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Handbook for Sampling and Sample Preservation of Water and Wastewater

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HANDBOOK FOR
SAMPLING AND SAMPLE PRESERVATION
OF WATER AND WASTE WATER

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati engages in the following activities:

- Develops and evaluates techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, waste water. bottom sediments, and solid waste.

- Investigates methods for the concentration, recovery and identification of viruses, bacteria, and other microbiological organisms in water. Conducts studies determine the responses of aquatic organisms in water.

- Conducts an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and waste water.

Standardized procedures for analyses of quality control become academic if samples are not representative of their original environment or if changes of constituent concentrations occur between time of sampling and analysis. This publication presents techniques for sampling and sample preservation to help alleviate these problems. Procedures have been standardized as much as possible throughout this document. However, sampling techniques could not be predetermined for all situations, so the use of statistical procedures to establish location and frequency of sampling, number of samples, and parameters to be analyzed is recommended when other guidelines do not exist. Sample preservation methods and holding times are included for the 71 parameters listed for the National Pollutant Discharge Elimination System program, priority pollutants, and selected biological species. Special handling or sampling techniques are also included for the individual constituents. Personnel establishing a sampling program should find sufficient information to determine the best techniques to apply.

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ABSTRACT

This research program was initiated with the overall objective of providing guidelines for sampling and sample preservation of waters and wastewaters.

Information obtained from a review of the literature and the results of a survey of field practices provides the basis for guidelines in general sampling techniques, automatic samplers, flow measuring devices, a statistical approach to sampling, preservation of physical, chemical, biological and radiological parameters, and sampling procedures for waters emanating from municipal, industrial, and agriculture sources. Sampling procedures for surface waters and sludges are also included.

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CHAPTER 1

INTRODUCTION

Obtaining representative samples and then maintaining the integrity of the constituents is an integral part of any monitoring or enforcement program. Standardization of the analytical techniques has been established to a high degree, but the result of analysis is only as good as the sampling and the sample preservation. The purpose of this handbook is to present the best techniques currently available for sampling and sample preservation. The recommendations were developed from an extensive research report which included a literature review and survey of current laboratory and field practices. The handbook will allow personnel to determine the most effective procedures for their specific applications.

In sampling, the objective is to remove a small portion of an environment that is representative of the entire body. It is then obvious that improper sampling will give erroneous results. Once the sample is taken, the constituents of the sample must stay in the same condition as when the sample was collected. The length of time that these materials will remain stable is related to the preservation method.

The sampling technique is determined by the type of water or wastewater to be sampled. Salt waters are not included. Therefore, the following areas are addressed in this handbook:

1. Municipal wastewaters
2. Industrial wastewaters
3. Surface waters and sediments
4. Agricultural runoff
5. Wastewater sludges
6. Groundwater

General information on automatic samplers and flow monitoring is also included.

Statistical methods have been presented in this handbook and will be used to determine the following aspects of sampling programs:

1. Number of samples
2. Frequency of sampling
3. Location of sampling
4. Parameters of measure

Special consideration is given to sampling for suspended solids, trace organics and radioactive substances.

Preservation methods are related to the parameters to be analyzed so, in this handbook, these techniques are classified by parameter. The (71) parameters specified for the National Pollution and Discharge Elimination System (NPDES) permit program in the Federal Register of October 16, 1973, priority pollutants, and selected biological parameters are included.

CHAPTER 2

GENERAL CONSIDERATIONS FOR A SAMPLING PROGRAM

Most definitions of water quality are use-related. Each water use produces wastewaters which are responsible for different types of pollution. For example, thermal pollution is associated with power plant discharges; eutrophication of lakes is due to nutrient discharges; fish kills result from dissolved oxygen deficiency or toxic substances from industrial discharges. The broad spectrum of waters (ground water, surface waters, lakes, estuaries, coastal waters) and an equally broad spectrum of wastewaters (municipal wastes, industrial wastewaters, surface run-offs) make monitoring of water quality a formidable task. Sampling is one of the key elements in a monitoring program. However, there is no unique sampling program that applies to all types of waters and wastewaters. Nevertheless, features of a sampling program which are included for all types of waters and wastewaters include:

1. Objectives of Sampling Program
2. Location of Sampling Points.
3. Types of Samples.
4. Sample Collection Methods.
5. Flow Measurements.
6. Field Procedures.

2.1 OBJECTIVES OF SAMPLING PROGRAMS

The objectives of a sampling program can be classified into four main

categories, namely, planning, research or design, process control and regulation. These objectives in an overall water quality program are interrelated and cover different stages from planning to enforcement. In relation to these objectives, the different sampling programs are compared in general terms in Table 2.1. Since the objectives of a program directly affect all aspects of sampling and laboratory analysis, determination of the objectives is the first step in planning a sampling program.

2.1.1 Planning Objectives

Monitoring objectives of interest to an areawide or basin planner include:

1. Establishment of baseline conditions.
2. Determining assimilative capacities of streams.
3. Follow effects of a particular project or activity.
4. Identifying pollutant source.
5. Assessing long-term trend.
6. Allocating waste load.
7. Project future water characteristics.

2.1.2 Research Objectives

Sampling is an essential part of most water/wastewater research projects and is conducted to accomplish one or more of the following objectives:

1. Determining the treatment efficiency for a unit process or overall treatment system.
2. Determining the effect of changes in process control variables.
3. Characterizing influent and effluent streams and sludges.
4. Optimizing chemical dosages, loadings for carbon adsorption columns,

TABLE 2.1 COMPARISON OF SAMPLING PROGRAMS BASED ON OBJECTIVES

Objective	Planning	Research Design	Process Control	Regulatory
Scope	General	Specific	Specific	Specific
Goals	Establish trends benchmarks background levels.	New developments Modifications Improvements	Operation quality control	Verification, compliance, enforcement
Effort	Nonintensive and unlimited	Intensive and limited	Nonintensive and limited	Nonintensive and limited

for advance waste treatment processes or treatment of drinking water.

5. Ascertaining health effects of effluents sludges, drinking waters and ambient waters.

2.1.3 Process Control Objectives

Sampling to control water/wastewater treatment process and associated systems is conducted primarily for internal use to accomplish one or more of the following objectives to:

1. Producing an effluent of the highest quality.
2. Optimizing and maintaining physical, chemical, and biological process control variables that affect treatment efficiency, i.e. mixed liquor suspended solids, sludge withdrawal rate, dissolved oxygen, chemical dosages, etc.
3. Determining resource recovery from unit processes.
4. Allocating the cost of treatment to a unit within a complex of unit processes.
5. Determining substances that are toxic or interfere with the treatment system.

2.1.4 Regulatory Objectives

Most sampling and subsequent analyses are performed to meet the requirements of federal, state, or local regulatory agencies; or regulatory agencies will sample and analyze to assure compliance. An example of regulatory monitoring is the National Pollutant Discharge Elimination System established in accordance with the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500). Specific objectives in collecting regulatory data vary con-

siderably and often overlap, but generally include the following:

1. Verifying compliance with effluent limitations.
2. Verifying self-monitoring data.
3. Verifying compliance with NPDES permit.
4. Supporting enforcement action.
5. Supporting permit reissuance and/or revision.
6. Supporting other program elements such as, water quality standards, requiring wastewater data.

2.2 SAMPLING LOCATIONS

2.2.1 General Considerations

Usually, the sampling program objectives define either the approximate or precise locations for sampling, e.g., influent and effluent to a treatment plant or water supply intake. Often, however, the sampling program objectives give only a general indication, e.g.,effect of a surface runoff on a river quality when assessing the quality of drinking water to a large community. For programs of this type, careful selection of sampling locations is required.

Since water quality varies from place to place in most water systems, locations appropriate to the information needs of a particular program must be selected. The nature and extent of spatial heterogeneity may vary with time, and can also differ markedly between systems of the same type, e.g., a typical case may be a zone of mixing of fresh and saline waters. Therefore, no specific guidelines can be given on the exact locations for sampling; however, some general points are worth bearing in mind when considering sampling locations.

2.2.2 Relevant Factors in Selecting Sampling Locations

The selected sampling locations must be representative sites. The term

"representative point" is defined in 40 CFR, Part 35, Appendix A, p. 224, 1976 as:

1. A location in surface waters or groundwaters at which specific conditions or parameters may be measured in such a manner as to characterize or approximate the quality or condition of the water body; or
2. A location in process waters or wastewaters where specific conditions or parameters are measured that adequately reflect the actual condition of those waters or wastewaters.

A major consideration influencing the selection of the sampling locations is the homogeneity of the water or wastewater. Turbulence and good mixing enhance the homogeneity or the uniform distribution of constituents within the body of water or wastewater, e.g., a stream just downstream of a hydraulic jump or a lake during spring or fall turnovers. Non-homogeneity, on the other hand results from:

1. Poor mixing, e.g., thermal stratification in lakes or a river downstream of a waste discharge.
2. Different densities of the constituents, e.g., floating oils or settling suspended solids.
3. Chemical or biological reactions, e.g., growth of algae in upper layers of water body causing changes in pH.

Other considerations for the selection of sampling locations are: establishment of general characteristics of a large body of water or wastewater, pronounced degradation of water quality in specific areas, suitability for flow measurements, convenience and accessibility.

