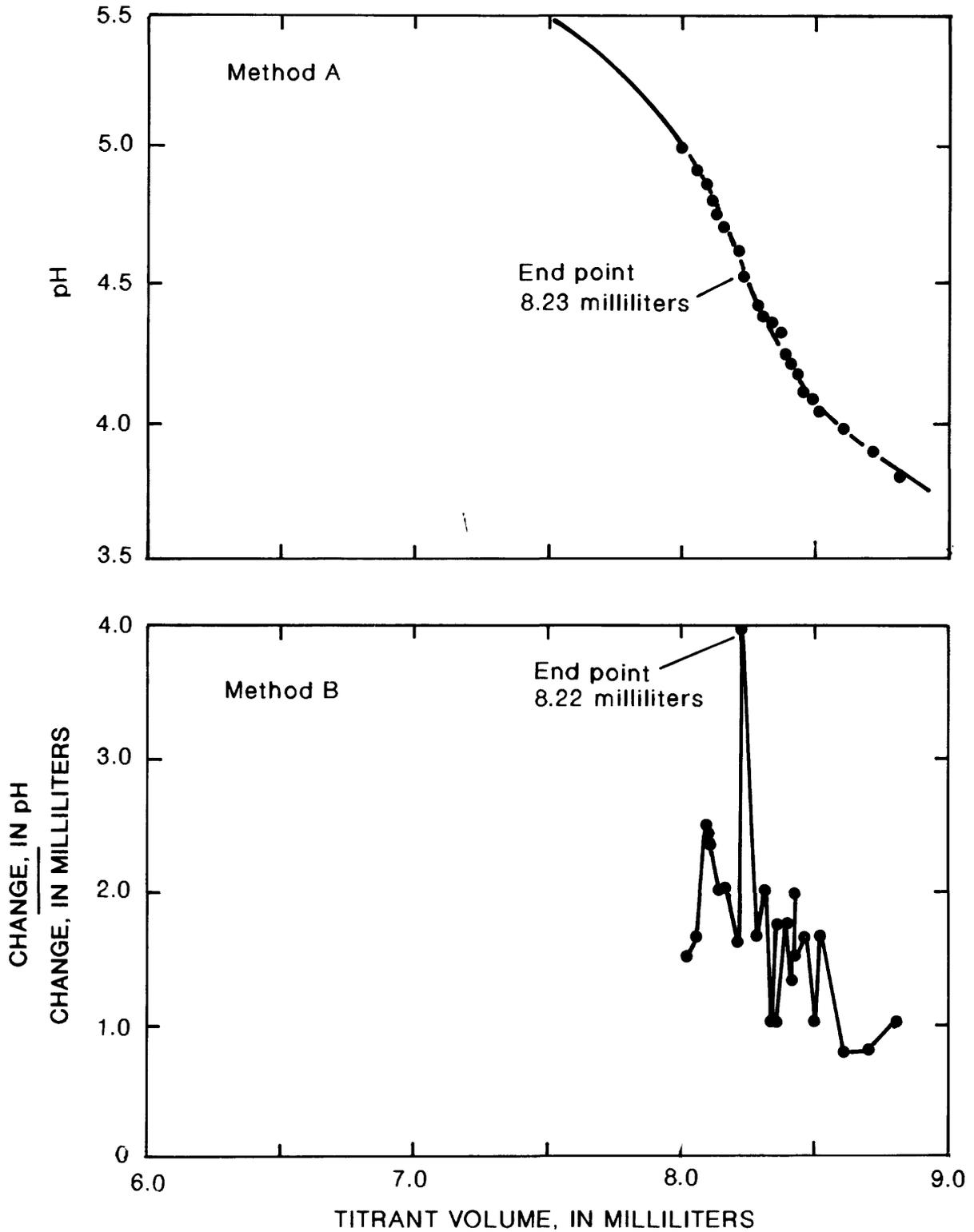


Figure 12.--Two methods of determining the end point for bicarbonate by incremental titration.

- titrator is to be attached to the laboratory stand, use a clean, 90-degree delivery tube. Do not insert the tube past the cartridge extension. Twist the cartridge into the titrator body.
2. Press the plunger release, then manually position the plunger against the cartridge seal. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant and then dry with a soft absorbent tissue. Reset the counter to zero using the counter reset knob.
 3. Pipet 50 mL of filtered sample into a clean dry 100-mL beaker.
 4. Rinse the pH electrode with an aliquot of the sample.
 5. Insert the pH electrode and a clean dry stirring bar into the sample.
 6. Place the beaker containing the sample on a portable magnetic stirrer and adjust stirrer speed to low.
 7. Measure and record pH value and counter number. (Counter should read 0000.)
 8. Immerse the end of the delivery tube in the sample. (The delivery tube must be immersed during all acid additions.)
 9. If the initial pH is less than 8.3, skip step 10 and go directly to step 11.
 10. If the pH is greater than 8.3, add the H₂SO₄ standard solution in counts of 2 increments and record the pH and counter number after each addition, allowing 15 to 20 seconds for equilibration after each addition. Continue until pH is below 8.0.
 11. Titrate to pH 5.0 and record the volume of titrant at pH 5.0 to the nearest counter number of 1. Allow 15 to 20 seconds for equilibration.
 12. From pH 5.0 to 4.0, add acid in counts of 2 increments and record the pH counter numbers after each addition, allowing 15 to 20 seconds for pH equilibration after each addition. The most sensitive part of the titration curve usually is between pH 4.8 and 4.3.

Calculate carbonate and bicarbonate according to the following instructions:

1. For those that have access to the Prime, use the Prime program (ALK.CPL) to compute the carbonate and bicarbonate alkalinity.
 - A. Type CPL PROGRAMS>RUN>ALK and follow program prompts for entering field pH and counter numbers.
 - B. Type CPL PROGRAMS>RUN>ALK and follow the program prompts to compute carbonate and bicarbonate alkalinity.
2. For those that do not have access to the Prime, use the following instructions:
 - A. Calculate the change in pH and the change in counter numbers and record these values on the field sheet.
 - B. Divide each change in pH by the change in counter numbers and record the results on the field sheet.
 - C. The end points are the counter numbers where maximum rates of change of pH per counter number increments occur. If a tie for the end point occurs, choose the last one (the one with the lower pH).
 - D. Calculate carbonate.

$$\text{CO}_3, \text{ mg/L} = [\text{counter number at CO}_3, \text{ endpoint}] \times [0.24 \times (50/\text{sample size})]$$
 - E. Calculate bicarbonate.

$$\text{HCO}_3, \text{ mg/L} = [(\text{counter number at HCO}_3, \text{ end point}) - (2 \times \text{counter number at CO}_3, \text{ end point})] \times [0.244 \times (50/\text{sample size})]$$

Report carbonate and bicarbonate alkalinity as follows: Less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

Dissolved Oxygen

Oxygen dissolved in surface water is derived from the air and from the oxygen generated by aquatic plants during the process of photosynthesis. The solubility of oxygen in water is dependent upon the partial pressure of oxygen in the air, the temperature of the water, and the mineral content of the water. Consequently, the barometric pressure, the temperature of the water or water vapor, and the specific conductance of the water must be known in order to determine the amount of oxygen that a solution or water vapor is capable of holding. The larger the barometric pressure, the more oxygen can be in solution. The lower the temperature, the more oxygen can be in solution, and the smaller the specific conductance, the more oxygen can be in solution. The solubility of oxygen in water at various water temperatures and pressures is given in table 5. The solubility correction factors for dissolved oxygen (DO) in water based on specific conductance are given in table 6.

