Water Quality Sampling and Shipping Procedures

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Introduction

Several procedures are outlined in this chapter for sampling different types of wastewater in various physical states. These procedures require a plan of action to maximize safety of sampling personnel, minimize sampling time and cost, reduce errors in sampling, and protect the integrity of the samples after collection.

Sampling and Laboratory Testing Methods

Wastewater Analyses

In order to demonstrate an impact, water samples should be collected upstream of the point source, at the point source, and downstream of the point source.

All sample collection must be conducted according to recommendations found in the latest edition of:

1. Standard Methods for the Examination of Water and Wastewater, 18th edition, American Public Health Association, Washington, D.C., 1992, or
2. U.S. Environmental Protection Agency manual, Methods for Chemical Analysis of Water and Wastes, or
3. U.S. Environmental Protection Agency manual, Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents.

Sample containers, holding times, preservation methods and the physical, chemical and microbiological analyses of effluents must meet the requirements specified in regulations published in the 40 Code of Federal Regulations (CFR) Part 136 pursuant to the Federal Water Pollution Control Act, Section 304(g) and be conducted according to this federal regulation. For pollutants not included in 40 CFR Part 136, the sampler may use TNRCC recommended analytical method(s) or an EPA approved method for detecting the specific compound in water/wastewater.

Flow measurements, equipment, installation, and procedures must conform to those prescribed in the Water Measurement Manual, U.S. Department of the Interior Bureau of Reclamation, Washington, D.C., or methods that are equivalent as approved by the TNRCC.

Soil Analyses

For soil samples a background sample should be collected outside of the area that is thought to be impacted. All laboratory testing of soils and solid waste must be conducted according to recommendations found in the latest edition of:

1. Methods of Soil Analysis, edited by Arnold Klute and published by the American Society of Agronomy, Inc. and the Soil Science Society of America, Inc., or
2. Test Methods for Evaluating Solid Waste, Physical and Chemical Methods, Environmental Protection Agency Publication SW-846, or
3. Standard Methods for the Examination of Water and Wastewater, 18th edition, American Public Health Association, Washington, D.C., 1992, or
4. Soil Testing Procedures - Soil Fertility, Texas Agriculture Extension Service, Texas A&M University System, March 1980.

Soil samples are normally sent to the laboratory under field moisture conditions. Usually the laboratory air dries, grounds, and sieves the soil samples. Chemical analyses are generally performed by the laboratory on air-dried samples; therefore, samples generally do not require any preservation. Samples collected for ammonia and nitrate nitrogen analyses should, however, be refrigerated.

Sewage Sludge Analyses

Sewage sludge analyses must be conducted according to the methods found in the latest edition or revision of:

1. Inorganic pollutants -- Test Methods for Evaluating Solid Waste, Physical and Chemical Methods, U.S. Environmental Protection Agency Publication SW-846.
2. Salmonella sp. bacteria -- Part 9260 D.1, Standard Methods for the Examination of Water and Wastewater, 18th edition, American Public Health Association, Washington, D.C., 1992.
3. Total solids, fixed solids, and volatile solids -- Part 2540 G, Standard Methods for the Examination of Water and Wastewater, 18th edition, American Public Health Association, Washington, D.C., 1992.
4. Percent volatile solids reduction -- Percent volatile solids reduction should be calculated using the procedure in Environmental Regulations and Technology - Control of Pathogens and Vectors in Sewage Sludge, EPA-625/R-92/013, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1992.
5. Specific oxygen uptake rate -- Part 2710 B. Standard Methods for the Examination of Water and Wastewater, 18th edition, American Public Health Association, Washington, D.C., 1992.
6. Fecal coliform -- Part 9221 E or Part 9222 D, Standard Methods for the Examination of Water and Wastewater, 18th edition, American Public Health Association, Washington, D.C., 1992.
7. Enteric viruses -- ASTM Method D 4994-89, Standard Practice for Recovery of Viruses From Wastewater Sludge, Annual Book of ASTM Standards: Section 11, Water and Environmental Technology, 1992.
8. Helminth ova -- Yanko, W.A., Occurrence of Pathogens in Distribution and Marketing Municipal Sludges, EPA 600/1-87-014, 1987. NTIS PB 88-

154273/AS, National Technical Information Service, Springfield, Virginia.

Sampling Equipment

This section describes EPA-approved equipment and procedures for obtaining representative samples. The information in this section is general in nature. Since each specific sampling situation is unique, the equipment and procedures described may need to be modified appropriately in an actual use situation to ensure that representative samples are collected.

All samplers must be thoroughly cleaned before use; it is recommended that they be washed, triple rinsed with water, and then rinsed with distilled water. This will help prevent cross contamination of samples.

Pond Sampler

Scope and Application - The pond sampler consists of a glass or plastic beaker clamped to the end of a 2 or 3 piece telescoping aluminum or fiberglass pole which serves as the handle. This instrument is used to collect samples of liquids, free-flowing slurries, and samples from sample points that are difficult to access.

General Comments and Precautions -

Do not use a plastic beaker to sample wastes containing organic materials. A glass beaker should always be used in this situation.

Procedure -

1. Clean beaker, clamp, and handle.
2. Assemble sampler by bolting adjustable clamp to the pole. Place beaker in clamp and fasten shut.
3. Turn sampler so the mouth of the beaker faces down and insert into waste material. Turn beaker right side up when dipper is at desired depth. Allow beaker to fill completely as shown by the cessation of air bubbles.
4. Raise pond sampler and transfer sample to container.

Sludge Judge

Scope and Application - The sludge judge is a 7/8" inside diameter clear plastic pipe consisting of three threaded joints with a total length of 15 feet. The total length of pipe is calibrated in one-foot intervals. It can be used to measure sludge depths.

Procedure -

1. Assemble sludge judge by threading the three separate joints together.
2. Slowly lower the sludge judge to the bottom.
3. Withdraw the sludge judge in a vertical manner. A plastic ball will seat in the

bottom of the sludge judge and will prevent the discharge of the sludge and water captured in the judge.

4. Read the volume or depth of sludge which was removed in the captured column. Also note the total water depth to calculate the depth occupied by the sludge blanket.
5. Place the bottom of the judge against a firm object and the plastic ball stem will cause the ball to unseat, and the contents will discharge from the pipe.
6. Take samples in multiple locations.
7. Disassemble, clean and return to carrying case.

ISCO Sampler

Scope and Application - The ISCO wastewater sampler is a portable device designed to collect up to 24 separate sequential samples of a predetermined volume from a liquid source. The samples can be collected on a time proportional basis using the internal sampler timing circuitry or on a flow proportional basis using flow inputs from an external flow meter. The interval in minutes or flow pulses remaining until the next sample is to be taken is displayed by an LED readout. The suction line is purged before and after each sample is taken to minimize cross contamination of samples. The flow rate of the pump is typically 1400 ml/min. to prevent sedimentation of large heavy particles during the sampling cycle. The controls and electronics are housed in a water-tight stainless steel container. Power sources can be either a "line" source of 117 volts AC, 50/60 Hz or an external battery of 12 volts DC. The sampler is basically made up of four sections which are held together by a series of clasps. These four sections are: the cover; the pump and control section; the distributor plate; and the sample bottle tub with a center section which will hold 10 pounds of uncontained cubed ice. The sampler is ideal for collecting 24-hour composite samples and can be used for a variety of situations.

Procedure -

1. Charge the external battery the day before planned use of the sampler.
2. Clean sampler, sample bottles and suction line. If additional line is available, it may be preferable to replace line to prevent cross contamination; however, that will depend upon the parameters being analyzed.
3. Locate sampler in a secure and safe location. Place an adequate amount of ice in center of tub.
4. Program the sampler according to mode desired. Refer to instructions in manual and/or inside the top cover of the unit.
5. Collect sample. One can periodically check the sampler to make sure that samples are being collected and to replenish ice as necessary.
6. Remove sample bottles at conclusion of sampling period and composite sample.
7. Clean sampler and bottles and store.

Sewage Sampler

Scope and Application - Sampler is designed for underwater sampling of sewage and/or wastewater without surface contamination. The outer bottle is resistant to corrosive agents and normally constructed of nickel plated brass. This outer bottle has a machine threaded cover which insures an air-tight closure with the outer bottle. A sample bottle (up to 300 ml) is positioned on a built-up platform in the lower section of the outer bottle. The cover of the outer bottle has a filling tube which fits into the sample bottle. The sampler is available with or without a messenger to operate the valve assembly located on the cover of the outer bottle. This sampler can be used to collect samples at varying depths.