2.2.3 Selection of Sampling Locations (1)

Locations of the sampling points based on the considerations mentioned in section 2.2.2 are:

1. Homogeneity of Water or Wastewater
   - At significant outlets and inputs of lakes, impoundments, estuaries or coastal areas that exhibit eutrophic characteristics.
   - At locations upstream and downstream of major population and/or industrial centers which have significant discharges into flowing stream.
   - Upstream and downstream of representative land use areas and morphologic zones.
   - From several locations to obtain the required information.
2. General Characteristics of Water or Wastewater (1):
   - At representative sites in mainstream of rivers, estuaries, coastal areas, lakes or impoundments.
   - In major water use areas, such as public water supply intakes, commercial fishing areas and recreational areas.
   - At representative sites in the individual waste streams.
   - At the mouths of major or significant tributaries to mainstreams, estuaries or coastal areas.
3. Pronounced Water Quality Degradation:
   - At critical locations (which have the potential for displaying the most pronounced water quality or biological problems) in water quality limiting areas.
   - At critical locations within eutrophic or potentially eutrophic lakes, impoundments, estuaries, or coastal areas.

4. Flow Measurement

   - Locations where corresponding discharges are known or can be estimated.

5. Convenience, accessibility and practicability are certainly important but they should be secondary to representativeness of sampling.

2.3 SAMPLE COLLECTION METHODS

Samples can be collected either manually or with automatic samplers. Whichever technique is adopted, the success of the sampling program is directly related to the care exercised in the sample collection. Optimal performance will be obtained using trained personnel.

2.3.1 Manual Sampling

Manual sampling is the oldest method of sample collection. There is minimal initial cost involved in manual sampling. The human element is the key to the success or failure of manual sampling programs. It is well suited to a small number of samples, but is costly and time consuming for routine and large sampling programs. Table 2.2 lists some of the advantages and disadvantages of manual and automatic sampling.

2.3.2 Automatic Samplers

Automatic Samplers usage has increased because of cost savings, capability of more frequent sampling, better reliability (2), and the NPDES permit program.

Currently, there are many automatic samplers available with widely varying levels of sophistication, performance, mechanical reliability and cost. Table 2.3 lists different automatic samplers and their characteristic features (3). However, no single automatic sampling device is ideally suited for all

TABLE 2.2. THE ADVANTAGES AND DISADVANTAGES OF MANUAL AND AUTOMATIC SAMPLING

Type	Advantages	Disadvantages
Manual	Low capital cost	Probability of increased variability due to sample handling
	Compensate for various situations	Inconsistency in collection
	Note unusual conditions	High cost of labor
	No maintenance	Repetitious and monotonous for personnel
	Can collect extra samples in short time when necessary	
Automatic	Consistent samples	Considerable maintenance for batteries & cleaning; susceptible to plugging by solids
	Probability of decreased variability caused by sample handling	Restricted in size to the general specifications
	Minimal labor requirement for sampling	Inflexibility
	Has capability to collect multiple bottle samples for visual estimate of variability & analysis of individual bottles	Sample contamination potential

TABLE 2.3 AUTOMATIC SAMPLERS AND THEIR CHARACTERISTIC FEATURES (3)

MANUFACTURER	MODEL NO.	APPROX. COST ($)	DIMENSIONS WD.x DPTH.x HT. or DIA.x HT. (cms)	WEIGHT (kg)	SAMPLE BOTTLES		TYPE COOLING	MATERIALS EXPOSED TO SAMPLES			Velocity sample line (cms/sec)	MAX. LIFT (cm H_2O)	INTAKE ID (mm)	TYPE OF PUMP	PURGE CYCLE	CONTROLS			POWER				PORTABLE or FIXED
					No.	Cap. (ml)		Bottles	Tubing	Other						Flow Prop.	Time Prop.	Solid State	AC	Batt.	Press.	Spring	
BIF Sanitrol	41-4	670	27.3 x 25.4 x VAR	18.16	1	7570		Nalgene	Tygon	Fiberglass		762		Dipper			X		X				F
Brailsford	EVS-38	672	30.5 x 22.9 x 48.3	8.72	1	3785		Polypropylene	Tygon	Plexiglas	10.2	182	3.16	Vacuum			X		X	X			P
Brailsford	DC-F	296	30.5 x 24 x 48.3	8.72	1	7570		Polypropylene	Tygon	Teflon	23.2	213	3.16	Piston			X			X			P
Brailsford	DU-2	373	30.5 x 22.9 x 48.3	8.72	1	7570		Polypropylene	Tygon	Teflon	23.2	213	3.16	Piston			X			X			P
Brailsford	EP	373	Small	L	1	3785		Polypropylene	Tygon	Teflon	23.2	213	3.16	Piston			X			X			P
BVS	PP-100	700	31.8 x 25.4 x 46	35	1	9463		Plastic	Tygon	PVC		6096	3.16	Pressure			X				X		P
BVS	PPR-100	900	43.2 x 49.5 x 45.1		1	5678	Ref.	Plastic	Tygon	PVC		6096		Pressure			X			X	X		P
BVS	SE-400	2700	61 x 61 x 122	79.5	1	18,925	Ref.	Polyethylene	Plastic	PVC		975	12.7	Submersible			X	X	X				F
BVS	SE-600	2900	61 x 61 x 122	79.5	1	18,925	Ref.	Polyethylene	Plastic	PVC			50.8	Submersible			X	X	X				F
Bristol	M-4KT	941	7.6 x 30.4	3.2	1	3785		Polypropylene		Stainless				Plunger into Pipeline			X	X	X				F
Chandler	SR-10	2245	27.2 x 59.7 x 108	45.4	1	8000	Ref.	Polyethylene	PVC	U	H	671		Vacuum	X		X	X	X				F
Collins	40-2R	1343	50.8 x 61 x 122	100	1	18,925	Ref.	Polyethylene	Polyethylene	Polypropylene	H	610	9.5	Moyno			X		X				F
EMA	200 AC	239	20 x 83	9.1	1	U	Ice	U	Plastic	Aluminum		77	9.5	Solenoid Plunger			X		X	X			F
ETS	FS-4	1100	108 x 46 x 55	31.8	12	3785		Plastic		Noryl	L	883		Peristaltic			X		X				P
Fluid Kinetics	Custom Design						Ref.									X	X	X	X				F
FMC Corp.	Tru-Test	2850	49.6 x 60.4 x 131	147.6	1	7500	Ref.	Polyethylene			93.3	457	50.8	Centrifugal			X	X	X				F
Horizon	7578	600	40.6 x 23.5 x 57.2	12.7	1	9463		Polyethylene	Tygon	Silicone		914	4.8	Peristaltic			X			X			P
Hydragard	FP	370	10.2 x 74	3.2	1	U		U	Plastic	Stainless			9.5	Pressure		X	X				X		P
Hydra-Numatic	HNS	1980	91.4 x 33.4 x 91.4	90.8	1	18,925		Polyethylene	Tygon	Bronze	75	457	12.7	Impeller		X	X		X				F
ISCO	1392	1200	49.5 x 53.3	18.2	28	500	Ice	Polyethylene	Tygon	Silicone	96.3	790	6.35	Peristaltic	X	X	X		X	X			P
ISCO	1480	800	48.5 x 64.8	14.1	1	11,350	Ice	Polyethylene	Tygon	Silicone	24.1	790	6.35	Peristaltic	X	X	X		X	X			P
ISCO	1580	900	48.5 x 64.8	14.1	1	11,350	Ice	Polyethylene	Tygon	Silicone	96.3	790	6.35	Peristaltic	X	X	X	X	X	X			P
Lakeside	T2	1855		25	1	U	Ref.	U	Plastic	Plexiglas			12.7	Scoop		X			X				F
Manning	S-4000	1350	43.8 x 57.2	18.1	24	500	Ice	Polyethylene	Tygon	Plexiglas	H	670	9.5	Vacuum	X	X	X	X	X	X			P
Markland	1301	1150	43.2 x 30.5 x 71.1	27.2	1	7570		Polyethylene	Tygon	E.P.T.		914	6.35	Pressure			X	X		X	X		P
Markland	2104T-CLK	1250			1	7570		U	Tygon	E.P.T.		914	6.35	Pressure			X	X	X		X		F
N-Con	Surveyor	275	Small	L	1	U		U	U	Buna-N	H	182	12.7	Impeller			X		X				P
N-Con	Scout	520	35.6 x 15.3 x 43.2	10	1	3785		Polypropylene	Tygon	Silicone	12.1	457	6.35	Peristaltic			X		X	X			P

X = HAS, U = USER SUPPLIED, L = LOW, H = HIGH

(continued)

TABLE 2.3 (continued)