DO meters used in the Texas District utilize a "Clark-type" polarographic oxygen probe. The Clark-type oxygen sensor is a complete polarographic system in itself. A thin membrane is stretched over the end of the sensor and isolates the sensor elements from their environment. The membrane is permeable to gases and allows them to enter the interior of the sensor. When a suitable polarizing voltage is applied across the cell, oxygen will react at the cathode (gold ring on the probe) causing a current to flow through the cell. The membrane passes oxygen at the rate that is proportional to the pressure difference across the membrane. Because oxygen is rapidly consumed at the cathode, it can be assumed that the oxygen pressure inside the membrane is zero. Hence, it can be seen that the force causing oxygen to diffuse through the membrane is proportional to the absolute pressure of oxygen outside the membrane. If the oxygen pressure outside the membrane increases, more oxygen diffuses through the membrane, and more current flows through the cell.

The Clark-type oxygen probes are temperature compensated. In the measurement of DO, temperature MUST be compensated for because the permeability of the membrane changes as a function of temperature. Thus a change in probe current could be caused by a change in membrane temperature rather than by a change in oxygen pressure. The solubility of oxygen in water is also temperature dependent. This factor must be considered if an instrument is to read the quantity of oxygen in the solution rather than read the oxygen pressure differential across the membrane. For these reasons, it is extremely important that the thermistor in the oxygen probes be checked for accuracy before each field trip.

Probe Preparation

Field probes commonly used in the Texas District are the YSI 5739 non-stirring in situ probe, the YSI 5750 nonstirring BOD bottle probe, the YSI 5720A stirring BOD probe, and the YSI probes used in our multiparameter instruments. These probes are shipped dry and require preparation before they can be used. In addition, all probes should be reconditioned prior to each field trip. The following procedure should be used to prepare YSI probes.

Table 5.--Solubility of oxygen in water at various temperatures and pressures
(dissolved oxygen in milligrams per liter)

[°C, degrees Celsius]

Temperature (°C)	Atmospheric pressure (millimeters mercury)																			
	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	700
0.0	15.3	15.2	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4
0.5	15.0	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2
1.0	14.8	14.7	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2	13.2	13.1
1.5	14.6	14.5	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2	13.2	13.1	13.0	12.9
2.0	14.4	14.3	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7
2.5	14.2	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.5
3.0	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.5	12.5	12.4
3.5	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4	12.3	12.2
4.0	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4	12.3	12.2	12.1	12.0
4.5	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.1	12.0	11.9
5.0	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7
5.5	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7	11.7	11.6
6.0	13.0	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4
6.5	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.9	11.8	11.7	11.6	11.5	11.5	11.4	11.3
7.0	12.7	12.6	12.5	12.4	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2	11.1
7.5	12.5	12.4	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0
8.0	12.4	12.3	12.2	12.1	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0	10.9
8.5	12.2	12.1	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7
9.0	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.8	10.7	10.6
9.5	11.9	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.6	10.5
10.0	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4
10.5	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2
11.0	11.5	11.4	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.3	10.2	10.1
11.5	11.4	11.3	11.2	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0
12.0	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.0	10.0	9.9
12.5	11.1	11.1	11.0	10.9	10.8	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8
13.0	11.0	10.9	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7
13.5	10.9	10.8	10.7	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.6
14.0	10.8	10.7	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5
14.5	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4
15.0	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3
15.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.2
16.0	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.1	9.1
16.5	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.4	9.3	9.2	9.2	9.1	9.0	9.0
17.0	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9
17.5	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.8
18.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.7
18.5	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6
19.0	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5
19.5	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.5	8.5	8.4
20.0	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.3
20.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3
21.0	9.3	9.2	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2
21.5	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1
22.0	9.1	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8.0
22.5	9.0	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9
23.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9
23.5	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8
24.0	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7
24.5	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6

Table 5.--Solubility of oxygen in water at various temperatures and pressures (dissolved oxygen in milligrams per liter)--Continued

Temperature (°C)	Atmospheric pressure (millimeters mercury)																			
	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	700
25.0	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6
25.5	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5
26.0	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4
26.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4
27.0	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3
27.5	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2
28.0	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2
28.5	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1
29.0	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0
29.5	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0
30.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9
30.5	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9
31.0	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8
31.5	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7
32.0	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7
32.5	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6
33.0	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6
33.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5
34.0	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5
34.5	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4
35.0	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3
35.5	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
36.0	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2
36.5	7.1	7.0	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2
37.0	7.0	7.0	6.9	6.9	6.8	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1
37.5	7.0	6.9	6.9	6.8	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1
38.0	6.9	6.9	6.8	6.8	6.7	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0
38.5	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0
39.0	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	6.0
39.5	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	6.0	5.9
40.0	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.9

Table 5.--Solubility of oxygen in water at various temperatures and pressures (dissolved oxygen in milligrams per liter)--Continued

Temperature (°C)	Atmospheric pressure (millimeters mercury)																			
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605	600
0.0	13.3	13.2	13.1	13.0	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5
0.5	13.1	13.0	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3
1.0	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2
1.5	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.0
2.0	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9
2.5	12.4	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.0	10.9	10.8	10.7
3.0	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.0	10.9	10.8	10.8	10.7	10.6
3.5	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7	10.6	10.5	10.4
4.0	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3
4.5	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.5	10.4	10.3	10.3	10.2
5.0	11.6	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2	10.1	10.0
5.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9
6.0	11.3	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.0	9.9	9.9	9.8
6.5	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.7	9.7
7.0	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.3	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.6	9.5
7.5	10.9	10.9	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4
8.0	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.6	9.5	9.5	9.4	9.3
8.5	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.6	9.5	9.4	9.3	9.3	9.3	9.2
9.0	10.5	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1
9.5	10.4	10.3	10.3	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.0	9.0
10.0	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	8.9	8.9
10.5	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8	8.8
11.0	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.7	8.7
11.5	9.9	9.9	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8	8.8	8.7	8.6	8.6
12.0	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.7	8.7	8.6	8.5	8.5
12.5	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.6	8.6	8.5	8.4	8.4
13.0	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.5	8.5	8.4	8.3	8.3
13.5	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.2	8.2
14.0	9.4	9.3	9.3	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1
14.5	9.3	9.2	9.2	9.1	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0
15.0	9.2	9.1	9.1	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9
15.5	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8
16.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.7
16.5	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7
17.0	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.6	7.6
17.5	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5
18.0	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.5	7.5	7.4
18.5	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.3
19.0	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3
19.5	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.2	7.2
20.0	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1
20.5	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.0
21.0	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0
21.5	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9
22.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.8
22.5	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8
23.0	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7
23.5	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6
24.0	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6	6.6
24.5	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5

Table 5.--Solubility of oxygen in water at various temperatures and pressures (dissolved oxygen in milligrams per liter)--Continued

Tem- per- ature (°C)	Atmospheric pressure (millimeters mercury)																			
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605	600
25.0	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.4
25.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.4	6.4
26.0	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.5	6.5	6.4	6.4	6.3
26.5	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
27.0	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2
27.5	7.2	7.1	7.1	7.0	7.0	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2
28.0	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.1	6.1
28.5	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.2	6.2	6.1	6.1	6.0
29.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.2	6.2	6.1	6.1	6.0	6.0
29.5	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9
30.0	6.9	6.8	6.8	6.7	6.7	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9
30.5	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8
31.0	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8
31.5	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7
32.0	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7
32.5	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6
33.0	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6
33.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5
34.0	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5
34.5	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4
35.0	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4
35.5	6.2	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3
36.0	6.2	6.1	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3
36.5	6.1	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.2
37.0	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2
37.5	6.0	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2	5.2
38.0	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2	5.2	5.1
38.5	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1
39.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0
39.5	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0	5.0
40.0	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0	5.0	4.9

Table 6.--Salinity correction factors for dissolved oxygen in water based on specific conductance