Procedure -

1. Place a clean sample bottle in sewage sampler and lower the unit to depth desired.
2. Activate valve assembly to allow sample to enter bottle and fill. Filling will be complete when bubbles floating to surface cease.
3. Remove sampler to surface and remove sample bottle for analysis.
4. Clean sampler and sample bottle.

Bucket

Scope and Application - Buckets are used for collection of water samples. Since they are constructed of unbreakable material, they may be used in a variety of sampling situations.

Procedure -

1. Clean the bucket.
2. The bucket may be lowered by rope to the sampling location or the bucket may be used by hand to collect the sample.
3. Rapidly, pour the liquid into the sample container. If any suspended matter begins to settle to the bottom, swirl the sample in the bucket to re-suspend the solids.

Sample Storage Containers

Scope and Application - In many instances, the sample storage container may be used in the sample collection. This may be advantageous because the transfer of sample from the collection vessel to storage container is eliminated. A list of approved containers is found in Table 1 at the end of this section.

General Comments and Precautions -

1. Rigid sample containers with wide mouths are the most convenient for use as samplers. Often, a cubitainer may be used to sample directly from the effluent stream, however, this may be difficult if effluent stream velocities are high.
2. Glass jars are required to be pre-cleaned if organic analyses are to be performed. Cubitainers do not need cleaning.

Sampling Procedures -

1. Clean sample container, if necessary.
2. Dip container into material to be sampled.
3. Close container.

Table 1 - Required Containers, Preservation Techniques, and Holding Times (Per 40 CFR Part 136.3, Table II)

Parameter No./Name	Container	Preservation	Maximum holding time
Bacteria Tests: Coliform, fecal and total	P, G	Cool, 4EC, 0.008% NaS_2O_3	6 hours.
Fecal streptococci	P, G.	Cool, 4EC, 0.008% NaS_2O_3	6 hours
Aquatic Toxicity: Toxicity, acute and chronic.	P, G	Cool, 4EC	6 hours.
Inorganic Tests: Acidity	P, G	Cool, 4EC	14 days
Alkalinity	P, G	Cool, 4EC	14 days
Ammonia	P, G	Cool, 4EC, to pH <2	28 days.
Biochemical oxygen demand	P, G	Cool, 4EC	48 hours.
Boron	P, PFTE, or Quartz.	HNO_3 to pH <2	6 months.
Bromide	P, G	None required	28 days
Biochemical oxygen demand, carbonaceous.	P, G	Cool, 4EC	48 hours.
Chemical oxygen demand	P, G	Cool, 4EC, to pH <2	28 days
Chloride	P, G	None required	28 days
Chlorine, total residual.	P, G	None required	Analyze immediately
Color	P, G	Cool, 4EC	48 hours.
Cyanide, total and amenable to chlorination.	P, G	Cool, 4EC, NaOH to pH>12, 0.6g ascorbic acid	14 days
Fluoride	P, G	None required	28 days
Hardness	P, G	HNO_3 to pH<2, to pH<2	6 months
Hydrogen ion (pH)	P, G	None required	Analyze immediately
Kjeldahl and organic nitrogen.	P, G	Cool, 4EC, to pH <2	28 days
Nitrate	P, G.	Cool, 4EC	48 hours
Nitrate-nitrite	P, G.	Cool, 4EC, to pH<2	28 days.
Nitrite.	P, G	Cool, 4EC	48 hours
Oil and grease	G	Cool, 4EC, HCl or to pH<2	28 days.
Organic Carbon	P, G	Cool, 4EC, HCl or H_2SO_4 to pH<2	28 days.
Orthophosphate	P, G	Filter immediately, Cool, 4EC	48 hours
Oxygen, Dissolved - Probe	G Bottle and top	None required	Analyze immediately.
Oxygen, Dissolved - Winkler	G Bottle and top	Fix on site and store in dark	8 hours.
Phenols	G only	Cool, 4EC, to pH<2	28 days.
Phosphorus (elemental)	G	Cool, 4EC	48 hours
Phosphorus, total	P, G	Cool, 4EC, to pH<2	28 days

Parameter No./Name	Container	Preservation	Maximum holding time
Residue, total	P, G	Cool, 4EC	7days
Residue, Filterable	P, G	Cool, 4EC	7days
Residue, Nonfilterable (TSS).	P, G	Cool, 4EC	7days
Residue, Settleable	P, G	Cool, 4EC	48 hours
Residue, volatile.	P, G	Cool, 4EC	days
Silica	P, PFTE, or Quartz.	Cool, 4EC	28 days.
Specific conductance	P, G	Cool, 4EC	28 days.
Silica	P, PFTE, or Quartz	Cool, 4EC	28 days.
Sulfate.	P, G	Cool, 4EC	28 days.
Sulfide	P, G	Cool, 4EC, add zinc acetate plus sodium hydroxide to pH>9.	7 days
Sulfite	P, G	None required	Analyze immediately
Surfactants	P, G	Cool, 4EC	48 hours
Temperature	P, G	None required	Analyze immediately
Turbidity	P, G	Cool, 4EC	48 hours
Metals: Chromium VI	P, G	Cool, 4EC	24 hours.
Mercury	P, G	HNO_3 to pH<2	28 days
Metals, except boron, chromium VI, and mercury	P, G.	HNO_3 to pH<2	6 months
Organic Tests: VOA (Volatile Organic)	G, Telflon-lined septum, no air bubbles	Cool, 4EC, 0.008% $Na_2S_2O_3$	14 days
BTEX (Benzene, Tolulene, Ethlybenzene, Xylene	G, Telflon-lined septum, no air bubbles	Cool, 4EC, 0.008% $Na_2S_2O_3$	14 days
Semi-volatiles (Includes acid and base neutral extractables, polynuclear aromatics, haloethers, and phenol compounds)	G, Telflon-lined cap.	Cool, 4EC, 0.008% $Na_2S_2O_3$	7 days until extraction, 40 days after extraction
Phenols	G, Telflon-lined cap.	Cool, 4EC, 0.008% $Na_2S_2O_3$	7 days until extraction, 40 days after extraction
PCBs	G, Telflon-lined cap	Cool, 4EC	7 days until extraction, 40 days after extraction
Pesticides Tests: Pesticides / Herbicides	G, Telflon-lined cap	Cool, 4EC, pH 5-9	7 days until extraction, 40 days after extraction
Radiological Tests: Alpha, beta, and radium	P, G	HNO_3 to pH<2	6 months

Equipment Decontamination

All reusable sampling equipment should be properly cleaned before going into the field. Sample containers for some organic analyses should also be cleaned. When sampling and field activities are completed, all equipment including safety equipment and field instrumentation should be decontaminated before leaving the site. The purpose of the field decontamination procedures is to protect the field equipment from cross contamination. It will also make it easier to clean the equipment before the next site inspection. The field decontamination procedure should provide a quick method of removing most sample residues from the equipment. Rinsing and/or wiping with paper towels is usually sufficient for field decontamination.

The sampler should consider designating some non-disposable samplers as "clean" or "environmental" sampling equipment. Generally, low (ppm) concentrations occur in contaminated ground or surface waters. If some samplers are designated for this type of sampling, there will be less chance of cross contamination from inadequately decontaminated sampling equipment.

- **Sample Equipment and Containers** - Sampling equipment should be cleaned with a non-phosphate detergent in hot water, tap water rinsed, solvent rinsed if necessary, and a final distilled water rinse. The best solvent to use will depend on the parameters that are requested, see Table 2 below. Methylene chloride, acetone, hexane and methanol are all appropriate solvents if semi-volatile organics are to be analyzed. If volatiles are to be analyzed, ultra pure methanol is the solvent of choice. Acetone may also be used if it is not an analyte of interest.

Table 2 - Type Container Rinse Required Per Parameter

PARAMETER	NONE	HEXANE	MCL	COMMENTS
BOD	P			
TSS	P			
COD	P			
TOC	P			
NH3N	P			
OIL AND GREASE		G		
PHENOLS			G	
METALS	P			
VOLATILE ORGANICS	VOA			pretreat w/HCl 2drops

PARAMETER	NONE	HEXANE	MCL	COMMENTS
SEMI-VOLATILE ORGANICS			G	
PESTICIDES			G	
TPH (fill 3/4 full of sample)	VOA			pretreat w/ NaHSO4
CYANIDE	P			
BTEX	VOA			pretreat w/HCl 2drops

G - glass
P - plastic

- **Instruments** - Decontamination of instruments should consist of a distilled water rinse of the probe or portion of the probe which was in contact with the sample. If contamination is difficult to remove, consult the owner's manual for specific instructions. Grossly contaminated samples should not be measured for field parameters if possible. Between use, probes should be stored according to manufacturer's instructions.
- **Safety Equipment** - Safety equipment should be decontaminated in the field. Most dealers of rubberized products have their own mild detergents. If not, use the same mild detergent used to clean sampling equipment.