MANUFACTURER	MODEL NO	APPROX. COST ($)	DIMENSIONS WD.x DPTH.x HT. or DIA.x HT. (cms)	WEIGHT (kg)	SAMPLE BOTTLES No.	SAMPLE BOTTLES Cap. (ml)	TYPE COOLING	MATERIALS EXPOSED TO SAMPLES Bottles	MATERIALS EXPOSED TO SAMPLES Tubing	MATERIALS EXPOSED TO SAMPLES Other	Velocity (in sample line (cms/sec)	MAX. LIFT (cm H_2O)	INTAKE ID (mm)	TYPE OF PUMP	PURGE CYCLE	CONTROLS Flow Prop	CONTROLS Time Prop.	CONTROLS Solid State	POWER AC	POWER Batt.	POWER Press.	POWER Spring	PORTABLE or FIXED
N-Con	Sentry	1100	40.6 x 35.6 x 33	15.9	24	450		Glass	Tygon	Silicone	12.1	457	6.35	Peristaltic	X		X		X	X			P
N-Con	Trebler	1600			1	U	REF.	U		PVC		L		Scoop		X			X				F
N-Con	Sentinel		58.5 x 25.4 x 147.4	84	1	7570	REF.	Polyethylene		PVC			50.8	U			X		X				F
NP Enterprises	NPE				1		REF.				H			Vacuum	X		X		X				F
Phips & Bird	8392-300	850			1	U		U		Stainless		305		Dipper			X		X	X			F
Pro-Tech	CG-125	800	33 x 25.4 x 43.2	9.1	1	5678		TFE Resins	TFE Resins	PVC		914	3.16	Pressure	X		X				X		P
Pro-Tech	CG-150	900	33 x 25.4 x 43.2	9.1	1	5678		TFE Resins	TFE Resins	PVC		914	3.16	Pressure	X		X				X	X	P
Pro-Tech	CEL-300	1500	33 x 48.3 x 43.2	13.7	1	5678		TFE Resins	PVC	PVC	99.7	914	12.7	Submersible			X		X				P
Pro-Tech	DEL-240S	5700	76.2 x 81.2 x 182.9		24	100	REF.	TFE Resins	Stainless	PVC	99.7	914	12.7	Submersible			X		X				F
QCEC	CVE	570	38.1 x 38.1 x 60.9	24.9	1	1893	ICE	Glass	Tygon	Plexiglas	H	610	6.35	Vacuum	X		X		X				P
QCEC	E	1000	20.3 x 33 x VAR.	45.4	1	U				Stainless				Dipper			X		X				F
QCEC	CVE II	950	38.1 x 43.2 x 38.1	15.9	1	3785	ICE	Glass	Plexiglas	Brass	H	610	12.7	Vacuum	X		X	X	X	X			P
QCEC	LF	960	39.4 x 7.7	10	1	U		U	U	Stainless				Plunger into pipeline			X		X				F
Sigmamotor	WD-1	650	34.3 x 25.4 x 36.9	14	1	9462		Plastic	Tygon		9.7	670	3.16	Nutating			X		X	X			P
Sigmamotor	WD-5	1100	50 x 37 x 64	27	1	18,925		Plastic	Tygon		4.2	548	6.35	Finger			X		X	X			P
Sigmamotor	WM-4-24	1100	50 x 37 x 64	25.4	24	450		Plastic	Tygon		9.7	670	3.16	Nutating	X		X		X	X			P
Sigmamotor	WM-6-24	1400	50 x 37 x 64	29	24	450		Plastic	Tygon		4.2	548	6.35	Finger	X		X		X	X			P
Sigmamotor	WAP-2	700	34.3 x 25.4 x 36.9	11.4	1	9462		Plastic	Tygon		9.7	670	3.16	Nutating		X			X				P
Sigmamotor	WAP-5	1050	50 x 37 x 64	19.1	1	18,925		Plastic	Tygon		4.2	548	6.35	Finger		X			X				P
Sigmamotor	WM-1-24R	1525	53.4 x 55.9 x 86.4	56.8	24	450	REF.	Plastic	Tygon		9.7	670	3.16	Nutating	X		X		X				F
Sigmamotor	WAC-5R	1300	53.4 x 55.9 x 125	44.5	1	18,925	REF.	Plastic	Tygon		VAR.	670	3.16	Finger		X			X				F
SIRCO	B/ST-VS	1670-2950		127	24	473	REF.	Polyethylene	Plexiglas		H		9.53	Vacuum	X		X		X				F
SIRCO	B/IE-VS	1100-2778		123	1		REF.	Stainless	PVC	PVC		6096		Dipper			X		X				F
SIRCO	B/OP-VS	1375-2772		91	24		REF.	Polyethylene	PVC.	Plexiglas				Pressurized Source			X		X				F
SIRCO	MK-VS	675-1364	40.7 x 40.7 x 55.9	17	1 24	15,140 500		Plastic	PVC	Plexiglas	140	670	9.53	Vacuum	X		X	X	X	X			P
Sonford	NW-3	1000	39.4 x 39.4 x 68	23.2	24	473		Glass	Tygon	Stainless		396	6.35	Evacuated bottles			X					X	P
Sonford	HG-4	500	33.8 x 31.4 x 33.5		1	3785		Polyethylene		Stainless		53		Telescoping tube			X		X	X			P
TMI	MARK 3B	845	36.8 x 66	14.5	12	570		Glass	Tygon	Stainless		300	6.35	Evacuated bottles			X					X	P
TMI	MARK 4B	950	38 x 38 x 47	20.2	24	570		Glass	Tygon	Stainless		300	6.35	Evacuated bottles			X			X		X	P
Tri-Aid Sciences	CUSTOM DESIGN						REF		Silicone			762	9.53	Peristaltic		X	X	X	X				F
Waste Watcher	CS/TP	1425	20 x 20 x 7	10.5	1	U		U	Tygon	Silicone	34	670	7.9	Peristaltic	X	X	X		X				F

X - HAS, U - USER SUPPLIED, L - LOW, H - HIGH

situations. For each application the following variables should be considered in selecting an automatic sampler (4):

- Variation of water or wastewater characteristics with time.
- Variation of flow rate with time.
- Specific gravity of liquid and concentrations of suspended solids
- Presence of floating materials.

Selection of a unit or a variety of units for sampling should be preceded by a careful evaluation of such factors as:

- The range of intended use.
- The skill level required for installation of the automatic sampler.
- The level of accuracy desired.

References 5,6,7,8 and 9, have useful information on the theoretical design considerations and actual field performance data for automatic samplers.

2.3.2.1 Criteria for Evaluating Automatic Sampler Subsystems

There are usually five interrelated subsystems in the design of an automatic sampler. The criteria for selecting subsystems are briefly described below; more detailed information can be found in references 5,6, and 9.

2.3.2.1.1 Sample Intake Subsystem

The success of an automatic sampler in gathering a representative sample is dependent upon conditions at a particular sampling site (4) and the design of the sample intake subsystem. The reliability of a sample intake subsystem is measured in terms of:

- Freedom from plugging or clogging.
- Non-vulnerability to physical damage.
- Minimum obstruction to flow
- Capability to draw a representative sample.

- Multiple intakes.
- Rigid intake tubing or facility to secure or anchor the intake tubing. Avoidance of sharp bends, twists, or kinks to prevent clogging of intake line.

2.3.2.1.2 Sample Gathering Subsystem

Three basic sample gathering methods: mechanical, forced flow, and suction lift are available in commercial samplers. Figures 2.1 and 2.2 illustrate forced flow and suction lift sample gathering subsystems, respectively. Figures 2.3 and 2.4 illustrate a mechanical sample gathering subsystem at weir and flume installations respectively. These subsystems are compared in Table 2.4.

2.3.2.1.3 Sample Transport System

The majority of the commercially available composite samplers have fairly small diameter tubing in the sample train. This tubing is vulnerable to plugging, due to the buildup of fats, etc. Adequate flow rates must be maintained throughout the sampling train in order to effectively transport suspended solids.

To optimize sampler performance and reliability, the following features and procedures are desirable:

- The minimum size of the sample transport line should be 6 mm (1/4 in.) internal diameter.
- For most applications, the sample should not contact metals during transport.
- The sample line should be transparent and flexible, and made of an inert material such as Tygon^{R}. If trace quantities are to be

TABLE 2.4 COMPARISON OF SAMPLE GATHERING SUBSYSTEMS

Feature	Mechanical	Forced Flow	Suction Lift
Lift	High	High	Limited to 7.6 m(25 feet) or less
Sample integration over the entire depth.	Possible	Possible with pumps but not with ejection units.	Possible with multiple intakes
Obstruction to flow	Significant	Less than mechanical subsystem	Very little
Explosion-proof	Some	Pneumatic ejection units meet this requirement	Some
Dissolved gasses	No problem	No problem	Not suited but if used, the initial flow should be discarded.
Fouling	Exposed parts have a tendency to foul	Not easily fouled	Intake tubing of less than 6mm(1/4") I.D. is prone to fouling
Sample Volume	Suitable for wide range	Pump suitable for wide range. Pneumatic ejection units suitable for sample volume	Should be independent of vertical lift
Flexibility	Limited	Moderate	Maximum
Maintenance	Heavy	Moderate but costly	Little

PRESSURE OPERATION

Propellant under pressure from a source (A) is metered by a control valve (B) for rate-meter (C) into accumulator tank (D). On reaching a preselected pressure, a pneumatic relay (E) releases the accumulated propellant through inlet line (F) to the sample intake chamber (G). Pressure in the chamber closes its check valve (H) and propels the sample through outlet line (I) and into the sample bottle (J). Excess propellant vents through the sample line, thereby purging it of liquid and incidentally providing protection against line freezing in cold weather. The resulting pressure drop recloses the relay (E) and the sampling cycle repeats at a repetition rate determined by adjusting the control valve (B).