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

Temperature (°C)	Specific conductance ($\mu\text{S}/\text{cm}$)															
	0	2,000	4,000	6,000	8,000	10,000	12,000	14,000	16,000	18,000	20,000	22,000	24,000	26,000	28,000	30,000
0.0	1.000	0.992	0.985	0.977	0.969	0.961	0.953	0.946	0.938	0.930	0.922	0.914	0.905	0.897	0.889	0.881
1.0	1.000	.992	.985	.977	.969	.962	.954	.946	.938	.930	.922	.914	.906	.898	.890	.882
2.0	1.000	.992	.985	.977	.970	.962	.954	.946	.938	.931	.923	.915	.907	.899	.891	.883
3.0	1.000	.993	.985	.977	.970	.962	.954	.947	.939	.931	.923	.915	.907	.899	.891	.883
4.0	1.000	.993	.985	.978	.970	.962	.955	.947	.939	.932	.924	.916	.908	.900	.892	.884
5.0	1.000	.993	.985	.978	.970	.963	.955	.947	.940	.932	.924	.917	.909	.901	.893	.885
6.0	1.000	.993	.985	.978	.970	.963	.955	.948	.940	.933	.925	.917	.909	.902	.894	.886
7.0	1.000	.993	.985	.978	.971	.963	.956	.948	.941	.933	.925	.918	.910	.902	.894	.887
8.0	1.000	.993	.986	.978	.971	.963	.956	.949	.941	.933	.926	.918	.911	.903	.895	.887
9.0	1.000	.993	.986	.978	.971	.964	.956	.949	.941	.934	.926	.919	.911	.904	.896	.888
10.0	1.000	.993	.986	.979	.971	.964	.957	.949	.942	.934	.927	.919	.912	.904	.897	.889
11.0	1.000	.993	.986	.979	.971	.964	.957	.950	.942	.935	.927	.920	.912	.905	.897	.890
12.0	1.000	.993	.986	.979	.972	.965	.957	.950	.943	.935	.928	.920	.913	.906	.898	.890
13.0	1.000	.993	.986	.979	.972	.965	.958	.950	.943	.936	.928	.921	.914	.906	.899	.891
14.0	1.000	.993	.986	.979	.972	.965	.958	.951	.943	.936	.929	.922	.914	.907	.899	.892
15.0	1.000	.993	.986	.979	.972	.965	.958	.951	.944	.937	.929	.922	.915	.907	.900	.893
16.0	1.000	.993	.986	.979	.972	.966	.958	.951	.944	.937	.930	.923	.915	.908	.901	.893
17.0	1.000	.993	.986	.980	.973	.966	.959	.952	.945	.938	.930	.923	.916	.909	.901	.894
18.0	1.000	.993	.987	.980	.973	.966	.959	.952	.945	.938	.931	.924	.917	.909	.902	.895
19.0	1.000	.993	.987	.980	.973	.966	.959	.952	.945	.938	.931	.924	.917	.910	.903	.896
20.0	1.000	.993	.987	.980	.973	.966	.960	.953	.946	.939	.932	.925	.918	.911	.903	.896
21.0	1.000	.993	.987	.980	.973	.967	.960	.953	.946	.939	.932	.925	.918	.911	.904	.897
22.0	1.000	.993	.987	.980	.974	.967	.960	.953	.947	.940	.933	.926	.919	.912	.905	.898
23.0	1.000	.994	.987	.980	.974	.967	.960	.954	.947	.940	.933	.926	.919	.912	.905	.898
24.0	1.000	.994	.987	.981	.974	.967	.961	.954	.947	.941	.934	.927	.920	.913	.906	.899
25.0	1.000	.994	.987	.981	.974	.968	.961	.954	.948	.941	.934	.927	.921	.914	.907	.900
26.0	1.000	.994	.987	.981	.974	.968	.961	.955	.948	.941	.935	.928	.921	.914	.907	.901
27.0	1.000	.994	.987	.981	.975	.968	.962	.955	.948	.942	.935	.928	.922	.915	.908	.901
28.0	1.000	.994	.987	.981	.975	.968	.962	.955	.949	.942	.936	.929	.922	.915	.909	.902
29.0	1.000	.994	.988	.981	.975	.969	.962	.956	.949	.943	.936	.929	.923	.916	.909	.903
30.0	1.000	.994	.988	.981	.975	.969	.962	.956	.950	.943	.936	.930	.923	.917	.910	.903
31.0	1.000	.994	.988	.982	.975	.969	.963	.956	.950	.943	.937	.930	.924	.917	.911	.904
32.0	1.000	.994	.988	.982	.975	.969	.963	.957	.950	.944	.937	.931	.924	.918	.911	.905
33.0	1.000	.994	.988	.982	.976	.969	.963	.957	.951	.944	.938	.931	.925	.918	.912	.905
34.0	1.000	.994	.988	.982	.976	.970	.963	.957	.951	.945	.938	.932	.925	.919	.912	.906
35.0	1.000	.994	.988	.982	.976	.970	.964	.957	.951	.945	.939	.932	.926	.919	.913	.906

Table 6.--Salinity correction factors for dissolved oxygen in water based on specific conductance--Continued

Temperature (°C)	Specific conductance (µS/cm)															
	32,000	34,000	36,000	38,000	40,000	42,000	44,000	46,000	48,000	50,000	52,000	54,000	56,000	58,000	60,000	62,000
0.0	.873	.865	.856	.848	.840	.832	.823	.815	.807	.799	.790	.782	.774	.766	.757	.749
1.0	.874	.866	.857	.849	.841	.833	.825	.816	.808	.800	.792	.783	.775	.767	.759	.751
2.0	.875	.867	.858	.850	.842	.834	.826	.818	.809	.801	.793	.785	.777	.768	.760	.752
3.0	.875	.867	.859	.851	.843	.835	.827	.819	.811	.803	.794	.786	.778	.770	.762	.754
4.0	.876	.868	.860	.852	.844	.836	.828	.820	.812	.804	.796	.788	.780	.771	.763	.755
5.0	.877	.869	.861	.853	.845	.837	.829	.821	.813	.805	.797	.789	.781	.773	.765	.757
6.0	.878	.870	.862	.854	.846	.838	.830	.822	.814	.806	.798	.790	.782	.774	.766	.758
7.0	.879	.871	.863	.855	.847	.839	.831	.824	.816	.808	.800	.792	.784	.776	.768	.760
8.0	.880	.872	.864	.856	.848	.840	.833	.825	.817	.809	.801	.793	.785	.777	.769	.761
9.0	.880	.873	.865	.857	.849	.842	.834	.826	.818	.810	.802	.794	.787	.779	.771	.763
10.0	.881	.874	.866	.858	.850	.843	.835	.827	.819	.811	.804	.796	.788	.780	.772	.764
11.0	.882	.874	.867	.859	.851	.844	.836	.828	.820	.813	.805	.797	.789	.781	.774	.766
12.0	.883	.875	.868	.860	.852	.845	.837	.829	.822	.814	.806	.798	.791	.783	.775	.767
13.0	.884	.876	.869	.861	.853	.846	.838	.830	.823	.815	.807	.800	.792	.784	.777	.769
14.0	.884	.877	.869	.862	.854	.847	.839	.832	.824	.816	.809	.801	.793	.786	.778	.770
15.0	.885	.878	.870	.863	.855	.848	.840	.833	.825	.817	.810	.802	.795	.787	.779	.772
16.0	.886	.879	.871	.864	.856	.849	.841	.834	.826	.819	.811	.804	.796	.788	.781	.773
17.0	.887	.879	.872	.865	.856	.850	.842	.835	.827	.820	.813	.805	.797	.790	.782	.775
18.0	.888	.880	.873	.866	.858	.851	.843	.836	.829	.821	.814	.806	.799	.791	.784	.776
19.0	.888	.881	.874	.867	.859	.852	.844	.837	.830	.822	.815	.807	.800	.792	.785	.777
20.0	.889	.882	.875	.867	.860	.853	.845	.838	.831	.823	.816	.809	.801	.794	.786	.779
21.0	.890	.883	.876	.868	.861	.854	.846	.839	.832	.825	.817	.810	.802	.795	.788	.780
22.0	.891	.884	.876	.869	.862	.855	.848	.840	.833	.826	.818	.811	.804	.796	.789	.782
23.0	.891	.884	.877	.870	.863	.856	.849	.841	.834	.827	.820	.812	.805	.798	.790	.783
24.0	.892	.885	.878	.871	.864	.857	.850	.842	.835	.828	.821	.814	.806	.799	.792	.785
25.0	.893	.886	.879	.872	.865	.858	.851	.843	.836	.829	.822	.815	.808	.800	.793	.786
26.0	.894	.887	.880	.873	.866	.859	.852	.844	.837	.830	.823	.816	.809	.802	.794	.787
27.0	.894	.887	.880	.874	.867	.860	.853	.845	.838	.831	.824	.817	.810	.803	.796	.789
28.0	.895	.888	.881	.874	.867	.860	.853	.846	.839	.832	.825	.818	.811	.804	.797	.790
29.0	.896	.889	.882	.875	.868	.861	.854	.848	.841	.834	.827	.820	.812	.805	.798	.791
30.0	.896	.890	.883	.876	.869	.862	.855	.849	.842	.835	.828	.821	.814	.807	.800	.793
31.0	.897	.890	.884	.877	.870	.863	.856	.850	.843	.836	.829	.822	.815	.808	.801	.794
32.0	.898	.891	.884	.878	.872	.864	.857	.851	.844	.837	.830	.823	.816	.809	.802	.795
33.0	.899	.892	.885	.879	.872	.865	.858	.851	.845	.838	.831	.824	.817	.810	.803	.797
34.0	.899	.893	.886	.879	.873	.866	.859	.852	.846	.839	.832	.825	.818	.812	.805	.798
35.0	.900	.893	.887	.880	.874	.867	.860	.853	.847	.840	.833	.826	.820	.813	.806	.799