Sampling Procedures

Sampling Safety

Proper safety precautions must always be observed when sampling. In all cases, the person collecting a sample must be aware of the potential dangers from the material to be sampled and from the site location. The background information obtained about the wastewater should be helpful in deciding the extent of sampling safety precautions to be observed. In some situations, obtaining a sample using normal sampling procedures may be too dangerous and should not be attempted.

The following general safety rules and practices should be implemented whenever sampling:

1. Each sample should be handled with care to minimize the risk of personal exposure.
2. If special handling of the sample is appropriate, you must also warn the laboratory which receives the sample.
3. Approved and appropriate safety equipment, such as safety glasses/goggles, hard hats, boots, gloves, and respirators, must be worn in areas where hazardous conditions are suspected. In addition, eye and hand protection should be worn when handling acidic, caustic, or other hazardous liquids (including preservative

chemicals).

Sample Handling

The portion of sample to be analyzed is transferred to the appropriate containers. It may be necessary to transfer the sample into two or more containers if multiple analyses will be requested and they require different preservatives or different container materials.

Preservatives should be added to water samples as soon as practical after collection (in general, within 15 minutes). Never add a chemical preservative to a sludge sample or any sample containing large amounts of solids. A list of preservation techniques and holding times is provided in Table 1 on Page 9.

Sufficient volume of sample must be collected for all the analytical needs. Table 3 below gives general guidelines for volume requirements. As each portion of sample is transferred to the various containers, it may be necessary to stir or agitate the samples so that suspended matter remains evenly distributed.

Table 3 – Minimum Sample Volumes

Parameter	**Required Sample Volume (ml)**
Alkalinity	200
Ammonia	500
BOD	1000
COD	100
Chloride	200
Chlorine	500
Cyanide	500
Fluoride	300
pH	100
Kjeldahl nitrogen	500
Nitrate-Nitrite	200
Oil and grease	1000
Orthophosphate	100
Phenols	500
Specific Conductance	100
Total Phosphorus	100
Total Residue	200
TDS	200
TSS	500
Sulfate	200
Sulfide	200

TOC	200

Table 3 – Minimum Sample Volumes (cont'd)

Parameter	**Required Sample Volume (ml)**
Metals	
Hexavalent Chromium	300
All Others	1000
Organics	
Volatiles	40(use VOA bottle)
Semi-volatiles	1000
Pesticides	1000

Field Log Book

All information pertinent to a field survey and/or sampling must be recorded in a log book. Entries in the log book should include the following types of information:

- Purpose of sampling (e.g., compliance, annual, etc.)
- Location of sampling (e.g., industrial, domestic, etc.) and address
- Name, address, affiliation and title of personnel contacted
- Type of process (if known) producing wastewater
- Type of waste (e.g., sludge, wastewater, etc.)
- Type of treatment system
- Number and volume of sample taken
- Description of sampling point
- Date and time of collection
- Collector's sample identification number(s)
- Chain of Custody tag numbers
- Sample distribution (e.g., laboratory, permittee, etc.)
- References such as maps or photographs of the sampling site
- Field observations
- Any field measurements made such as pH, temperature, etc.
- Calibration record of field equipment
- Permit number (if applicable)

Sampling situations vary widely. No general rule can be given as to the extent of information that must be entered in the log book. A good rule, however, is to record sufficient information so that someone can reconstruct the sampling situation without relying on the collector's memory.

Sample Identification and Seals

Immediately after the samples have been collected and placed in the proper containers, it

is necessary to label. Samples are labeled by writing the associated chain-of-custody identifier number on the sample container.

Chain-of-Custody

After the samples have been labeled and sealed, they should be stored in a cooler which is kept in view or within a limited access, locked storage area until custody is relinquished and formal documentation of the transfer is completed. Chain-of-Custody (COC) requires permanent records of all sample handling and shipment. Chain-of-custody procedures must be used to ensure sample integrity and legally and technically defensible data. The sampler is responsible for initiating chain-of-custody procedures and documenting the sample source.

In completing the tag, care should be utilized to insure that all necessary information is correct and is legibly entered onto the tag with a black waterproof ink pen.

Shipping of Samples

Samples should be delivered to the laboratory for analysis as soon as possible - usually within one day after sampling. The samples must be accompanied by the chain-of-custody record and by a sample analysis request sheet. The samples must be delivered to the person in the laboratory authorized to receive samples (often referred to as the sample custodian).

When a sample is shipped to the laboratory, it must be packaged in a proper shipping container to avoid leakage and/or breakage.

All packages must be accompanied by the chain-of-custody record. Complete address of the sender and the receiving laboratory must legibly appear on each package. When sent by common carrier, obtain a copy of the bill of lading. Receipts and bill of lading copies may be used as part of the chain-of-custody documentation.

Quality Assurance and Quality Control Practices

All quality assurance/quality control practices must strictly adhere to those outlined in each EPA approved analytical method. Assurance of the quality of all effluent measurements is performed through the use of blanks, standards, duplicate analyses, and spikes. At a minimum, the quality assurance requirements specified in 30 TAC §319.9(c) must be used.

Laboratories must routinely use and document intra-laboratory quality control practices as recommended by the U. S. Environmental Protection Agency manual, Handbook for Analytical Quality Control in Water and Wastewater Laboratories. These practices will include the use of internal quality control check samples.

Quality control guidelines for sampling are based on the references listed at the end of this section.

If method specific or program specific QC requirements are more stringent than those listed in here, then the method specific QC or program specific QC requirements will supersede these guidelines.

For some analytical procedures, such as oil and grease, pesticides, semi-volatile and volatile organics, replicates must be collected to provide the laboratory with sufficient sample to perform the appropriate QC, since the entire sample quantity in a single container may be consumed by the analytical procedure.

The frequencies listed in the definitions below only apply to CBOD, BOD, TSS and Ammonia Nitrogen. For all other parameters, the frequency shall be one in every 10 sampling events or one per month, whichever comes first.

Definitions

Environmental Sample - a representative portion of any material (aqueous, nonaqueous, or mixed matrix) collected from any source to determine composition or contamination. It may be collected for laboratory analysis or for analysis in the field.

Equipment Blank - An equipment blank applies to any matrix. It is a sample of reagent water poured into or over a sampling device or pumped through the sampling device. An equipment blank is collected in the same type of container as the environmental sample, preserved in the same manner, and analyzed for the same parameters. It should be collected immediately after the equipment has been decontaminated. If more than one type of container is used (i.e., VOA, metals, etc.), then one container of each type must be filled as an equipment blank. The same paperwork should be filled out for the equipment blank as for the environmental sample. An equipment blank is not necessary when disposable sampling equipment is used.

Frequency - An equipment blank should be collected per equipment type, per matrix, per 1 in every 10 sampling events.

Field Blank - A field blank applies to any matrix except soils. It is used to assess the potential introduction of contaminants from field sources such as air borne materials, containers, preservatives, and contaminants that are not representative of the site. A field blank consists of reagent grade (ASTM Type II) water poured into a sample container. It is handled like an environmental sample (same type of container, preservative, if applicable, etc.) and is analyzed for the same parameters. If several different containers are used, a blank must be prepared for each container type. For example, in the Public Water Supply Program, different containers or preservatives are used to collect SOC 1, SOC 3, and SOC 5; therefore, individual field blanks for SOC 1, SOC 3 and SOC 5 must be included. A field blank should be labeled on the container and paperwork filled out the same as for the environmental sample. It should be shipped under chain-of-custody (when

appropriate) and submitted with a request for analysis. The analyses requested should be the same as for the environmental sample.

Frequency - One set of field blanks should be included for 1 in every 10 sampling events, per matrix type.

Field Duplicate - A field duplicate applies to any matrix and to field measurements for chlorine residual, dissolved oxygen, pH or temperature. It is used to document the precision of the environmental sample collection process. Duplicates are collected either simultaneously (preferably) or in immediate succession to the original environmental sample, whichever is possible under field conditions. The field duplicate should be collected, handled and analyzed in the same manner as the original environmental sample. The environmental sample should be submitted under separate chain-of-custody. A duplicate should be collected for each container type used to collect the environmental sample. For field measurements, precision limits should be applied on-site to determine if the measurement is acceptable. Until sufficient data have been generated to calculate the precision for each instrument, use either the precision specifications listed by the instrument manufacturer, or the current edition of Standard Methods for the Examination of Water and Wastewater, Section 1-4, Table 1020-I.