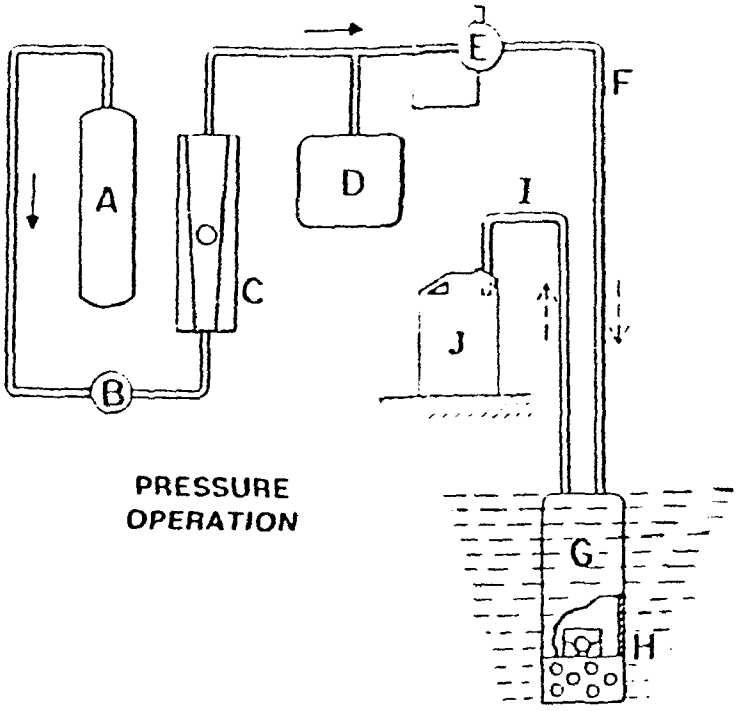

Figure 2.1 Schematic of Forced Flow Type Sampler.

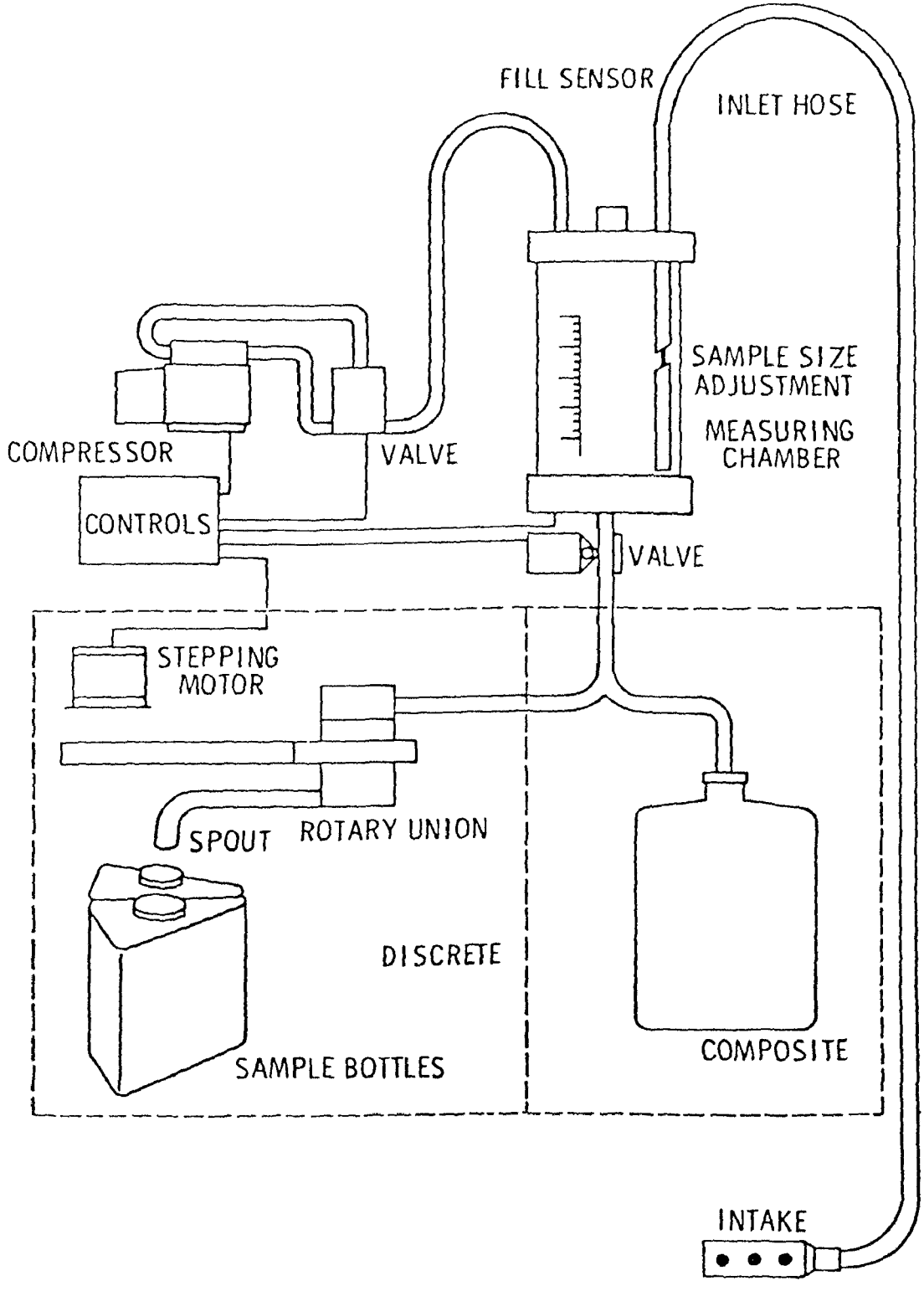

Figure 2.2 Schematic of Suction Lift Type Sampler

Parts List

No.	Description
1.	Motor-Reducer
2.	Drive Sprocket
3.	Driven Sprocket
4.	Roller Chain
5.	Scoop
6.	Scoop Counter Weight(not shown)
7.	Limit Switch
8.	Time Clock
9.	Alum. Sampler Casting
10.	Alum. Sampler Support
11.	Outlet Coupling
12.	Unilet Body & Cover

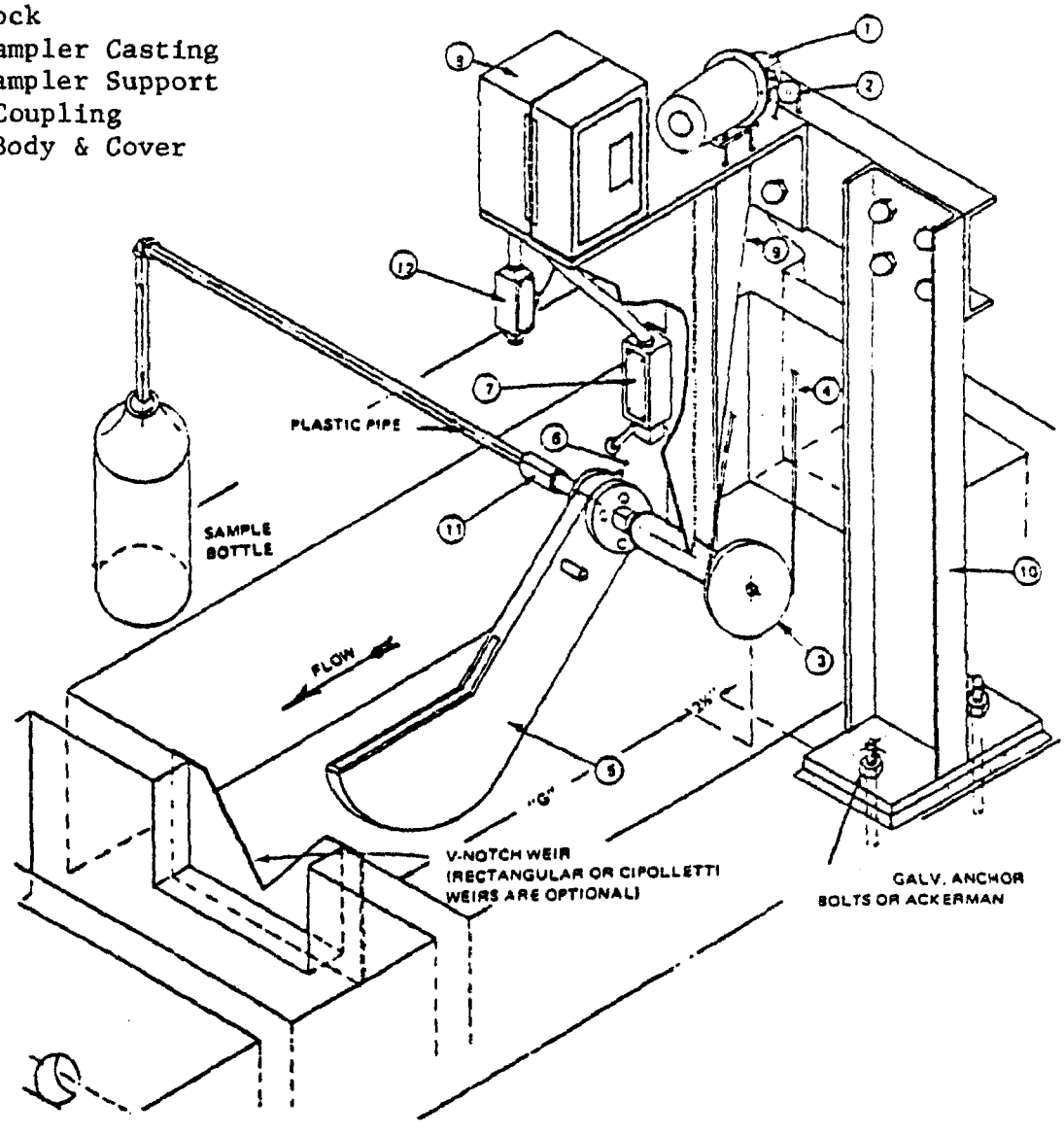

Figure 2.3 Schematic of Mechanical Type Sampler (Weir Installation).