1. Remove the sensor guard from the bottom of the probe (the YSI nonstirring BOD bottle probe and the YSI 5720 stirring BOD probe do not have a sensor guard). Remove the O-ring and membrane.
2. Turn the probe upside down and shake out the old KCl electrolyte. If the probe has a pressure compensating port, use the eraser end of a pencil, or a similar soft blunt tool, to pump the pressure compensating diaphragm until all KCl is expelled from the chamber.
3. Inspect the gold cathode at the probe tip. It should always be bright and untarnished. If it is tarnished (which can result from contact with certain gases) or plated with silver (which can result from extended use with a loose or wrinkled membrane), the surface should be restored as follows:
 - A. Use the eraser end of a pencil to gently buff the gold cathode until it appears bright and untarnished. Never use abrasives or chemicals.
 - B. Flush the probe and probe chamber with deionized water to remove eraser debris.
4. Thoroughly rinse the sensor tip and chamber, and when applicable, the pressure compensating chamber with KCl solution.

NOTE: The KCl filling solution is available from the District office. If it is necessary to prepare the KCl filling solution from a vendor kit, follow the instructions supplied with the kit.

5. To fill the probe with electrolyte and install a new membrane, follow these steps:
 - A. Grasp the probe in your left hand with the probe tip pointing up. When preparing the YSI 5739 probe, the pressure compensating port should be to the right. Successively fill the sensor body with electrolyte solution while pumping the diaphragm with the eraser end of a pencil or a similar soft, blunt tool. Continue filling and pumping until no more air bubbles appear. When preparing a probe without a pressure compensating port, simply fill the sensor body until no more air bubbles appear.
 - B. Tap the probe body lightly with a pen or pencil to remove air trapped in the silver anode.
 - C. Remove a membrane from the kit. Secure the membrane between your left thumb and side of probe near the probe tip. Add more electrolyte to the probe until a large meniscus completely covers the gold cathode. Handle the membrane only at the ends, keeping it clean and dust free.
 - D. Grasp the free end of the membrane with the thumb and forefinger of the right hand. With one continuous motion, stretch the membrane up and over the probe tip and down the other side.
 - E. Secure the end of the membrane under the forefinger of the left hand holding the probe.
 - F. Roll a NEW O-ring over the probe. There should be no wrinkles in the membrane or air bubbles trapped under the membrane. Wrinkles may be removed by tugging lightly on the edge of the membrane beyond the O-ring. Lightly tap probe to check for bubbles.

NOTE: The O-rings that come with the YSI 5739 probe should be replaced with the smaller diameter O-rings used on the 5720A probe. They provide a tighter

seal for the 5739 probe and help reduce electrolyte contamination. NEW O-rings should always be used each time a probe is reconditioned.

- G. Trim excess membrane with scissors or a sharp knife. Check that the stainless steel temperature sensor is not covered by excess membrane.
6. Replace the sensor guard where applicable.

Calibration

The three most common methods for calibrating the YSI oxygen meters are (a) air calibration chamber in water, (b) air-saturated deionized water, and (c) air calibration chamber in air. The Texas District uses (a) air calibration chamber in water. For a more thorough discussion of this and other methods of calibration, personnel are referred to USGS Quality of Water Branch Technical Memorandum No. 79.10.

1. For all needle movement instruments, start with the switch in the OFF position and adjust the meter pointer to 0 with the screw in the center of the meter panel. (This adjustment, calibration, and all readings made thereafter should be done with the instrument in the same general position.)
2. Attach the prepared probe to the PROBE connector of the instrument and adjust the retaining ring until finger tight. (Skip this step if using a multiparameter instrument.)
3. Turn the operating switch to the 0 to 20 position and allow sufficient time for the probe to polarize (5 to 10 minutes).
4. For needle movement instruments, turn the switch to RED LINE position and adjust the RED LINE knob until the meter needle aligns with the red mark at the 31 °C position.
5. For needle movement instruments, switch to ZERO position and adjust to 0 with ZERO CONTROL.
6. Prior to the initial daily calibration, insert the probe into a sodium sulfite solution (DO free solution) prepared as outlined in the section on "Reagents for Field Determination," and check to insure that the instrument reads zero. If the instrument reading exceeds 0.2 mg/L, take appropriate steps to remedy the problem (this problem is usually caused by a defective or improperly prepared probe).
7. Dip the calibration chamber into the stream or container of native water, pour out excess water, and insert the DO probe snugly into the wet chamber. If the YSI 5739 probe is used, insure that the pressure compensating diaphragm on the side of the probe is enclosed within the calibration chamber during calibration. For multiparameter instruments, fill the calibration cup with native water to a level just below the DO membrane. Cover the calibration cup with one of the plastic cup lids.
8. Immerse the calibration chamber into the stream or bucket of native water for 10 to 15 minutes to allow the temperature of the system to equilibrate. Skip this step for multiparameter instruments.
9. Determine true atmospheric pressure with a pocket altimeter-barometer to the nearest 5 mm of mercury. (NOTE! Atmospheric pressure reported by the Weather Service is not "true" atmospheric pressure, but is corrected to sea level.)
10. Turn the function switch to TEMPERATURE and observe readings until the meter stabilizes. Note the temperature reading to the nearest 0.5 °C.

11. Refer to the oxygen solubility table (table 5, p. 57) to determine the saturated DO value corresponding to the measured air chamber temperature and true atmospheric pressure.
12. Turn the operating switch on the oxygen meter to the 0 to 10 or 0 to 20 scale and calibrate the meter using the saturated value determined in step 11. Do not change scales without recalibrating or verifying that identical readings are obtained on both scales.