Frequency - A field duplicate should be collected for 1 in every 10 sampling events, per matrix type.

Field Measurement - an analysis conducted in the field (in situ) on an environmental sample. Typical field measurements are chlorine residual, dissolved oxygen, pH and temperature.

Matrix - defined by EPA as the component or substrate (e.g., surface water, drinking water, effluent waters, soil, sediment, tissue, etc.) which contains the analytes of interest. In the TNRCC, a matrix is defined as a medium for which a body of regulations governing testing exists. In other words, if a program exists for the medium (e.g., wastewater liquid, wastewater sludge, drinking water, surface water), that medium should be considered a matrix. A matrix is generally either soil or water. Additional matrices include oils, solvents or anything that is not soil or water.

Matrix Duplicate - A matrix duplicate applies to organic analyses or any matrices except soils and *is required for organic sample collection only*. A matrix duplicate consists of additional environmental samples collected at one site for organic analysis. The additional environmental samples are needed by the laboratory to provide a sample for the method required spiked samples. One environmental sample during each sampling event must be collected in triplicate for volatiles using 40-mL VOA vials and in triplicate for semi-volatiles

or pesticides using one liter (1-L) glass containers. One or two additional containers (depending on the program) that are the same as used for collecting the original environmental sample are used for each analysis. For example, for SOC 1, SOC 3 and SOC 5 in the Public Water Supply Program, two containers would be filled for each analysis for a total of six containers and preservative added just as for the original environmental samples. For oil and grease, three containers would be filled. The chain-of-custody forms or sample submission forms for samples submitted as the matrix duplicate should be filled out the same as the original sample. The paperwork should indicate that additional quantity of the original sample was collected for the matrix spike and/or matrix spike duplicate. The sample ID number should be written on the original sample container and on the matrix duplicate sample containers.

Frequency - A matrix duplicate should be collected for 1 in every 10 sampling events. However, if the environmental samples are for groundwater monitoring at a particular site, then one of the environmental samples from the site should be collected in triplicate for volatiles. A matrix duplicate should be collected during every sampling event when *groundwater monitoring* is performed.

Reagent Water - Is deionized, distilled, or otherwise purified water which meets ASTM standards and is free of contaminants that may interfere with the analytical test in question.

Trip Blank - A trip blank is used *only when a volatile sample is taken* and is analyzed only for volatile analytes. It is used to check for possible sample contamination that may originate from site conditions or from sample transport or shipping. A trip blank is not opened in the field.

Frequency - One trip blank should be placed in each cooler that contains samples to be analyzed for volatiles.

QC Sampling for Municipal/Industrial Sites

Some QC samples apply only to specific analyses (e.g., volatile organic compounds) and therefore are not required if the analysis is not requested. The recommended QC tests for sampling at municipal and industrial sites are summarized in Tables 4 and 5 below.

For some analytical procedures, such as oil and grease, pesticides, semi-volatile and volatile organics, replicates must be collected to provide the laboratory sufficient sample to perform the appropriate QC, since the entire sample quantity in a single container may be consumed by the analytical procedure.

If there are multiple sampling locations at one site, each of the sampling locations should

be counted as a separate set of samples when determining whether QC tests need to be conducted.

References

30 TAC §319.9, Table 3.
Chapter Nine, Section 9.2, EPA SW 846, Revision 0, September 1986.
Chapter One, Section 1.0, EPA SW 846, Revision 1, July 1992.
Handbook for Analytical Quality Control in Water and Wastewater Laboratories, Chapter 10, EPA-600/4-79-019.

Table 4-Required QA Sampling for Municipal

Wastewater Collection QA/QC Form Municipal						
	Field Dup **1**	Matrix Dup **2**	Field Blank **3**	Trip Blank **4**	Equip. Blank **5**	Notes
pH	**X**					
Cl_2	**X**		**X**		**X**	
D.O.	**X**					
CBOD	**X**		**X**		**X**	
TSS	**X**		**X**		**X**	
VSS	**X**		**X**		**X**	
NH_3-N	**X**		**X**		**X**	
FECAL	**X**		**X**		**X**	

Field Duplicate - Just take an additional sample, either at the same time as, or right after, the first one.
Field Blank - Fill containers in the field with Type II* water.
Equipment Blank - After equipment has been cleaned, pour Type II* water over equipment, into container.

* Note: Reagent grade water types

Type II water - used for wet chemistry, including oil & grease and phenols.
Volatile organic water - used for VOA samples
Semi-volatile organic water - used for semi-volatile and pesticide samples
Metal free water - used for metals samples.

Table 5-Required QA Sampling for Industrial

Wastewater Collection QA/QC Form Industrial						
	Field Dup **1**	Matrix Dup **2**	Field Blank **3**	Trip Blank **4**	Equip. Blank **5**	Notes
pH	**X**					
Oil/Grease	**X**	**X**	**X**			
CBOD	**X**		**X**		**X**	
COD	**X**		**X**		**X**	
TOC	**X**		**X**		**X**	
TSS	**X**		**X**		**X**	
VSS	**X**		**X**		**X**	
VOA	**X**	**X**	**X**	**X**	**X**	
SemiVOA	**X**	**X**	**X**		**X**	
Metals	**X**		**X**		**X**	
Phenols	**X**	**X**	**X**		**X**	

Field Duplicate - Just take an additional sample, either at the same time as, or right after, the first one.
Matrix Duplicate -Organics only!! Just like a field duplicate, except label extra container(s) "Matrix Duplicate".
Field Blank - Fill containers in the field with the applicable reagent grade water type* .
Trip Blank - Volatiles only!! Volatile organic free-reagent grade water.
Equipment Blank -After equipment has been cleaned, pour the applicable reagent grade water* over equipment, into container.

* Note: Reagent grade water types
Type II water - used for wet chemistry, including oil & grease and phenols.
Volatile organic water - used for VOA samples
Semi-volatile organic water - used for semi-volatile and pesticide samples
Metal free water - used for metals samples.

Field Analyses

Upon arrival at a sampling site, record visual observations on the appearance of the water and other information related to water quality and water use.

Water Appearance	Color, unusual amount of suspended matter, debris or foam, etc.
Weather	Recent meteorological events that may have impacted water quality; heavy rains, cold front, very dry, very wet, etc.
Biological Activity	Excessive macrophyte, phytoplankton or periphyton growth, The observation of water color and excessive algal growth is very important in explaining high chlorophyll *a* values. Other observations such as fish, birds and spawning fish are noted.
Unusual Odors	Hydrogen sulfide odor, musty odor, sewage odor, etc.
Watershed or Instream Activities	Instream or drainage basin activities or events that are impacting water quality; bridge construction, shoreline mowing, livestock watering upstream, etc.
Record of Pertinent Observations Related to Water Quality and Stream Uses	If the water quality conditions are exceptionally poor, note that standards are not met in the observations, for example, dissolved oxygen is below minimum criteria. Uses-swimming, wading, boating, fishing, irrigation pumps, navigation, etc. Eventually, for setting water quality standards, the level of use will be based on comments related to the level of fishing and swimming activities observed at a station.
Specific Sample Information	Specific comments about the sample itself that may be useful in interpreting the results of the analysis; number of sediment grabs, or type and number of fish in a tissue sample. If the sample was collected for a complaint, or fish kill, make a note of this in the observation section.
Missing Parameters	If a scheduled parameter or group of parameters are not collected, make some note of this in the comments.

The most common field measurements are temperature, pH, residual chlorine, dissolved oxygen and flow.

All field meters should be calibrated prior to sampling. The maintenance and calibration performed on the instrument should be recorded in the field log book. A supply of replaceable parts should be carried into the field with each meter. The meter should be checked just prior to taking the field measurement. The complete calibration does not need to be performed; it is usually sufficient to follow the manufacturers recommendations for instrument checks. The results of the meter checks and the field sample results should be recorded in the field log book.

Instantaneous Flow Measurement

Flow Measurement Equipment

Flow meter - One of the following or an equivalent:

- Marsh-McBirney Electronic meter
- Montedoro-Whitney Electronic meter
- Price Pigmy meter (with timer and beeper)
- Price meter, Type AA (with Columbus weight)

Additional Equipment

- Top-setting wading rod (preferably measured in tenths of feet).
- Tape measure (with gradations every tenth of a foot).