Parts List

No.	Description
1.	Motor - Reducer
2.	Drive Sprocket
3.	Driven Sprocket
4.	Roller Chain
5.	Scoop
6.	Scoop Counter Weight(not shown)
7.	Limit Switch
8.	Time Clock
9.	Alum. Sampler Casting
10.	Alum. Sampler Support
11.	Outlet Coupling
12.	Unilet Body & Cover

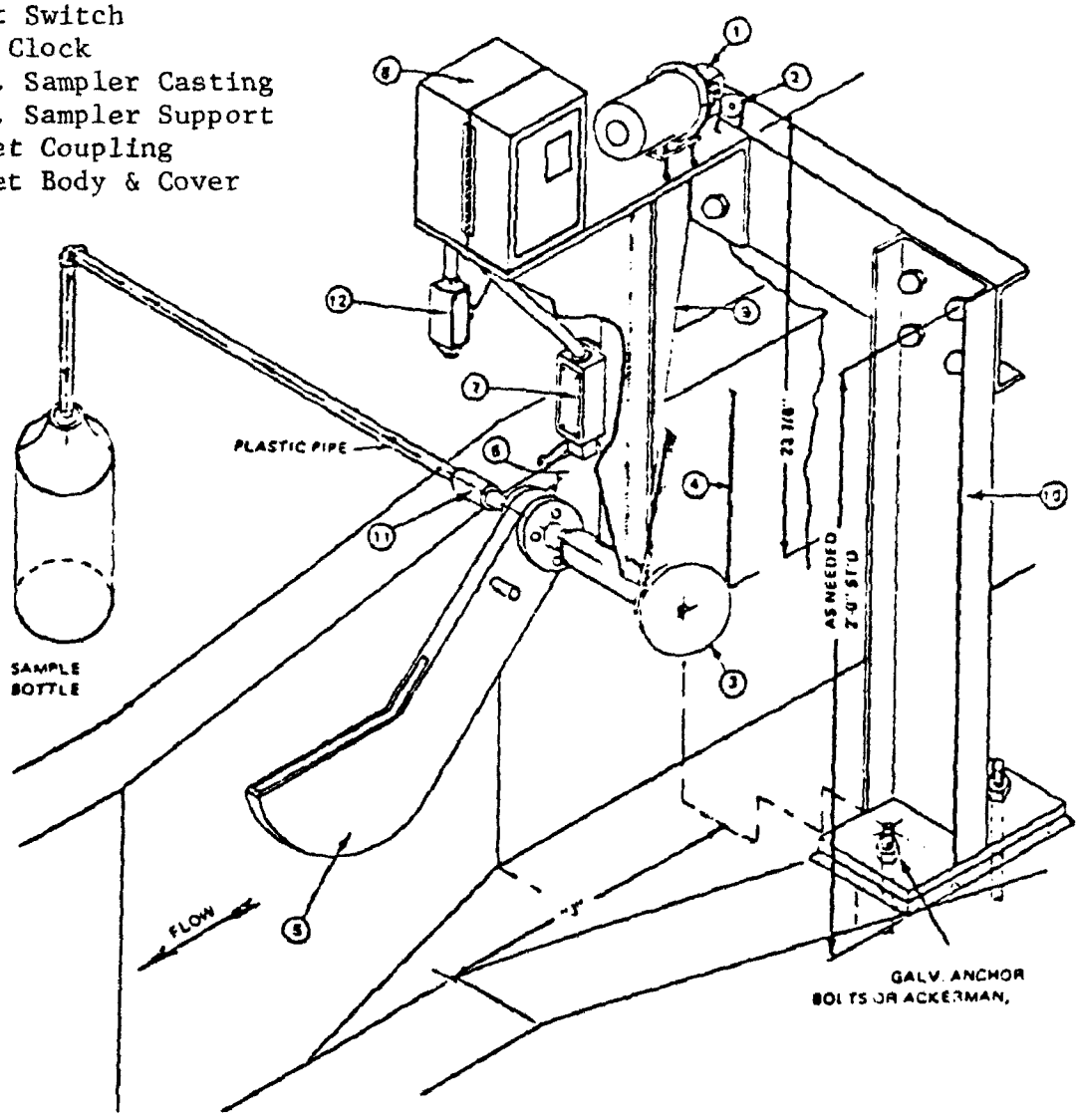

Figure 2.4 Schematic of Mechanical Type Sampler (Flume Installation).

measured, a method of testing for tube contamination is needed. Avoid sharp bends, twists, or kinks to prevent clogging.

- The sample line should be purged prior to and immediately after each sample collection. A clean water purge is effective (4) but not feasible in most instances. A complete air purge is sufficient for non-permanent or winter operation.
- The sampler should be capable of lifting a sample a vertical distance of 6.1 m (20 ft.) (7).
- The sampler should be capable of maintaining line velocity of 0.6 to 3.0 m/sec. (2-10 ft/sec.) for vertical transport. (7).
- The importance of line velocity and isokinetic conditions (intake velocity same as velocity of flow of water) depends on the concentration and density of the non-filterable suspended solids in the water, the program requirements for accuracy of suspended solids determinations, and any other parameters affected by suspended solids concentrations. If a program requires maintaining isokinetic conditions, dial adjustmant of intake velocity is a desired feature.

2.3.2.1.4 Sample Storage Subsystem

Both discrete samples and composite samples are desirable for certain applications. Discrete samples are subject to considerably more error introduced through sample handling, but do provide opportunity for manual flow compositing and time history characterization of a waste stream during short period studies. The desired features of sample storage subsystems are:

- Flexibility of discrete sample collection with provision for single composite container.

- Minimum discrete sample container volume of 500 mℓ (0.13 gal.) and a minimum composite container capacity of 7.57 ℓ (2.0 gal.).
- Storage capacity of at least 24 discrete samples.
- Containers of conventional polyethylene or borosilicate glass and of wide mouth construction.
- Capability for cooling samples by refrigeration or a space for packing ice and maintaining samples at 4° to 6°C (39° to 43°F) for a period of 24 hours at ambient temperature range between -30° to 50°C. (-22° to 122°F)
- Adequate insulation available for the sampler to be used in either warm or freezing ambient conditions.

2.3.2.1.5 Controls and Power Subsystem

The following are desired power and controls features, many of which will depend upon whether or not the sampler is to be portable or a permanent installation:

- Capability for either AC or DC operation.
- Battery life for 2 to 3 days of reliable hourly sampling without recharging.
- Battery weight of less than 9 kg (20 lb.) and sealed so no leakage occurs.
- Solid state logic and printed circuit boards.
- Timing and control systems contained in a waterproof compartment and protected from humidity. Timer should use solid state logic and a crystal controlled oscillator.
- Controls to allow both flow-proportional sampling (directly linked to a flow meter) and periodic sampling at an adjustable

interval from 10 minutes to 4 hours.

- Capability of multiplexing, i.e. drawing more than one sample into a discrete sample bottle to allow a small composite over a short interval. Also capability for filling more than one bottle with the same aliquot for additon of different preservatives.
- Capability of adjusting sample size and ease of doing so.

2.3.2.1.6 General Desirable Features

From the view of safety, maintenance, reliability and security in field applications, the following general features are desired in an automatic sampler:

- Water tight casing to withstand total immersion and high humidity.
- Vandal-proof casing with provisions for locking.
- A secure harness or mounting device if sampler is placed in a sewer.
- Explosion-proof construction.
- Sized to fit in a standard manhole without disassembly.
- Compact and portable for one-man installation.
- Overall construction, including casing, of materials resistant to corrosion (plastics, fiberglass, stainless steel).
- Sampler exterior surface painted a light color to reflect sunlight.
- Low cost, availability of spare parts, warranty, ease of maintenance, reliability and ruggedness of construction.