Field Measurements

DO should be measured in situ at the centroid of flow. If the velocity of the stream at the point of measurement is less than 1 ft/s, manual stirring must be provided by raising or lowering the probe about 1 ft/s (do not break the surface of the water). If the stream velocity is so fast that the probe cannot be submerged, the probe can be attached to a sounding weight on a separate line and the sounding weight and probe submerged. (Do not support the sounding weight with the probe cable!)

After the probe has been submerged and the stirring rate of at least 1 ft/s has been established, complete the DO measurement as follows:

1. Turn function switch to the 0 to 20 mg/L range.
2. After the reading on the meter has stabilized (at least 2 minutes), read and record the DO value. Report values of less than 20.0 mg/L to the nearest 0.1 mg/L. If the value exceeds 20 mg/L, record ">20 mg/L."
3. Turn the function switch to the OFF position if no other measurements will be made that day. If more measurements are needed, leave the meter on until after the final daily measurement.
4. Remove the probe from the water, rinse with deionized water, and store it with the probe tip in a container of 100-percent humidity.

Trouble-Shooting Guide

<u>Symptom</u>	<u>Possible problems and solutions</u>
Meter does not read line consistently	1. Weak batteries--replace.
Meter drift or excessive time for meter to stabilize	1. Temperature compensator has not equilibrated with stream. 2. Weak batteries--replace. 3. Probe needs reconditioning. See probe preparation section.
Erratic meter readings	1. Break in cable--replace cable. 2. Bad connection at meter or probe. 3. Hole in membrane--recondition. 4. Air bubble in probe--recondition.
Meter slow to react	1. Gold cathode tarnished--buff with pencil eraser and recondition probe. 2. Fouled membrane--recondition probe and replace membrane.

Meter will not zero in sodium sulfite solution

1. Add additional Na_2SO_3 to insure solution contains no oxygen. If meter still does not zero, recondition the probe.

Cannot adjust calibration to read standards

1. If unable to adjust in an upward direction, check to see if more than one membrane is on the probe.
2. If unable to adjust in a downward direction, the membrane is probably stretched too tight or thin--replace with new membrane.

Bacteriological Analyses

Bacteriological determinations indicate the degree of contamination of the water with wastes from human or animal sources. Traditionally, analyses for detection and enumeration of these indicator organisms have been used rather than direct analysis for the pathogens. The coliform group of bacteria has been the principal indicator of the suitability of a particular water for domestic, dietetic, and similar uses. Increasing attention is being given to the potential value of fecal-streptococcal bacteria as indicators of substantial contamination of water. Fecal-streptococcal data may also provide information concerning the probable origin of contamination.

Bacteriological analyses of surface waters in the Texas District usually include determinations of fecal-coliform and fecal-streptococcal bacteria. For the purpose of the method described in this section, the fecal-coliform group is defined as all the organisms which produce blue colonies within 24 hours when incubated at $44.5 \text{ }^\circ\text{C} \pm 0.2 \text{ }^\circ\text{C}$ on M-FC medium. The fecal-streptococcal group is defined as all the organisms which produce red or pink colonies within 48 hours when incubated at $35 \text{ }^\circ\text{C} \pm 0.5 \text{ }^\circ\text{C}$ on KF streptococcal medium.

The standard tests for presence of fecal-coliform and fecal-streptococcal bacteria may be carried out by membrane-filter techniques. Tests usually utilized in the Texas District are the membrane-filter techniques which are described in the following sections and are discussed in more detail in USGS Techniques of Water Resources Investigations, Book 5, Chapter A4, "Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples."

Preparation for Field Trip

Glassware preparation

Residual chlorine in a water sample will destroy the biological population and may prevent an accurate determination of bacteria, unless the chlorine is destroyed at the time of sample collection. Consequently, 1.0 mL of a 10-percent solution of sodium thiosulfate should be added to the 1-L sample bottle before sterilization in the field service unit. This reagent will neutralize about 15 mg/L of residual chlorine in the sample.

Glassware should be sterilized in a hot-air oven not less than 1 hour at a temperature of 170 °C. Glassware may also be sterilized by autoclaving for 20 minutes at 121 °C at 15 lb/in².

Buffered dilution water

When necessary, dilution of samples for bacteriological examination should be made with a sterile buffered solution. To prepare the stock phosphate buffer solution, dissolve 34.0 g potassium dihydrogen phosphate (KH₂PO₄) in 500 mL deionized water. Adjust to pH 7.2 with 1 N sodium hydroxide (NaOH). Dilute to 1 L with deionized water. Sterilize (autoclave) in a glass bottle for 20 minutes at 121 °C at 15 lb/in². If an autoclave is not available, the solution may be sterilized in a covered glass beaker by boiling for 30 minutes or by filtering with a sterile filter assembly through a sterile membrane filter into a sterile glass bottle. After a bottle of this stock solution is opened for use, the unused part should be refrigerated. Buffered stock solutions may become contaminated. This is usually indicated by the solution becoming turbid or a precipitate forming. Contaminated solutions should be discarded.

To prepare the sterile buffered dilution water, add 1.2 mL of the stock phosphate buffer solution to 1 L of deionized water containing 1 g of Difco peptone (0118) or equivalent. Sterilize (autoclave) in a glass bottle for 20 minutes at 121 °C at 15 lb/in². If an autoclave is not available, the solution may be sterilized in a covered glass beaker by boiling for 30 minutes or by filtering aseptically through a sterile membrane filter. Dispense 99 ±2.0 mL portions in sterile glass dilution bottles.

Preparation of media

Bacteria media should be prepared in the laboratory or field service unit prior to each field trip. The media should be obtained from the Water-Quality Service Unit in Ocala, Florida. The media, and all necessary reagents are contained in a package and ready for preparation. Follow the instructions in the package for preparation of the media. Once the media have been prepared, the plates must be refrigerated or kept on ice. The maximum storage time for the fecal streptococcal plates is 2 weeks. The maximum storage time for fecal coliform plates is 3 days.

Sample Collection and Analysis

Sample collection

Samples for bacteriological examination are collected in clean sterile glass bottles. Field sterilization of depth-integrating water-sediment samplers available in the Texas District is impractical; consequently, these samplers should not be used for the collection of bacteriological samples.

Samples from shallow streams should be collected from a single vertical near the centroid of flow by wading. When collecting the sample, personnel should face upstream, hold the bottle near its base, and immerse the bottle with the mouth directed toward the current.

Samples from deep streams can be collected from a bridge or cableway with a weighted bottle sampler by immersing the sampler at a single vertical near the centroid of flow. The empty sampler should be immersed in the stream before the sample bottle is inserted in order to avoid the possibility of contamination of the sample. When the sample is collected, air space should be left in the bottle to facilitate mixing the sample. Do not use the USGS churn splitter for compositing samples for bacteriological examination!

Bacteriological determinations should be initiated as soon as possible after sample collection, preferably within 1 hour of the time of collection. Data have shown that bacteria do not survive long in a harsh stream environment. Approximately 80 to 90 percent of fecal bacteria die within 24 hours after discharge into a stream environment.

Selection of sample volumes

The selection of sample volume is sometimes difficult to determine unless prior sampling has given an indication of bacterial densities. Five plates with selected sample volumes usually can give a coverage that will provide at least one plate within the ideal range (unless stream bacteria densities are very small). The volume of sample to be filtered must be such that after incubation one or more of the plates will have a count of 20 to 60 fecal-coliform colonies or 20 to 100 fecal-streptococcal colonies.

In some instances it is difficult, if not impossible, to process a sample volume large enough to provide the minimum plate count (20 colonies). For routine field work with raw water, the maximum sample volume should be 100 mL.