Flow Measurement Procedure (USGS, 1969)

Select a stream reach with the following characteristics:

- Straight reach with laminar flow (threads of velocity parallel to each other) and bank to bank. These conditions are typically found immediately upstream of riffle areas or places where the stream channel is constricted.

- The site should have an even streambed free of large rocks, weeds, and protruding obstructions that create turbulence. The site should not have dead water areas near the banks, and a minimum amount of turbulence or back eddies.

Flat Streambed Profile (cross section)

Stretch the measuring tape across the stream at right angles to the direction of flow. When using an electronic flow meter, the tape does not have to be exactly perpendicular to the bank (direction of flow). When using a propeller or pigmy type meter, however, corrections for deviation from perpendicular must be made.

If necessary and possible, modify the measuring cross section to provide acceptable conditions by building dikes to cut off dead water and shallow flows, remove rocks, weeds, and debris in the reach of stream one or two meters upstream from the

measurement cross section. After modifying a streambed, allow the flow to stabilize before starting the flow measurement.

Record the following information.

- Location
- Date
- Time measurement is initiated and ended
- Name of person(s) measuring flow
- Note if measurements are in feet or meters
- Total Stream Width and Width of Each Measurement Section
- Flow measuring method used
- Flow measuring equipment used
- For each cross section, record the mid-point, section depth and flow velocity

If the *stream width is less than 5 feet*, use flow sections with a width of 0.5 feet. See Example 1 at the end of this section. If the *stream width is greater than 5 feet*, the minimum number of flow measurements is 10. The preferred number of flow measurement cross sections is 20-30. See example 2 at the end of this section: The total stream width is 26 feet with 20 measurements, section widths will be 1.3 feet (26/20 = 1.3).

Determining the Mid-Point of the Cross Section

To find the mid-point of a cross section, divide the cross section width in half. Using Example 2 at the end of this section; The total stream width is 26 feet with 20 cross sections and each cross section width is equal to 1.3 feet. Divide 1.3 feet in half and the mid-point of the first section is 0.65 feet. In this example the tape at waters edge is set at zero (0) feet. By adding 0.65 to zero the mid-point of the first section is 0.65 feet. Each subsequent mid-point is found by adding the section width (1.3 feet) to the previous mid-point. For example; MIDPOINT #1 is 0.65 + 0.0 = 0.65; MIDPOINT #2 is 0.65 + 1.3= 1.95 feet; MIDPOINT #3 is 1.95 + 1.3 = 3.25 feet and ....MIDPOINT # 20 is 24.05 +1.3.

Using a top setting wading rod, measure the depth at the mid-point of the first flow measurement section and record to the nearest 0.01 feet.

Adjusting the Sensor Depth at a Cross Section

Adjust the position of the sensor to the correct depth at each mid-point. The purpose of the top setting wading rod is to allow the user to easily set the sensor at 20%, 60% and 80% of the total depth. The total depth can be measured with the

depth gauge rod. Each single mark represents 0.10 foot, each double mark represents 0.50 foot, and each triple mark represents 1.00 foot (see Figure 1 below).

For Depths # 2.5 Feet

If the depth is less than 2.5 feet, only one measurement is required at each measurement section. To set the sensor at 60% of the depth, line up the foot scale on the sliding rod with the tenth scale in the top of the depth gauge rod. If, for example, the total depth is 2.0 feet, then line up the 2 on the foot scale with the 0 on the tenth scale (Marsh McBirney 1990).

For Depths $ 2.5 Feet

If the depth is greater than 2.5 feet, two measurements should be taken at 20% and 80% of the total depth. To set the sensor at *20%* of the depth, multiply the total depth by two. For example, the total depth is 2.7 feet the rod would be set at 5.4 feet (2.7 x 2). Line up the 5 on the foot scale with the 4 on the tenth scale.

To set the sensor at 80% of the depth, divide the total depth by two. For example, the total depth is 2.7 feet the rod would be set at 1.35 feet (2.7/2). Line up the 1 on the foot scale with the 0.35 on the tenth scale (see Figure 1) (Marsh McBirney 1990). The average of the two velocity measurements is used in the flow calculation. See Example 3 for an example of a flow form recording measurements for depths greater than 2.5 feet.

NOTE: The point where the rod is set for 20 and 80% of the depth will not equal the values derived from calculating 20 and 80% of the total depth.

Measuring Velocity

- Position the meter at the correct depth and place at the mid-point of the flow measurement section. Measure and record the velocity and depth. The wading rod is kept vertical and the *flow sensor kept perpendicular to the tape* rather than perpendicular to the flow while measuring velocity with an electronic flow meter. When using a propeller or pigmy-type meter, however, the instrument should be perpendicular to the flow.
- Permit the meter to adjust to the current for a few seconds. Measure the velocity for a minimum of 20 seconds with the Marsh-McBirney and Montedoro-Whitney meters. Measure velocity for a minimum of 40 seconds (preferably 2 minutes with the Price and pigmy meters).
- When measuring the flow by wading, stand in the position that least affects the velocity of the water passing the current meter. The person wading stands a

minimum of 1.5 feet downstream and off to the side of the flow sensor.

- A flow sensor, equipped with cable and weight may be used to measure flows where the water is too deep to wade. Follow the procedure involving meters attached to wading rods.
- Report flow values less than 10 ft^2 /s to two significant figures. Report flow values greater than 10 ft^3/s to the nearest whole number, but no more than three significant figures.
- In cases where the flow is low and falling over an obstruction, it may be possible to measure the flow by timing how long it takes to fill a bucket of known volume.

Calculating Flow

To calculate flow, multiply the width x depth (ft^2) to derive the area of the flow measurement section. The area of the section is then multiplied by the velocity (ft/s) to calculate the flow in cubic feet per second for that flow measurement section. When flow is calculated for all of the measurement sections, they are added together for the total stream flow (see Figure 2 below).

Q=Total Flow (or discharge), W=Width, D=Depth, V=Velocity.

$$Q = (W_1 * D_1 * V_1) + (W_2 * D_2 * V_2) + ... (W_n * D_n * V_n)$$

Figure 1. Top-Setting Wading Rod
(Marsh-McBirney)