2.3.2.2 Installation and Use

2.3.2.2.1 General Consideration

Well designed equipment will yield good results only when properly

installed and maintained. A few general guidelines follow:

- When a sampler is installed in a manhole, secure it either in the manhole (e.g. to a rung) above the high water line or outside of the manhole (e.g. to an above ground stake by means of a rope).
- Place the intake tubing vertically or at such a slope to ensure gravity drainage of the tubing between samples, avoiding loops or dips in the line.
- Clean sample bottles, tubing and any portion of the sampler which contacts the sample between setups. Whatever methods of cleaning are used, all parts of the sampler which come in contact with the sample should be rinsed with tap water and then given a final rinse with distilled water. A distilled water rinse may not be necessary between setups on the same waste stream.
- Inspect the intake after each setup and clean, if necessary. Exercise care when placing the intake(s) in a stream containing suspended solids and run the first part of the sample to waste. The velocity of flow should at all times be sufficient to prevent deposition of solids. When a single intake is to be used in a channel, place it at six-tenths depth (point of average velocity) (10,11). For wide or deep channels where stratification exists, set up a sampling grid.
- Maintain electrical and mechanical parts according to the manufacturer's instructions. Replace the desiccant as needed. If

a wet-cell lead-acid battery is used, neutralize and clean up any spilled acid.

- Position the intake in the stream facing upstream. In any case limit the orientation of the intake with ±20 degrees on either side of the head-on. Secure the intake by a rope at all times with no drag placed on the inlet tubing.
- After the installation is complete, collect a trial sample to assure proper operation and sample collection. The sampler must give replicate samples of equal volume throughout the flow range. If the sampler imposes a reduced pressure on a waste stream containing suspended solids, run the first part of the sample to waste.

2.3.2.2.2 Winter Operation

For outdoor use in freezing temperatures special precautions should be used to insure reliable sample collection and to prevent the collected sample(s) from freezing:

- Place the sampler below the freezing level or in an insulated box.
- When AC is available, use a light bulb or heating tape to warm sampler. When installation below the freezing level is not possible and line current is available wrap 1.2 to 1.8 m (4 to 6 ft.) heat tapes [thermostatically protected 3°C (38°F)] around the sample bottle and the intake lines. Loosely wrap a large plastic bag (airline trash bags, 10 mil, GSA #8105-808-9631) over the heat tape on the intake lines. Place a large plastic bag over the sampler as loosely

as possible. (7)

- Be certain to place the line vertically or at such a slope to ensure gravity drainage back to the source. Even with a back-purge system some liquid will remain in the line unless gravity drainage is provided. If an excess length of tubing exists, cut it off. Keep all lines as short as possible.
- Do not use catalytic burners to prevent freezing since vapors can affect sample composition. When power is unavailable, a well insulated box containing the sampler, a battery and small light bulb are effective in preventing freezing.

2.3.2.3 Selection of an Automatic Sampler

To choose an automatic sampler, list the desired features needed for a particular sampling program and select the sampler that best fits the requirements consistent with the sampling objectives.

The following is a check list for selecting an automatic sampler:

1. Vertical lift
2. Submergence
3. Explosion proof
4. Intake tube: diameter/material
5. Dissolved gases
6. Suspended solids
7. Oils and grease and floating material
8. Organic priority pollutants
9. Isokinetic sampling

10. Sample type: continuous, composite: time proportional, flow proportional, etc.
11. Multiple intakes
12. Multiplexing
13. Dependability
14. Ease of operation
15. Maintenance
16. Availability

2.4 TYPE OF SAMPLE

Selection of the type of sample to be collected depends upon a number of factors such as the variability of flow, variability of water or wastewater quality, the accuracy required and the availability of funds for conducting the sampling and analytical programs. All samples collected, either manually or with automatic equipment, are either grab or composite samples.

2.4.1 Grab Samples

A grab sample is defined as an individual sample collected over a period of time not exceeding 15 minutes. It can be taken manually, using a pump, scoop, vacuum, or other suitable device. The collection of a grab sample is appropriate when it is desired to:

1. Characterize water quality at a particular time.
2. Provide information about minimum and maximum concentrations.
3. Allow collection of variable sample volume.
4. Corroborate composite samples.

2.4.2 Composite Samples

A composite sample is defined as a sample formed by mixing discrete samples taken at periodic points in time or a continuous proportion of the flow. The number of discrete samples which make up the composite depends upon the variability of pollutant concentration and flow. A sequential composite is defined as a series of short period grab samples each of which is held in an individual container, then composited to cover a longer time period. Six methods are used for compositing samples. Table 2.5 lists those methods with their advantages and disadvantages. Choice of composite type is dependent on the program and relative advantages and disadvantages of each composite type.

2.4.3 Selection of Sample Type

Use grab samples when: (12,13,14)

1. The stream does not flow continuously, e.g. batch dumps.
2. The water or waste characteristics are relatively constant.
3. The parameters to be analyzed are likely to change (i.e. dissolved gases, residual chlorine, soluble sulfide, oil and grease, microbiological parameters, organics, etc.).
4. Information on maximum, minimum or variability is desired.
5. The history of water quality is to be established based on relatively short time intervals.
6. The spatial parameter variability is to be determined e.g. the parameter variability throughout the cross-section and/or depth of a stream or large body of water.

TABLE 2.5 COMPOSITING METHODS

Sample mode	Compositing priciple	Advantages	Disadvantages	Comments
1. Continuous	Constant pumping rate	Minimal manual effort, requires no flow measurement.	Requires large sample capacity; may lack representativeness for highly variable flows.	Practical but not widely used.
2. Continuous	Sample pumping rate proportional to stream flow.	Most representative especially for highly variable flows; minimal manual effort.	Requires accurate flow measurement equipment, large sample volume, variable pumping capacity, and power.	Not widely used.
3. Periodic	Constant sample volume, constant time interval between samples.	Minimal instrumentation and manual effort; requires no flow measurement.	May lack representativeness especially for highly variable flows	Widely used in both automatic samplers and manual sampling.
4. Periodic	Constant sample volume, time interval between samples proportional to stream flow.	Minimum manual effort.	Requires accurate flow measurement/ reading equipment Manual compositing from flow chart.	Widely used in automatic as well as manual sampling.

(continued)

TABLE 2.5 (continued)

Sample mode	Compositing principle	Advantages	Disadvantages	Comments
5. Periodic	Constant time interval between samples, sample volume proportional to total stream flow since last sample.	Minimal instrumentation	Manual compositing from flow chart. In abscence of prior information on the ratio of minimum to maximum flow, there is a chance of collecting either too small or too large individual discrete samples for a given composite volume.	Not widely used in automatic samplers but may be done manually.
6. Periodic	Constant time interval between samples, sample volume proportional to total stream flow at time of sampling.	Minimal instrumentation.	Manual compositing from flow chart. In abscence of prior information on the ratio of minimum to maximum flow, there is a chance of collecting either too small or too large individual discrete samples for a given composite volume.	Used in automatic samplers and widely used as manual method.

Use composite samples when :

1. Determining average concentrations.
2. Calculating mass/unit time loading.

2.4.4 Method of Manual Compositing

When using a constant volume/ time proportional compositing method, previous flow records should be used to determine an appropriate flow volume increment so a representative sample is obtained without over-running the bottle capacity or supply.

The preparation of the flow rated composite is performed in various ways. Table 2.6 summarizes the techniques necessary for preparing composites from time constant/variable volume samples.

2.4.5 Examples of Manual Compositing

Example 2.1 illustrates the method of manual compositing for time constant/volume proportional to discharge since last sample, when records of totalized flow are available.

Example 2.1A illustrates the method of manual compositing for time constant/volume proportional to discharge since last sample, when records of flow rates are available.

Example 2.2 illustrates the method of manual compositing for time constant/volume proportional to instantaneous flow rate.

Example 2.3 illustrates the method of manual compositing for the constant volume/time proportional to equal increment discharge passing the sampling point, based on the past records of totalized flow.

Example 2.3A Illustrates the method of manual compositing for the constant volume/time proportional to equal increment discharge passing the sampling point, based on the past records of flow rates.

TABLE 2.6 MANUAL PREPARATION OF VARIABLE VOLUME COMPOSITE

Type	Preparation	Equation
Time constant/proportional	Determine volume since last sample by integration	$a_i = \frac{\Delta Q_i}{\Sigma \Delta Q_i} V_c$
		a_i = aliquot volume to be extracted from ith discrete sample
		V_c = composite volume (known)
		q_i = flow rate when ith discrete sample was taken (from flow record)
		Q_i = flow volume when ith discrete sample was taken
		Q_{i-1} = flow volume when ith-1 discrete sample was taken
		ΔQ_i = flow volume or rate since last sample (integration)
		$\Sigma \Delta Q_i$ = total flow volume (estimated)
Time constant/volume proportional to instantaneous flow rate	Note flow rate at each time of discrete sample collection	$a_i = \frac{q_i}{\sum_{i=i}^{n} q_i} V_c$
		Where, a_i = aliquot volume to be extracted from ith discrete sample
		q_i = flow rate when ith discrete sample was taken (from flow record)
		V_c = composite sample volume desired
		n = number of discrete samples

Example 2.1: Manually Preparing a Composite Sample for:

Time Constant/Volume Proportional to Discharge Since Last Sample.