The following sample volumes can be used when no prior experience exists:

1. Fecal coliforms
 - A. Unpolluted raw surface water: Sample volumes of 1.0, 3.0, 10.0, 30.0, and 100.0 mL will cover a range of 20 to 6,000 cols./100 mL (colonies per 100 mL).
 - B. Polluted raw surface water: Sample volumes of 0.001, 0.003, 0.01, 0.03, and 1.0 mL will cover a range of 2,000 to 6,000,000 cols./100 mL.
2. Fecal streptococci
 - A. Unpolluted raw surface water: Sample volumes of 0.20, 1.0, 5.0, 25.0, and 100.0 mL will cover a range of 20 to 50,000 cols./100 mL.
 - B. Polluted raw surface water: Sample volumes of 0.0005, 0.002, 0.01, 0.05, and 0.20 mL will cover a range of 10,000 to 20,000,000 cols./100 mL.

Analytical procedures

After the sample has been collected and the appropriate volumes of sample to be filtered have been selected, label the petri dishes with the station number, date, and the volume to be filtered and proceed with the analysis.

1. Sterilize the filter apparatus as follows:
 - A. Remove the stainless steel receiver flask from the base assembly.
 - B. Saturate the asbestos ring (wick) around the base assembly with methanol (about 2 mL).

NOTE: Only METHANOL can be used. Do not use any other type of alcohol. The reason is that the incomplete combustion of methanol produces formaldehyde gas which actually does the sterilization. It is NOT the heat produced by the burning of methanol.

- C. Ignite the methanol on the asbestos wick and allow it to burn for 30 seconds.
- D. Invert the stainless steel receiver flask over the funnel and the burning asbestos ring. Leave the flask in place for 15 minutes.
- E. Remove the flask and rinse it thoroughly with sterile water.
2. Sterilize stainless steel forceps by immersing tips in ethanol and passing them through a flame. (Do not hold forceps in flame.) Resterilize forceps before each use. Cool forceps several seconds to prevent scorching the membrane filter.
3. Assemble filtration equipment. Insert filter base into receiver flask, plug the suction tube adapter into the hole on the filter holder base, and connect the opposite end of the suction tube to the syringe inlet valve.
4. Unlock and remove the sterilized funnel and, using sterile forceps, place a sterile membrane filter (0.7- μ m pore size, 47-mm diameter) over the porous plate of the filter base, grid side of the membrane up. Replace the funnel on the filter base carefully to avoid tearing or creasing the membrane. Apply twist lock.
5. Before any actual samples are run, process a blank sample for each of the media types being used. The blanks should consist of 20 to 50 mL of buffered dilution water processed and incubated in the same manner as the actual sample (described below). After incubation, the absence of colonies on the blank plates confirms that contamination of the filtration apparatus as well as the media has not occurred. After the blank plates have been run, the actual sample(s) can be processed.
6. Shake the sample vigorously, as least 25 times, before each volume is withdrawn and immediately withdraw the sample volume to be filtered. Filter the smallest sample volume first.

If the volume of sample to be filtered is 10 mL or more, transfer the sample with a sterile pipet or graduated cylinder directly into the funnel.

If the volume of sample to be filtered is between 1.0 and 10.0 mL, pour about 10 mL of sterile buffer dilution water into the funnel before pipeting the sample.

If the volume of the original water sample to be filtered is less than 1.0 mL, prepare dilutions with sterile buffer-dilution water in sterile milk-dilution bottles and transfer the appropriate volume of dilution to the membrane filter. One of the dilutions in table 7 probably will be applicable.

7. After the sample has been transferred to the filter funnel, apply vacuum by pumping the syringe plunger slowly.
8. Rinse the side of the funnel twice with 20 to 30 mL of sterile buffer-dilution water while applying vacuum.
9. Release vacuum by briefly removing suction tube adapter from the hole on the filter holder base.

Table 7.--Methods of dilution for obtaining small sample volumes for bacterial analysis

[mL, milliliter]

Dilution (mL)	Volume of sample added to 99 mL sterile dilution water	Equivalent volume of original sample per mL of dilution
1:10	11.0 mL of original sample	0.1
1:100	1.0 mL of original sample	.01
1:1000	1.0 mL of 1:10 dilution	.001
1:10000	1.0 mL of 1:100 dilution	.0001

NOTE: When preparing dilutions, use a sterile pipet or hypodermic syringe for each dilution. Before each transfer between bottles, close and shake the bottle vigorously at least 25 times. Diluted samples are to be filtered within 20 minutes after preparation.

10. Remove the funnel and hold it in one hand until the membrane filter has been removed.
11. With sterile forceps, remove the membrane filter from the filter base. Replace the funnel on the filter holder base.
12. Open a petri dish and place the membrane filter (grid side up) on agar in the petri dish. Use a rolling action starting at one edge to avoid trapping air bubbles under the membrane. Inspect the membrane in the petri dish for uniform contact with the agar. If air is trapped under the membrane, remove the membrane and roll it on again.
13. Replace the top of the petri dish and record the time. Invert the petri dish so that the plated membrane filter is upside down.
14. Continue with filtration of the other volumes of samples, in the order of increasing sample volume. Record the volumes filtered on the field notes. Rinse the filter funnel with sterile buffer-dilution water between filtrations.
15. After the sample volumes have been filtered, place the inverted petri dishes in the preheated incubator, incubate, and count as follows:
 - A. Fecal coliforms: (22 to 24 hours at 44.5 °C ±0.2 °C). Remove and count, recording the values for each petri dish on the field form. Counts need to be made within 20 minutes after the plates have been removed from the incubator. Fecal-coliform colonies have a deep blue color and any that are gray to cream color are not counted. The counts are best made with the aid of 10X to 15X magnification.
 - B. Fecal streptococci: (48 ±2 hours at 35 °C ±0.5 °C). Remove and count, recording the values for each petri dish on the field form. The colonies may be deep red to pink in color and generally are of a smaller size than the fecal-coliform bacteria colonies. The counts are better made with the aid of 10X to 15X magnification.

If plates of a group have colonies that are in excess of the ideal range, and colonies of another plate(s) are within the accepted statistical range or close, counting the plates having excessive colonies is not necessary.

16. Calculate the number of bacteria colonies per 100 mL of sample as follows:

A. For colony counts within the ideal range use the following formula:

$$\text{Bacteria (cols./100 mL)} = \frac{\text{Bacteria colonies counted} \times 100}{\text{volume (mL of original sample filtered)}}$$

B. If dilutions of the original sample were made before filtration, calculate the volume (milliliters) of the original sample from the following formula:

$$\begin{array}{rcl} \text{Volume (mL of} & = & \text{Volume (mL)} \\ \text{original sample)} & & \text{of diluted} & \times & \text{Equivalent} \\ & & \text{sample} & & \text{volume (mL) of} \\ & & \text{filtered} & & \text{original sample} \\ & & & & \text{per mL of dilution} \end{array}$$

Assume for example that a 1:100 dilution was made, that a volume of 10 mL of the diluted sample was filtered, and that the colony count on the filter was 50. (See table 7.)

$$\begin{aligned} \text{Volume (mL) of original sample} &= (10) \times (0.01) \\ &= 0.1 \text{ mL} \end{aligned}$$

and

$$\begin{aligned} \text{Bacteria (cols./100 mL)} &= \frac{50 \times 100}{0.1} \\ &= 50,000 \end{aligned}$$

- C. Counts less than the ideal of 20 colonies or counts greater than the maximum listed for each bacteria type are calculated and reported as cols./100 mL, followed by the statement "estimated count based on nonideal colony count" or by an appropriate remarks code.
- D. If no sample filtered develops characteristic colonies, calculate assuming that the largest sample volume filtered had 1 bacteria colony.

For example, if the largest sample filtered was 25 mL, and no bacteria colony was found, calculate assuming 1 bacteria colony as follows:

$$\begin{aligned} \text{Bacteria (cols./100 mL)} &= \frac{<1 \times 100}{25} \\ &= <4 \end{aligned}$$

Report: "<4" cols./100 mL. Estimated count based on nonideal colony count or by an appropriate remarks code.