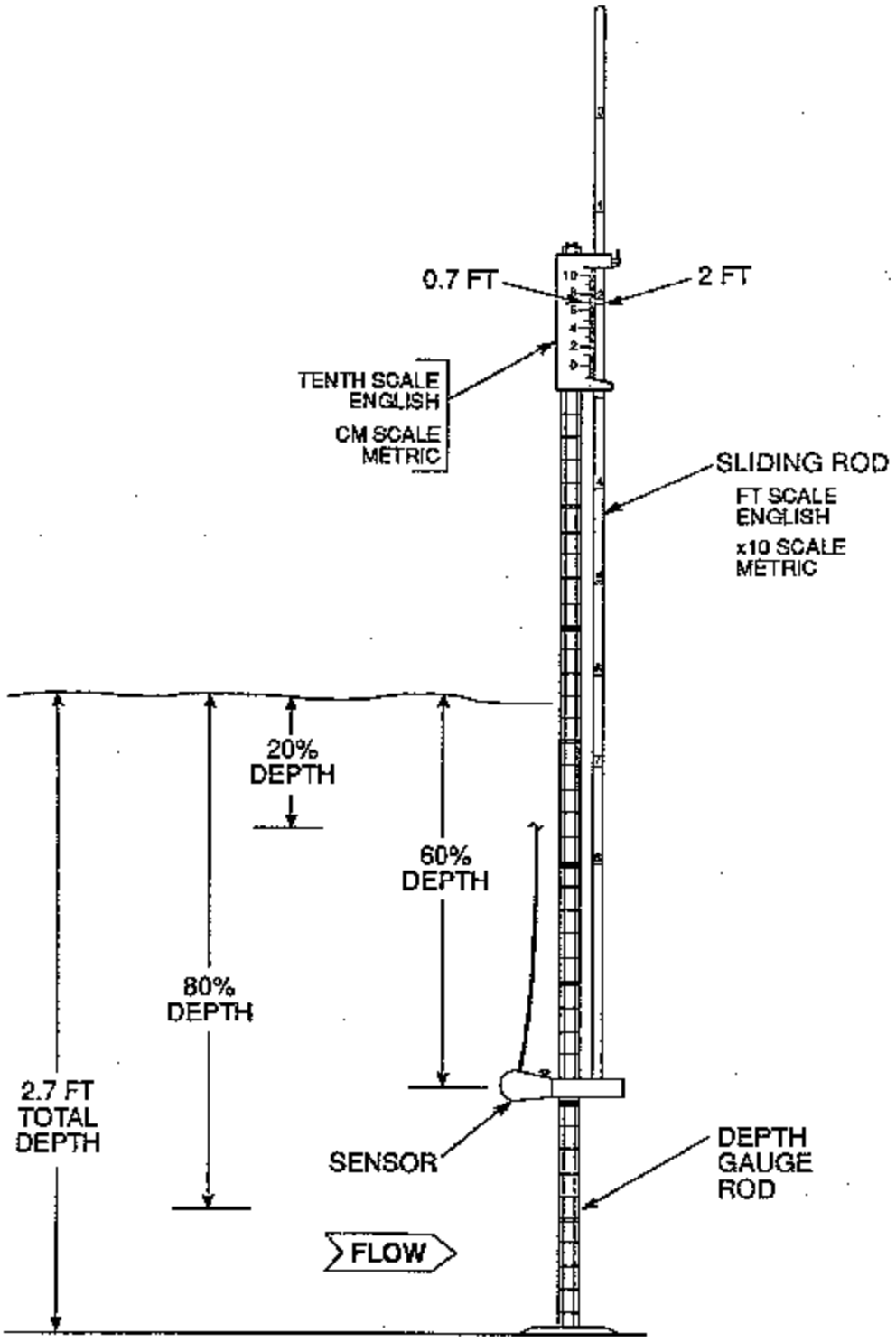
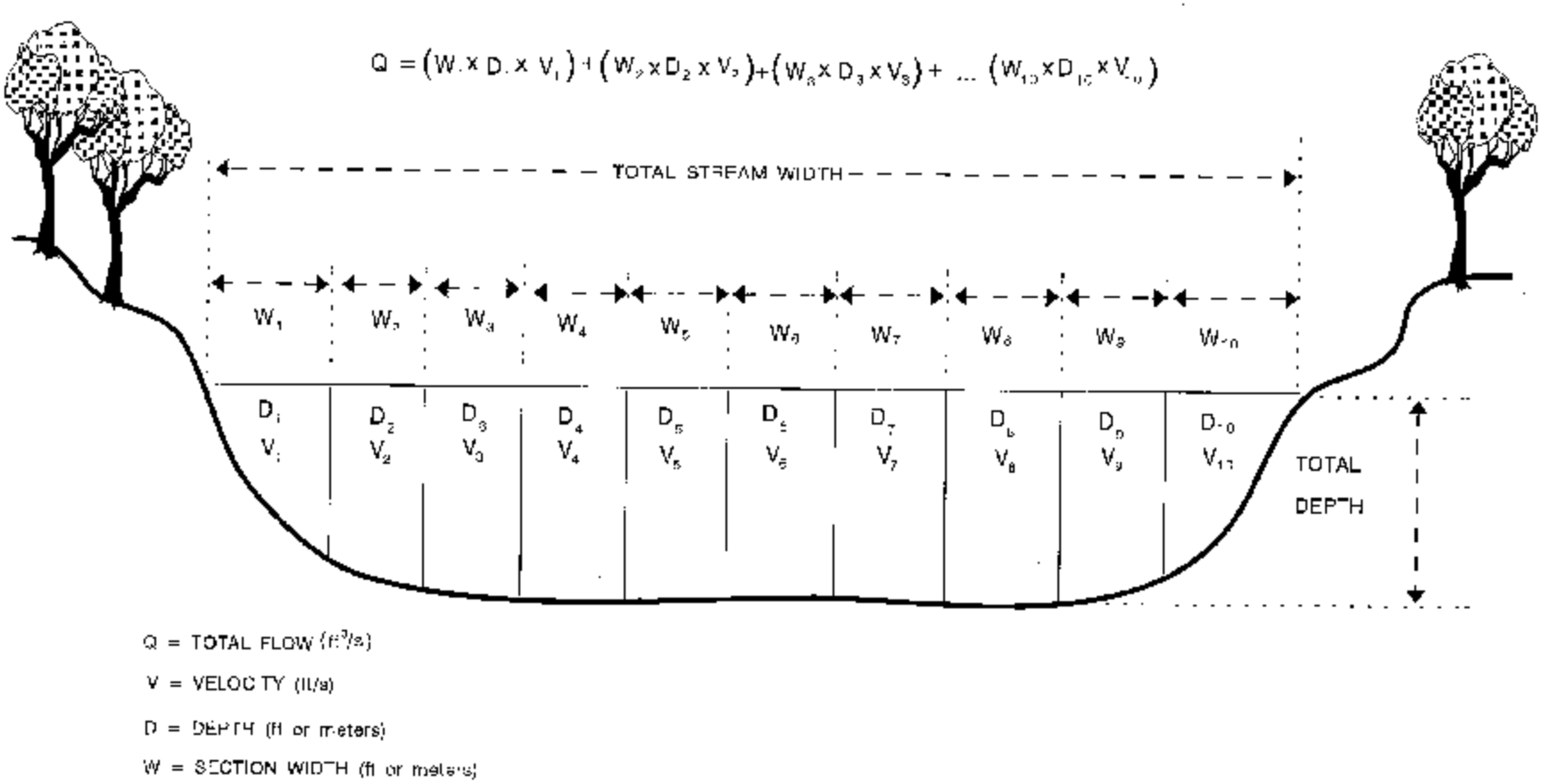


Figure 2. Stream Flow (Discharge) Measurement



Flow Estimate (ft^3/s)

Flow estimate data may be recorded for a non-tidally influenced stream when it is not possible to measure flows by one of the methods described above. Flow estimates are subjective measures based on field personnel's experience and ability to estimate distances, depths, and velocities.

Flow Estimate Procedure

- Observe the stream and choose a reach of the stream where it is possible to estimate the stream cross section and velocity.
- Estimate stream width (feet) at that reach and record.
- Estimate average stream depth (feet) at that reach and record.
- Estimate stream velocity (ft/s) at that reach and record. A good way to do this is to time the travel of a piece of floating debris. If doing this method from a bridge, measure the width of the bridge. Have one person drop a floating object (something that can be distinguished from other floating material) at the upstream side of the bridge and say start. The person on the downstream side of the bridge will stop the clock when the floating object reaches the downstream side of the bridge. Divide the bridge width by the number of seconds to calculate the velocity. The velocity can be measured at multiple locations along the bridge. These velocities are averaged. If this is done alone, watch for road traffic.
- Multiply stream width (feet) times average stream depth (feet) to determine the cross sectional area (in ft^2) which when multiplied by the stream velocity (in ft/s) and a correction constant, gives an estimated flow (ft^3/s).

Example: A stream sampler conducted a sampling visit to a stream while the flow meter was being repaired. The sampler looked at the creek downstream from the bridge and saw a good place to estimate flow. The stream width was around 15 feet. It appeared the average depth on this reach was about 0.75 feet. The sampler timed a piece of floating debris as it moved a distance of ten feet in 25
seconds downstream over the reach. An estimated flow with a smooth bottom was calculated using the following formula.

Width x Depth x Velocity x A (correction factor)= estimated flow
15 ft (width) x 0.75 ft (depth) x 2.5 ft/s (velocity) x A =25 ft^3/s (cfs)

A is a correction constant: 0.8 for rough bottom and 0.9 for smooth bottom

Estimated flow should be reported to one or two significant figures.

Example 1

Stream Flow (Discharge) Measurement

Small Stream < 5 Feet Wide and #2.5 Feet Deep

Stream:____OAK CREEK_____Date:__5/29/91_____

Station Description:_____at US Hwy XYZ_____

Time Begin:__1545_____Time End:__1630_____Meter Type:__Marsh-McBirney_____

Observers:_____BK/MK_____Stream Width*:____5 ft_____ Section Width:____0.5 ft_____

Observations:_____

_____

Section Midpoint (ft)	Section Depth (ft)	Observational Depth** ft	Velocity		Area W x D (ft^2)	Discharge (Q) V x A (ft^3/s)
			At Point (ft/s)	Average (ft/s)		
0.50	**0.55**			**0.05**		**0.01375**
1.00	**0.80**			**0.11**		**0.044**
1.50	**0.85**			**0.27**		**0.42635**
2.00	**0.90**			**0.49**		**0.2205**
2.50	**1.10**			**0.58**		**0.275**
3.00	**1.50**			**0.72**		**0.540**
3.50	**1.20**			**0.76**		**0.456**
4.00	**0.90**			**0.76**		**0.342**
4.50	**0.75**			**0.44**		**0.165**
5.0	**0.30**			**0.00**		**0.00**

m^3/s x 35.3 = ft^3/s

Total Discharge (∑Q) (ft^3/s) **2.4826**

* Make a minimum of 10 measurements when the total width is > 5.0 ft, 20 measurements preferred.
**Measure at 0.6 of depth from surface where < 2.5 ft deep. Measure at 0.2 and 0.8 of depth in waters >2.5 ft deep.