Given: A 500 mℓ discrete sample was taken at the end of each hour over an 8 hour shift. A 3000 mℓ composite is desired. A recording of totalized flow is available.

Sample No. (i)	Q_i (liters)	ΔQ_i (liters)	a_i (mℓ)	a_i (adjusted) = a_i (500/max a_i) (mℓ)
0	0	-	-	-
1	858	858	100	77
2	3,462	2,604	303	232
3	8,254	4,792	558	427
4	12,347	4,093	477	365
5	17,950	5,603	653	500
6	21,225	3,275	382	292
7	24,600	3,375	393	301
8	25,750	1,150	134	103
		$\Sigma\Delta Q_i$ = 25,750	Σa_i = 3,000	2,297

Max a_i = 653 mℓ

Steps:

1. Enter Q_i from record and calculate $\Delta Q_i = Q_i - Q_{i-1}$
2. Calculate $a_i = \frac{V_c}{\Sigma\Delta Q_i}(\Delta Q_i)$, where V_c = 3000 mℓ.
3. Check to see if maximum a_i exceeds discrete sample volume, i.e. 653 mℓ > 500 mℓ.
4. If it does, adjust aliquot sizes using the relationship:

$$a_i \text{ (adjusted)} = a_i \left(\frac{\text{discrete sample volume}}{\max\ a_i}\right) = \frac{500}{653} = 0.77$$

5. Determine the adjusted composite volume from a_i (adjusted). This example illustrates that although desired composite volume was 3,000 mℓ (V_c) because of discrete sample volume size, only 2,297 mℓ of composite sample can be obtained.

Example 2.1A: Manually Preparing a Composite Sample for:

Time Constant/Volume Proportional to Discharge Since Last Sample

Given: A 500 mℓ discrete sample was taken at the end of each hour over an 8 hour shift. A 3,000 mℓ composite is desired. A recording of flow rate is available.

Sample No. (i)	q_i (liters)	ΔQ_i (liters)	a_i (mℓ)	a_i (adjusted) = a_i (500/max a_i) (mℓ)
0	961	-	-	-
1	2,025	1,483	146	132
2	3,700	2,862	282	255
3	5,212	4,456	439	397
4	6,004	5,608	553	500
5	5,018	5,511	543	491
6	4,002	4,510	444	401
7	3,089	3,546	349	316
8	1,847	2,468	244	221
		$\Sigma\Delta Q_i$=30,444	Σa_i=3,000	2,713

Max a_i = 553 mℓ

Steps:

1. Enter q_i from record and use trapezoidal rule to calculate $\Delta Q_i = (q_i + q_{i-1})/2$ (another integration scheme could be used if warranted).
2. Calculate $a_i = \frac{V_c}{\Sigma\Delta Q_i}(\Delta Q_i)$ where V_c = 3,000 mℓ.
3. Check to see if maximum a_i exceeds discrete sample volume.
4. If it does, adjust aliquot sizes using the relationship:

$$a_i \text{ (adjusted)} = a_i \left(\frac{\text{discrete sample volume}}{\max a_i}\right).$$

5. Determine the adjusted composite volume from a_i (adjusted). This example illustrates that although desired composite volume was 3,000 mℓ (V_c) because of discrete sample volume size, only 2,713 mℓ of composite samples can be obtained.

Example 2.2: Manually Preparing a Composite Sample For:

Time Constant/Volume Proportional to Instantaneous Flow Rate.

Given: 500 mℓ discrete samples were taken at hourly intervals over an 8 hour shift. A 2000 mℓ composite is desired. A recording of flow rate is available.

Sample No. (i)	q_i (liters)	a_i (mℓ)	a_i (adjusted) = $a_i \times 500 / \max a_i$ (mℓ)
1	600	109	107
2	1,000	182	179
3	1,700	309	304
4	2,800	509	500
5	1,800	327	321
6	1,400	255	250
7	1,000	182	279
8	700	127	125
	$\Sigma q_i = 11{,}000$	$\Sigma a_i = 2{,}000$	1,965

$\max a_i = 509$ mℓ

Steps:

1. Enter q_i from record and sum.
2. Calculate $a_i = q_i V_c / q_i$.
3. Check to see if maximum a_i exceeds discrete sample volume.
4. Adjusted aliquot volume = a_i (500/509) = a_i (adjusted). This example illustrates that with an individual discrete sample capacity of 500 mℓ only 1,965 mℓ volume of composite sample can be obtained. If it is desired to collect a composite sample of 3,000 mℓ volume, obviously larger sized (750 mℓ) capacity bottles or greater sampling frequency will be required for collecting individual discrete samples.

Example 2.3; Manually Preparing a Composite Sample For:

A Constant Volume/Time Proportional to Equal Increment Discharge.

Given: A 500 mℓ discrete sample was taken each time an average hourly flow flowed past the sample point. Sampling period is 8 hours. In addition, a 500 mℓ sample was taken at the end of the sampling period. A composite of 4,000 mℓ is desired. A recording of totalized flow (from past record) is available.

	Past Record		Actual			
Period ith hour	$Q_{i(past)}$ (liters)	ΔQ_{i} (past) (liters)	Q_{i} (actual) (liters)	ΔQ_{i} (actual) (liters)	a_{i} (mℓ)	Sample No.
0	0	0	0	0		
1	868	868	797	797		
					500	1
2	4,024	3,156	3,648	2,851		
					500	2
3	7,616	3,592	8,002	4,354		
					500	3
4	11,453	3,837	11,709	3,707	500	4
					500	5
5	16,629	5,176	16,056	4,347		
					500	6
6	20,377	3,748	19,763	3,707		
					500	7
7	22,625	2,248	24,321	4,558		
					500	8
8	25,000	2,375	26,650	2.229	264	9

$\Sigma\Delta Q_{i}$ (past) = 25,000 $\Sigma\Delta Q_{i}$ (actual) = 26,650

Steps:

1. Enter Q_{i} from past record and calculate $\Delta Q_{i} = Q_{i} - Q_{i-1}$.
2. Determine the number of samples for the overall sampling period. On the basis of the number of samples required for the overall sampling period, P, determine the average flow from the past records for the time interval, T, between the successive discrete samples.

In our case, the number of samples for the sampling period = 8

Overall sampling period, P = 8 hours.

Time interval, $T = \frac{8 \text{ hrs}}{8}. = 1$ hour

Average flow for the time interval between successive samples from past $= \frac{\Sigma Q_i \text{ (past)}}{P} = \frac{25,000}{8} = 3,125$ liters.

3. Aliquot size a_i = 500 mℓ.
4. Collect each discrete sample every time 3,125 liters passes the sampling point; and an additional one 500 mℓ sample aliquot at the end of the sampling period.
5. Record the actual flow.
6. Note the total flow for the sampling period. In our case it is $\Sigma\Delta Q_i$ (actual) = 26,650 liters.
7. Calculate the difference between $\Sigma\Delta Q_i$ (actual) and $\Sigma\Delta Q_i$ (past) which is 26,650 - 25,000 = 1,650 liters. This is the flow which passes the sampling point after taking the last sample for equal incremental discharge, up to the end of sampling. This flow is sampled by the sample taken at the end of the sampling period.
8. Compute the representative aliquot required for the unbalanced flow in step 7 in proportion to the equal increment flow.

$$\text{Required aliquot volume} = \frac{\Sigma\Delta Q_i \text{ (actual)} - \Sigma\Delta Q_i \text{ (past)}}{\text{equal increment discharge volume}} (a_i)$$

$$= \frac{26,650\,\ell - 25,000\,\ell}{3.125\,\ell}(500 \text{ m}\ell) = 264 \text{ m}\ell$$

9. Composite volume:= Σa_i = 8 aliquots of 500 mℓ + 264 mℓ from the aliquot taken at the end of the sampling period for a total of 4,264 mℓ.

Example 2.3A Manually Preparing a Composite Sample For:

A Constant Volume/ Time Proportional to Equal Increment Discharge.

Given: A 500 mℓ discrete sample was taken each time an average hourly flow flowed past the sample point. Sampling period is 8 hours. In addition, a 500 mℓ sample was taken at the end of the sampling period. A composite of 4,000 mℓ is desired. A recording of instantaneous flow rate (from past records) is available.

Period ith hour	q_i(past) (liters)	ΔQ_i(past) (liters)	q_i(actual) (liters)	ΔQ_i(actual) (liters)	a_i (mℓ)	Samp. No.
0	40	-	30	-		-
		50		40		
1	60		50			
		80		80	500	1
2	100		110			
		110		110	500	2
3	120		110			
		140		130	500	3
4.	160		150		500	4
		160		165	500	5
5.	160		180		500	6
		155		180		
6.	150		180		500	7
		130		145		
7.	110		110		500	8
		105		100		
8.	100	———	90	———	86	9

$\Sigma\Delta Q_i$(past) = 930 $\Sigma\Delta Q_i$(actual) = 950

Steps:

1. Enter q_i from past record and use trapezoidal rule to calculate ΔQ_i $=(q_i + q_{i-1})/2$ (another integration scheme could be used if warranted.
2. Determine the number of samples for the overall sampling period. On the basis of number of samples required for the overall sampling period

P, determine the average flow from the past records for the time interval T, between the successive discrete samples.