- E. If all filters bear colonies too numerous to count, a minimum estimated value can be reported by assuming a maximum count within the ideal count range on the smallest volume filtered (fecal coliform--60, fecal streptococcus--100). For example, if the small-

est sample volume filtered was 1 mL, and more than 80 total coliform colonies developed on the filter, calculate as follows:

$$\text{Coliforms (cols./100 mL)} = \frac{>80 \times 100}{1} \quad \text{or } > 8,000$$

Report >8,000 cols./100 mL "estimated count based on nonideal colony count."

- F. Sometimes, two or more filters of a series will produce colony counts within the recommended range. The method of calculating and obtaining a weighted average is as follows:

Volume filtered	Colony count
Volume 1 (mL)	Colony count for filter 1
+ volume 2 (mL)	+ colony count for filter 2
Volume, sum (mL)	Colony count, sum

$$\text{Bacteria (cols./100 mL)} = \frac{\text{Colony count, sum} \times 100}{\text{Volume, sum (mL)}}$$

NOTE: Do not calculate the cols./100 mL for each filter and then average the results.

For example, assume that sample volumes of 1, 5, 20, and 100 mL were filtered and that the total coliform colony counts for the 5-mL and 20-mL samples were 20 and 75, respectively. Calculate as follows:

Volume filtered	Colony count
5 mL	20
+ 20 mL	+ 75
25 mL	95

$$\text{Bacteria (cols./100 mL)} = \frac{95 \times 100}{25} = 380$$

- G. Water samples with a large concentration of suspended sediment may preclude the filtration of adequate sample volumes to produce the ideal number of colonies. Under such circumstances a sample volume may be divided into two or more portions and filtered through separate membrane filters.

For example, assume that the sediment content precludes the filtration of more than 5 mL of a sample (that is, the accumulation of sediment on the membrane filter prevents the development of colonies). However, past analyses indicate that water from the site usually contains 100 to 200 cols./100 mL. Filter four or five 5-mL portions of the sample through separate membrane filters and calculate as follows:

Sample volume (mL)	Colony count
5 (first filter)	6
5 (second filter)	10
5 (third filter)	8
5 (fourth filter)	6
20 (total volume)	30 (total colonies)

Theoretically, an infinite time is required for complete biological oxidation of organic matter; but, for all practical purposes, the reaction may be considered complete in 20 days. However, a 20-day period is too long to wait for results in most instances. Investigations have shown that a reasonably large percentage of the total BOD is exerted in 5 days; consequently, the standard BOD test has been developed on the basis of a 5-day incubation period.

The oxidative reactions involved in the BOD test are a result of biological activity, and the rate at which the reactions proceed is governed to a great extent by the temperature and bacterial population. The temperature effects are held constant by performing the test at 20 °C. Samples that do not contain sufficient bacterial populations (some untreated industrial wastes, disinfected wastes, high-temperature wastes, or wastes with extreme pH values) can be reseeded by adding a population of microorganisms. The seed should be domestic, untreated (not chlorinated), wastewater that has settled at 20 °C for at least 1 hour but no longer than 36 hours.

SAMPLE STORAGE AND PRETREATMENT

Samples for BOD analysis may degrade substantially during storage between collection and analysis, resulting in small BOD values. The reduction of BOD can be minimized by analyzing the sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep the holding time to a minimum.

1. Collect sample in a 1-L plastic bottle.
2. Test for residual chlorine and dechlorinate if present. (See section on BOD sample dechlorination, p. 73.)
3. Store the sample in an ice chest on crushed ice during transit to the lab.

DISSOLVED OXYGEN METER CALIBRATION

The BOD test is based upon determination of DO; consequently, the accuracy of the results is influenced greatly by the care given to its measurements. Since the DO measurements are made using a DO probe equipped with a mechanical stirrer, the DO meter should be calibrated using the air saturated water method.

1. Aerate some deionized water that has been aged at 20 °C for 24 hours.
2. Turn the operating switch to temperature and allow 5 to 10 minutes for the probe to polarize. For needle-movement instruments use the following instructions:
 - A. Start with the switch in the OFF position and adjust the meter pointer to 0 with the screw just below the meter face.
 - B. Turn the switch to RED LINE and adjust the RED LINE knob until the meter needle aligns with the red line mark at the 31 °C position.
 - C. Turn the switch to the ZERO position and adjust to 0 using the ZERO knob.
 - D. Turn the operating switch to TEMPERATURE and allow 5 to 10 minutes for the probe to polarize.
3. Prepare a sodium sulfide solution (DO free solution) and check to insure that the instrument reads zero. If the instrument reading exceeds 0.2

mg/L, take appropriate steps to remedy the problem. (This problem usually is caused by a defective or improperly prepared probe.)

4. Flush the DO probe with deionized water to remove all sodium sulfite residue.
5. Fill a BOD bottle with aerated deionized water making sure no air bubbles are trapped in the BOD bottle.
6. Carefully insert the probe into the air saturated deionized water making sure no air bubbles are trapped below the probe tip.
7. Turn the stirrer on, and for needle-movement instruments, recheck the RED LINE and ZERO readings.
8. Turn the meter operating switch to TEMPERATURE and record the temperature reading to the nearest 0.5 °C.
9. Determine true atmospheric pressure with a pocket altimeter-barometer to the nearest 5 mm of mercury.
10. Refer to the oxygen solubility table to determine the saturated DO value corresponding to the measured temperature and true atmospheric pressure (table 5).
11. Turn the meter to the 0 to 20 scale and adjust the meter to the value determined in step number 10 by using the CAL adjustment knob.

METHODS OF MEASURING BIOCHEMICAL OXYGEN DEMAND

The BOD of some samples may be measured directly; that is to say, the samples for which the 5-day BOD does not exceed 7 mg/L require no dilution. Samples collected at or below point source discharges or samples collected after storm runoff must be diluted to insure that the DO uptake does not exceed 7 mg/L in one or more of the dilution samples.

Direct Method

1. Adjust the temperature of the sample to 20 °C.
2. For all samples that are collected below sewage discharges, test for residual chlorine and dechlorinate, if required. (See section on BOD sample dechlorination, p. 73.)
3. Aerate sample to saturation.
4. Fill a BOD bottle with the aerated sample and immediately insert the DO probe and turn on the mechanical stirrer. Measure and record the DO value and associated BOD bottle number in the proper section of the TX-72Q field form. Note: For all samples collected below sewage discharges, add 0.6 mL of settled sewage to the BOD bottle before filling it with the sample.
5. Turn off the DO stirrer and remove probe. Carefully place a glass BOD stopper in the BOD bottle making sure no air bubbles are trapped inside the bottle.
6. Add some sample water to the stoppered flared mouth of the BOD bottle to provide a water seal. Place a plastic cup over the flared mouth of the BOD bottle to reduce evaporation of the water seal during incubation.
7. Incubate the samples for 5 days at 20 °C.
8. After 5 days, determine the amount of DO remaining in the incubated samples.
 - A. Take the samples from the incubator and remove the plastic cups.
 - B. Hold the BOD bottle in one hand with one finger over the glass stopper and pour off the water seal. Remove the remaining water-seal residue by blotting with a tissue or paper towel.

$$\text{Bacteria (cols./100 mL)} = \frac{30 \times 100}{20} = 150$$

Report 150 cols./100 mL. "Count based on nonideal colony count" or by appropriate remark code.

Fortunately, experience has shown that samples containing large amounts of sediment also contain large amounts of bacteria, especially coliform. Therefore, at some sites, a diluted sample may be used to eliminate the interference of the sediment concentration.