Example 2.

Stream Discharge Measurement

Larger Stream > 5 Feet and #2.5 Feet Deep

Stream:____RED RIVER_____Date:__5/28/91_____

Station Description:_____40 meters below XYZ Outfall Below XYZ Outfall_____

Time Begin:__1542_____Time End:__1601_____Meter Type:_Marsh-McBirney_____

Observers:_____CM, EW, DO_____Stream Width*:____26 ft___ Section Width:___1.3 ft_____

Observations:_____

Section Midpoint (ft)	Section Depth (ft)	Observational Depth** ft	Velocity		Area W x D (ft^2)	Discharge (Q) V x A (ft^3/s)
			At Point (ft/s)	Average (ft/s)		
0.65	0.55			2.03	0.715	1.451
1.95	0.40			2.04	0.520	1.061
3.25	0.42			2.02	0.546	1.103
4.55	0.38			1.77	0.494	0.874
5.25	0.40			1.75	0.520	0.910
7.15	0.42			1.93	0.546	1.054
8.45	0.40			1.99	0.52	1.035
9.75	0.37			1.92	0.481	0.924
11.05	0.37			1.56	0.481	0.750
12.35	0.43			1.32	0.559	0.738
13.65	0.40			1.36	0.520	0.707
14.95	0.42			1.33	0.546	0.726
16.25	0.40			1.35	0.520	0.702
17.55	0.45			1.64	0.585	0.959
18.85	0.48			1.70	0.624	1.061
20.15	0.48			2.00	0.624	1.248
21.45	0.50			1.95	0.650	1.268
22.75	0.40			2.18	0.520	1.134
24.05	0.48			1.71	0.624	1.067

25.35	**0.50**			**0.60**	**0.650**	**0.390**

m^3/s x 35.3 = ft^3/s | Total Discharge (3Q) (ft^3/s) | **19.162**

Example 3
Stream Flow (Discharge) Measurement
Larger Stream > 5 Feet and >2.5 Feet Deep

Stream:____ARROYO COLORADO_____Date:__**6/16/98**__
Station Description:_____Downstream of XYZ Company_____
Time Begin:__**1400**_____Time End:__**1445**_____Meter Type:___**Marsh-McBirney**_____
Observers:_____**JD, CK**_____Stream Width*:___**47.5 ft**___ Section Width:___**2.375 ft**_____
Observations:_____

Section Midpoint (ft)	Section Depth (ft)	Observational Depth** ft	Velocity		Area W x D (ft^2)	Discharge (Q) V x A (ft^3/s)
			At Point	Average		
4.70	**0.73**			**0.65**	**1.73**	**1.127**
7.08	**1.10**			**1.08**	**2.61**	**2.822**
9.45	**1.85**			**0.90**	**4.39**	**3.954**
11.83	**2.20**			**1.05**	**5.23**	**5.486**
14.20	**2.20**			**1.44**	**5.23**	**7.531**
16.58	**2.45**			**1.09**	**5.82**	**6.342**
18.95	**2.55**	**0.20** **0.80**	**1.75** **1.76**	**1.76**	**6.06**	**10.659**
21.33	**2.60**	**0.20** **0.80**	**1.79** **1.32**	**1.56**	**6.18**	**9.633**
23.70	**2.70**	**0.20** **0.80**	**1.63** **1.26**	**1.45**	**6.41**	**9.298**
26.10	**3.05**	**0.20** **0.80**	**1.68** **1.15**	**1.42**	**7.24**	**10.286**
28.48	**3.10**	**0.20** **0.80**	**1.23** **0.69**	**0.96**	**7.36**	**7.068**
30.85	**2.90**	**0.20** **0.80**	**1.22** **0.89**	**1.06**	**6.89**	**7.301**
33.23	**2.84**	**0.20** **0.80**	**0.60** **0.37**	**0.49**	**6.75**	**3.305**
35.60	**2.65**	**0.20** **0.80**	**0.80** **0.21**	**0.51**	**6.29**	**3.210**
37.98	**2.65**	**0.20** **0.80**	**0.85** **0.96**	**0.91**	**6.29**	**5.727**
40.35	**2.20**			**0.28**	**5.23**	**1.464**

42.73	**2.30**			**0.16**	**5.46**	**0.874**
45.10	**2.05**			**0.51**	**4.87**	**2.483**
47.48	**1.10**			**0.49**	**2.61**	**1.280**
49.86	**0.65**			**0.62**	**1.54**	**0.957**
m^3/s x 35.3 = ft^3/s			**Total Discharge (ΣQ) (ft^3/s)**			**100.8**

Fecal Coliform

Flowing Streams

Dip the open bag to a depth of about four inches with the open end facing upstream. Push the mouth of the bag upstream at this depth until full. The mouth of the bag is always held upstream of the sampler, sampling apparatus, and any disturbed sediments.

Reservoirs and Coastal Waters

Dip the open bag to a depth of about four inches. The mouth of the bag is pushed at this depth away from the boat, the sampler, sampling apparatus, and any disturbed sediment.

Sample Container

Use a new, unused Whirlpack bag or a sterile plastic or glass bottle as the sample container. The sample container should never be pre-rinsed. When submerging the sample container, take care to avoid contamination by surface scums (Rawson, 1982). The surface film is enriched in particles and bacteria and is not representative of the water mass.

Sealing Container

Squeeze out the top one inch of water from the bag and whirl the bag to seal. The sealed bag must retain at least 50 ml of sample but leave a small pocket of air. This airspace will help mix the sample when it is shaken just before the filtration.

Labeling

Label each sample with the location.

Preservation

If the sample contains residual chlorine, add 0.1 ml of 10% sodium thiosulfate ($Na_2S_2O_3$) to the sample. Addition of sodium thiosulfate is not necessary if the sample is collected in a Whirlpack bag containing a sodium thiosulfate tablet.

Place sample(s) on ice immediately after collection.

Hold Time

The approved hold time for fecal coliform samples is six hours. Hold time is defined as the amount of time between when a sample is collected and sample filtration is initiated. Field collection is planned to ensure samples are set up within the six-hour holding time. Samples that are not prepared within the time limit or are reported from the laboratory as exceeding the holding time limit will not be considered as meeting the sampling commitments on the current surface water monitoring schedule. Resampling of the site(s) is strongly recommended in order to completely meet current monitoring commitments.

Temperature

The TNRCC rules require that temperature of effluent be determined in-situ. It is not acceptable to collect a sample for temperature analysis. The EPA approved method for temperature analysis requires that the thermometer be calibrated semi-annually with an National Institute of Standards and Technology (NIBS) standard thermometer.

Procedure for Temperature

1. Hold the thermometer by its top and immerse it in the water. Position the thermometer so that the scale can be read.
2. Allow the thermometer to stabilize for at least one minute; then without removing the thermometer from the water, read the temperature to the nearest 0.lE and record in field log book and/or on the chain of custody tag.

pH

The analysis of pH may be performed in-situ or it may be performed on a grab sample if analysis is begun within 15 minutes of sample collection. The use of the pH meter is the only approved method for pH analysis (pH paper is not acceptable for measuring and reporting pH values for the compliance inspection program). However, it would be valuable to record pH indicated by pH paper in the field notebook when the pH meter is inoperable.

Procedure for pH

1. Calibrate pH meter. The pH function should be calibrated each day of use and checked at each sampling site.
   a. pH buffers with values of 4.0, 7.0,and 9.2 (or 10.0) should be available.
   b. Working buffer solutions should be less than four weeks old. Bottles of buffer prepared from reagent powder or concentrate should be labeled with date of preparation.
   c. Do not return used buffer solution to the bottle of buffer.
2. Measure pH.
   a. Preferably, pH is measured in-situ. Allow the pH probe to equilibrate for at least one minute before pH is recorded to the nearest 0.1 pH unit.
   b. If pH cannot be measured in-situ, it should be measured in the container used for collection of water samples, i.e. bucket. The container must be large enough to allow full immersion of the probe and the container must be brought to the same temperature as the water, before it

is filled. The container and water must provide sufficient thermal mass to ensure that the temperature or pH does not change while it is being measured. The bucket should be shaded from direct sunlight and strong breezes prior to, and during pH measurement. Place the probe into the bucket as soon as possible. Allow the probe to equilibrate for at least one minute before recording pH to the nearest 0.l pH unit.

c. If the pH meter value does not stabilize in several minutes, outgassing of carbon dioxide or hydrogen sulfide may be occurring. If outgassing is suspected as the cause of meter drift, collect a fresh sample, immerse the pH probe and read pH at one minute.
d. With care, pH measurements can be accurately measured to the nearest 0.1 pH unit.
e. Record the pH results in the field log book and on the chain-of-custody tag.

Dissolved Oxygen

The analysis of dissolved oxygen (D.O.) may be performed in-situ if a D.O. meter is used or it may be performed on a grab sample using either the Winkler titration or the D.O. meter.

Procedure for Dissolved Oxygen (Meter)

1. Calibrate meter using either l00 percent humid atmosphere or Winkler titration according to the manufacturer's instructions.
2. Preferably, D.O. is measured in-situ. The D.O. probe should be allowed to equilibrate for at least 1.5 minutes before D.O. is measured and recorded to the nearest 0.1 mg/l. Care must be taken to insure that the reading is stable.
3. If D.O. cannot be measured in-situ, it should be measured in the container used for collection of water samples, i.e. bucket. The container must be large enough to allow full immersion of the probe and the container must be brought to the same temperature as the water, before it is filled. The container and water must provide sufficient thermal mass and volume to ensure that the temperature or D.O. does not change while it is being measured. The bucket should be shaded from direct sunlight and strong breezes prior to, and during D.O. measurement. Place the probe into the bucket as soon as possible. Allow the probe to equilibrate for at least 1.5 minutes before recording D.O. to the nearest 0.1 mg/l. During equilibration and reading, water should be moved past the membrane surface by gently raising and lowering the probe.
4. Record the D.O. results in the field log book and on the chain-of-custody tag.

Procedure for Dissolved Oxygen (Winkler)

If the electronic D.O. meter is inoperable, D.O. should be measured by Winkler titration. A sample for titration is collected by placing a 300 ml BOD bottle in a sewage sampler and lowering the top of the sewage sampler to the desired depth. The sewage sampler will fill in 30 to 45 seconds. The sampler is filled with water when it ceases bubbling. The sewage sampler should not be withdrawn until it has completely filled. The sampler should be carried upright until the BOD bottle is removed.

1. Remove the BOD bottle from sewage sampler carefully. The bottle should be filled to the top of the lip. Gently pour the upper 3-4 ml out of the flared mouth of the bottle.
2. Add the contents of one manganous sulfate powder pillow to the full bottle.

3. Add the contents of one alkali-iodide-azide powder pillow to the full bottle.
4. Touch the top of the liquid with the stopper tip and then drop it into position making certain that no bubbles are trapped in the BOD bottle.
5. Invert the bottle about 20 times to mix and set the bottle aside out of direct sunlight.
6. When the floc has settled so the upper one-third of the bottle is clear or after waiting two minutes, repeat the mixing procedure. Allowing the floc to settle twice ensures reaction of the chemicals with all of the dissolved oxygen present. The floc will settle very slowly in saline waters. A minimum of two minutes reaction time is required for sea water. Results will not be affected if the floc refuses to settle or if some of the reagent powder does not dissolve.
7. When the floc has settled so the upper one-third of the bottle is clear or after waiting two minutes, add the contents of one sulfamic acid powder pillow.
8. Restopper and gently invert the bottle about 20 times. The solution should be clear and straw-colored in appearance. The intensity of the yellow color is directly related to the original concentration of D.O. in the sample. A clear, pale solution suggests very low original D.O. levels. A dark, clear, yellow solution suggests high original D.O. levels.
9. Samples prepared through the addition of sulfamic acid may be stored for four hours before completion of the Winkler titration. Samples can be stored for a maximum of six hours in the dark if the bottle is stored at the temperature of collection or water-sealed by putting water around the lip, and kept at 10-20EC.
10. As soon as the precipitate has completely dissolved as a result of acidification, the sample is ready to titrate. Transfer 200 ml of the solution to a 300-ml Erlenmeyer flask (a 300-ml BOD bottle may be substituted for this purpose).
11. Titrate with 0.025N PAO until the solution is pale yellow in color. The PAO titrant is not affected by bacterial action, however, it is affected by ultraviolet radiation and should be protected from direct sunlight. An opened bottle of PAO should be discarded after one year in a regularly used field kit and after two years if it is stored in the stockroom. Unopened bottles have a shelf life of about five years. The strength of the solution can be checked using an Iodate-Iodide Standard solution which is equivalent to 10.00 mg/l as dissolved oxygen. Repeat steps 7-13. using the Iodate-Iodide Standard solution in place of the sample. The volume of PAO used to titrate should be 10 ml. If more than 10.5 ml of PAO is required to reach the endpoint, the PAO should be discarded. Alternately, the D.O. value from a well mixed body of water can be titrated using both a fresh bottle of PAO and the bottle in question. If the old solution requires 0.2 ml more to reach the endpoint in several titrations it should be discarded.
12. Add two ml of stable starch reagent and note the blue color which indicates the presence of iodine. The starch solution degrades rapidly in high temperatures. Monthly renewal of the supply in the field kit is recommended. Opened bottles should be stored in the refrigerator and discarded after two years. Unopened bottles have a shelf life of about five years when protected from high temperatures. A few drops should give the blue indicator color (not gray). If it takes more than 1 or 2 mls of starch solution to produce the color, the sample titration results should be rejected and the starch solution replaced.

13. Continue to titrate until the blue color just disappears. Titration should be completed against a white background. This step requires vigorous swirling to ensure that the titration endpoint is accurate. The blue color may reappear after a few minutes. The reappearance of the blue color should be disregarded.
14. The total number of milliliters of PAO used in the titration is equal to the D.O., expressed in mg/l. The D.O. (mg/l) value obtained from the titration should be recorded to the nearest 0.1 mg/l in the field log book and on the chain-of-custody tag.

Residual Chlorine

Residual chlorine should be analyzed on a grab sample. The analysis may be performed using the DPD-ferrous ammonium sulfate titration or using the DPD colorimetric procedure.

Procedure for Residual Chlorine (Titration)

1. Standard ferrous ammonium sulfate (FAS) must be made up fresh monthly. This should be stored in a cool, dark place. It is recommended that small portions of the standard solution be carried into the field; these should be replaced daily.
   a. Make a small amount of (1 + 3) H_2SO_4 by adding 5 mls of concentrated sulfuric acid to 15 mls of water in a 200 ml beaker. CAUTION: Always add acid to water!!! A large beaker is required so that the heat generated by the mixing of acid to water will dissipate. This solution may be stored in a glass bottle.
   b. In a 1000 ml volumetric flask, add approximately 500 ml of distilled water and then add 1 ml of (1 + 3) H_2SO_4. Add l.l06 grams of FAS crystals to this solution in the volumetric flask. After the crystals are completely dissolved, add enough distilled water to bring the volume to exactly 1000 ml. Transfer the FAS standard solution to a dark plastic bottle. Invert the bottle several times to mix the solution. Store the solution in a cool, dark place.

2. Sample Analysis
   a. Measure 100 ml of sample in a graduate cylinder, transfer to a 250 ml Erlenmeyer flask or beaker.
   b. Add the contents of 4 DPD-powder pillows for total chlorine analysis. A red or pink color should develop if chlorine is present. High chlorine residuals may produce a temporary red color followed by a yellow color. If this occurs, perform the analysis using a smaller volume of sample diluted to l00 mls with distilled water. Allow 3 minutes for color development.
   c. Fill a pipette with FAS. Titrate to the disappearance of the red color. Record the volume of FAS used. Disregard the reappearance after a few minutes of the pink color.
   d. If manganese is present in the sample, it will cause an interference in the chlorine analysis which must be corrected. Collect the same volume of sample used for the sample analysis described above. Add 0.5 ml of sodium arsenite solution (5 grams/liter) and 4 DPD powder pillows for total chlorine analysis. Wait three minutes, then titrate to the disappearance of the red color and record the volume of FAS used.
   e. Calculation

$$\text{mg/l of total chlorine} = \frac{[\text{mls titrant step c} - \text{mls titrant step d}] \times 100}{\text{mls of sample used}}$$

Record the final results in the field log book and/or on the chain-of-custody tag.

3. If using another EPA approved method, follow the manufacturer's directions for running residual chlorine and manganese interference**.**