17. After the appropriate calculation has been made, report the number of colonies to whole numbers for values less than 100 and to two significant figures for values of 100 and greater.
18. After counting and before discarding, the bacteria plates are to be autoclaved at 121 °C (250 °F) and 15 lb/in² for 15 minutes.

Field Test for Residual Chlorine and Dechlorination of Sample for Determination of Biochemical Oxygen Demand

Chlorination of water and wastewater destroys the biological population capable of oxidizing the organic matter in the water, oxidizes some of the organic matter, and prevents an accurate measurement of the BOD, unless the chlorine is destroyed at the time of sample collection. Consequently, BOD samples collected downstream from waste-treatment facilities must be tested for residual chlorine at the time of collection. When the field test for residual chlorine is positive, a sufficient reducing agent must be added to the sample in the field to destroy the chlorine. If residual chlorine is found and a dechlorinating agent is added to the sample, the sample must be reseeded with bacteria capable of oxidizing the organic matter (settled non-chlorinated sewage effluent) before BOD is determined.

The following section outlines the field test and dechlorination procedure for residual chlorine.

1. Measure 50 mL of sample into a 100-mL beaker using a pipet, graduated cylinder, or graduated beaker.
2. Add 10 mL 1:1 acetic acid.
3. Add about 1 g of KI and stir until dissolved.
4. Add about 1 g of thyodene and stir until dissolved.
5. If a blue color develops within 5 minutes, dechlorinate the sample by titrating with a Na₂SO₃ solution until the blue color disappears.
 - A. Prepare FRESH a 0.063 N Na₂SO₃ solution. Use a 1-g scoop to measure 1 g of anhydrous Na₂SO₃ into 250 mL deionized water. Use an 8-oz plastic sample bottle to prepare the solution.
 - B. Titrate using a 1-mL syringe. If the titration requires the addition of more than 1 mL, start over at step 1 and prepare a stronger solution of Na₂SO₃--in step 5.A use two scoops of anhydrous Na₂SO₃ sulfite in 250 mL of deionized water (0.126 N). Repeat until the titration volume equals or is less than 1 mL.
6. Calculate the volume of Na₂SO₃ solution required to dechlorinate the 1-L sample from the following equation.

$$\text{Volume Na}_2\text{SO}_3 \text{ required per liter of sample} = 20 \times \text{Volume of Na}_2\text{SO}_3 \text{ required for 50 mL of sample}$$

7. Add the volume of Na_2SO_3 (as determined in step 6) to the 1-L BOD sample.
8. Note on the field notes and the BOD sample container that the qualitative test for residual chlorine was positive and record the normality and volume of Na_2SO_3 added to the 1-L BOD sample.

POST FIELD TRIP INSTRUCTIONS

As the old cliché goes, "the job is not over until the paper work is done." This also applies to a field trip. It is imperative that the samples collected are shipped to the NWQL as soon after collection as possible. It is also imperative that the field data collected be entered into computer storage as soon as possible. Analytical data from the laboratory cannot be approved without this information in computer storage.

The following guidelines are presented to enable data-collection personnel to "complete" the field trip and the required paper work. These guidelines are extracted from the "Quality-Assurance Plan for Water-Quality Activities of the Texas District" and therefore constitute District policy:

1. BOD analyses will be initiated immediately upon return from the field trip. Ideally, BOD's should be set up on Wednesday, Thursday, or Friday of the week the sample was collected to prevent the final reading from falling on a weekend.
2. All chilled samples will be shipped to the laboratory within 3 working days of return from the field.
3. Field sheets (TX-72Q) will be turned in for review, and all field data will be entered into computer storage within 2 working days upon completion of the BOD analysis. If BOD is not determined, field data will be turned in for review and all data entered into computer storage within 5 working days of return from the field.
4. All field sheets will be reviewed by appropriate Subdistrict personnel. This review will be completed within 5 working days from the time the field sheets are turned in for review.

Remember, YOU are responsible for the data you collect. YOU are responsible for making sure that YOU collect the data according to procedures outlined in this report, and that the data YOU collect are entered into computer storage according to the guidelines outlined in this report.

BIOCHEMICAL OXYGEN DEMAND

The biochemical oxygen demand (BOD) is usually defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions. The method of determining BOD consists of placing a water sample in a full, airtight bottle and incubating the bottle under specified conditions for a specific time period. Dissolved oxygen (DO) is measured initially and after incubation. The BOD is computed from the difference between initial and final DO.

- C. Using the BOD bottle number, locate associated TX-72Q field form. Measure and record the DO remaining in the incubated samples in the proper section of the TX-72Q field form.
9. Calculate the 5-day BOD by subtracting the 5-day results from those obtained on day 0. If the sample was reseeded, subtract the average 5-day dilution BOD (blanks) from the 5-day sample BOD.

Dilution Method

1. Prepare dilution water.
 - A. Use deionized water aged at 20 °C for at least 24 hours.
 - B. Place the desired volume of deionized water in a suitable bottle and add 1 mL each of phosphate buffer, magnesium sulfate, calcium chloride, and ferric chloride solutions for each liter of dilution water. (These solutions will be prepared by the District office and can be obtained upon request.)
 - C. Add 2 mL of settled sewage (not chlorinated) per liter to provide the required population of microorganisms.
 - D. Aerate for 10 to 15 minutes after adding the seed.
2. Fill three bottles with dilution water (dilution water blanks) and measure and record the 0-day DO reading and associated BOD bottle numbers. Place glass stoppers in the BOD bottles, add a water-seal cap to prevent evaporation, and place in the incubator. (Siphon the dilution water avoiding contact with air as much as possible.)
3. Use the previously described direct method to set up straight samples.
4. Prepare dilutions that will result in a residual DO of at least 1 mg/L and a DO uptake of at least 2 mg/L after the 5-day incubation period. Several dilutions may be required to obtain DO uptake in this range.
 - A. For BOD's between 60 and 210 mg/L use a sample volume of 10 mL.
 - B. For BOD's between 30 and 105 mg/L use a sample volume of 20 mL.
 - C. For BOD's between 12 and 42 mg/L use a sample volume of 50 mL.
 - D. For BOD's between 6 and 21 mg/L use a sample volume of 100 mL.
 - E. For BOD's between 0 and 7 mg/L use a sample volume of 300 mL.
5. Pipet the sample volume(s) determined in step 4 into clean BOD bottle(s).
6. Fill the bottle(s) with dilution water using a siphon. While filling, the discharge end of the siphon tube should be held below the water surface.
7. Measure the 0-day DO of the dilution samples and record the DO values and associated BOD bottle numbers in the proper section of the TX-72Q field form.
8. Place a glass stopper in the BOD dilution bottles making sure no air bubbles are trapped inside the bottles.
9. Add some dilution water to the stoppered flared mouth of the BOD bottles to provide a water seal. Place a plastic cup over the flared mouth of the BOD dilution bottles.
10. After 5 days, determine the amount of DO remaining in the samples and the dilution water blanks.
 - A. Take the bottles from the incubator and remove the plastic cups.
 - B. Hold the BOD bottle in one hand with one finger over the glass stopper and pour off the water seal. Remove the remaining water-seal residue by blotting with a tissue or paper towel.

- C. Using the BOD bottle number, locate associated TX-72Q field form. Measure and record the DO remaining in the incubated samples and the dilution water blanks in the proper section of the TX-72Q field form.
11. Calculate the 5-day BOD using the Prime program FIELD CALC.CPL or use the following equation:

$$\text{BOD} = \frac{(D1 - D2) - (B)f}{p}$$

- where: D1 = initial DO of diluted sample;
D2 = final DO of diluted sample;
P = decimal volumetric fraction of sample used;
B = average of the three 5-day dilution BOD's (blanks); and
f = ratio of seed in sample to seed in dilution water (blanks).

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