In our case the number of samples for the sampling period = 8.

Overall sampling period, P = 8 hours.

Time interval, $T = \frac{8 \text{ hours}}{8} = 1$ hour.

Average flow for the time interval between successive samples from past records $= \frac{\Sigma q_i}{P} = \frac{930}{8} = 116$ liters.

3. Aliquot Size a_i = 500 mℓ.
4. Collect each discrete sample every time 116 liters passes the sampling point and one additional aliquot of 500 mℓ at the end of the sampling period.
5. Record the actual flows per unit of time interval selected. e.g. hours, minutes, days.
6. Calculate the total actual flow for the sampling period. In our case it is $\Sigma\Delta Q_i$ (actual) = 950 liters.
7. Calculate the difference between $\Sigma\Delta Q_i$ (actual) amd $\Sigma\Delta Q_i$ (past) which is 950-930 = 20 liters. This is the flow which passes the sampling point after taking the last sample for equal incremental discharge, up to the end of the sampling period.
8. Compute the representative aliquot required for the unbalanced flow determined in step 7 in proportion to the equal increments.

Required aliquot volume $= \frac{\Sigma\Delta Q_i(\text{actual}) - \Sigma\Delta Q_i(\text{past})}{\text{equal increment discharge volume}} (a_i) = \frac{(20\ell)(500\ m\ell)}{116\ell}$

$= 86\ m\ell$

9. Composite volume = Σa_i

= 8 aliquots of 500 mℓ + 86 mℓ from the aliquot taken at the end of the sampling period.

= 4,086 mℓ.

2.5 PLANNING A SAMPLING PROGRAM

To achieve desired goals and performance, it is imperative that adequate consideration is given to both the planning and execution of a sampling program. While no ready made sampling program can be formulated which is applicable to all situations, the following considerations are provided to help plan an appropriate sampling program. The overall planning process can be divided into four stages:

1. Preliminary Plan
2. Evaluation of Preliminary Plan
3. Final Plan
4. Program Evaluation

2.5.1 Preliminary Plan

In this stage emphasis is upon collection of preliminary information on the entity to be sampled, the sampling sites and the flow characteristics. This information may be available from records of previous surveys. Where such information is not available reconnaissance should be carried out to become thoroughly familiar with actual site conditions. Table 2.7 shows the type of information needed in most cases. The appropriate information for Table 2.7 should be collected with a minimum of effort and cost. Based on this information, a preliminary sampling plan is drawn up. Preliminary sampling objectives should be delineated and then details of plan such as anticipated parameters, sample type, sample size, frequency, etc. specified. This information should

TABLE 2.7 PRESURVEY INFORMATION

Entity:		Process details
_____	Treatment Plant ( )	1._____
_____	Industry ( )	2._____
_____	River ( )	3._____
_____	Estuary ( )	4._____
_____	Sewer ( )	5._____
_____	Water mains ( )	6._____

Plans:	Yes	No	Waste sources	flows	
sewer maps	( )	( )	1._____	_____	P/C
water line network maps	( )	( )	2._____	_____	P/C
river and tributary maps	( )	( )	3._____	_____	P/C
treatment plant maps	( )	( )	4._____	_____	P/C
estuary zone maps	( )	( )	5._____	_____	P/C

Channel

Width_____

Depth_____

Pipe

Diameter_____

Material_____

Flow Variability

Hourly max_____

Hourly min_____

Hourly average_____

Daily max_____

Daily min_____

Daily average_____

Manholes ( )
other _____

Diameter
or width_____

Depth_____

P = pipe flow C = open channel flow

(continued)

TABLE 2.7 (Continued)

Topography		Physical Characteristics of Flow		Safety		Security	
Level	( )	Odor_____		Steep banks	( )	Fence	( )
Slopes	( )	Temperature _____		Soft grounds	( )	Open	( )
Vegetation	( )	Oil and grease	( )	Gases	( )	Guarded	( )
				Specifiy _____			
Swamp	( )	Clear	( )			Lighted	( )
		Turbid	( )	Stream Currents			
Other	( )	Suspended solids concentration		Tubulent	( )	Other	( )
Specify_____						Specify	
				Sluggish	( )	_____	
_____		_____					

Sampling Sites

Distance:		Numbers:		Accessibility:		Convenience:	
Near	( )	Few	( )	Road	( )	Sheltered	( )
Remote	( )	Many	( )	Bridge	( )	Power available	( )
				Other Specifiy	( )	Other Specify	( )
				_____		_____	

Additional Information

_____

_____

_____

_____

_____

_____

be recorded in a tabular form similar to Table 2.8.

An estimate of the resources (manpower and equipment) needed for the sampling program should be made. Table 2.9 illustrates one form for keeping records of available resources and estimated needs of a sampling program. A preliminary sampling plan should include sample preservation and chain of custody procedures.

2.5.2 Evaluation of Preliminary Plan

Circulate the preliminary sampling plan among other divisions (laboratory, field personnel, quality assurance branch, etc.) connected with the sampling program for their considerations and further deliberations before drawing up a final sampling program.

2.5.3 Final Plan

The final sampling plan is based on the preliminary plan and subsequent deliberations and coordination with the various personnel involved. The final plan should spell out in detail and with clarity the various aspects of sampling such as: objectives, sampling locations, number and frequency of samples, sample types, preservation and chain of custody procedures, designation of authorities, field procedures and other pertinent information so that the sampling plan is executed in an efficient and well coordinated manner. Pre-sampling briefing should be a key element in any sampling program.

2.5.4 Program Evaluation

The entire program should be evaluated after the samples are collected and analyzed. This evaluation is to determine the effectiveness of the final plan and should serve to avoid future pitfalls and problems. The performance evaluation should act as a tool to enhance the efficiency of the program and quality of the data generated from a sampling program.

TABLE 2.8 DETAILS OF SAMPLING

Parameters of Interest	Sample Type	Sample Frequency	Number of Samples	Field or Lab Analysis	Sample Volume	Preservation	Holding Times	Analytical Methods	Chain of Custody Procedure	Remarks

TABLE 2.9 MANPOWER AND EQUIPMENT FOR A SAMPLING PROGRAM

Manpower:	Available	Needed
Sampling Program Coordinator		
Quality Assurance Coordinator		
Laboratory Custodian		
Field Sampling Crew Chief		
Sampling Crew Journeymen		
Field Laboratory Crew		
Shipment Truck Driver		
Others		
_____		
_____		
_____		
Equipment:		
Automatic Samplers:		
Type _____		
_____		
_____		
_____		
_____		
Manual Samplers:		
Type _____		
_____		
_____		
_____		

(continued)

TABLE 2.9 (continued)

	Available	Needed
Flow meters:		
Type		
Portable weirs:		
Size		
Portable flumes:		
Size		
Sounding Equipment:		
Wading rods		
Cable lines		
Sounding rods		
Sounding Weight		
Boats:		

(continued)

TABLE 2.9 (continued)

	Available	Needed
Trucks:		
Field Laboratory:		
Other Equipment:		

2.6 FIELD PROCEDURES

The importance of a good sampling program cannot be overemphasized. The heart of the sampling program is field operations. If proper precautions and care are not exercised in the field procedures, the entire sampling program will become meaningless despite adequate planning, analytical facilities, and personnel. The key to the success of a field sampling program lies in good housekeeping, collection of representative samples, proper handling and preservation of samples, and appropriate chain of custody procedures.

2.6.1 Good Housekeeping

1. Written specific instructions on field sampling procedures should be composed.
2. Prior to use, sampling equipment should be checked to insure good operating conditions and cleanliness. Always keep the equipment ready to be used. After the sampling has been completed, clean the equipment and keep it in neat environments. Follow manufacturer's specifications in carrying out routine maintenance of the equipment.
3. Check primary and secondary devices for the following:
    a. Locations
        - At appropriate place as defined in sampling program.
        - Upstream and downstream conditions meet the requirement of specific installation of primary and secondary devices.
    b. Dimensions of primary devices like flumes and weirs, and still wells are within tolerance limits,
    c. General conditions of channel, primary and secondary devices and stilling wells. Notice any unusual wear, debris in channel, and distortion of chart paper, etc.

d. Calibration of primary and secondary devices before actual measurements of flow are taken.

4. Check all sample bottles to avoid contamination. Clean bottles as indicated in Section 4.2.5. If this cannot be done, do not collect the sample.
5. In the laboratory clean sample intake tubing by flushing with hot water and then rinsing. In field rinse several times with sample water.
6. Maintain records of the breakdowns in the sampling operations and the problems encountered with different equipment and how they were resolved. This information indicates the reliability of the equipment, the problem areas that need to be brought to the manufacturer's attention, and considerations for future procurements.

2.6.2 Representative Sample

To obtain representative samples, follow these guidelines:

1. Take sample where water is well mixed (e.g. near a Parshall flume or at a point of hydraulic turbulence such as downstream of a hydraulic jump). Weirs tend to enhance the settling of solids upstream and accumulate floating solids and oil downstream, therefore such locations should be avoided as a sample source. For low level turbulence, mechanical or air mixing should be used to induce turbulence except when dissolved gases or volatile materials are being sampled.
2. Take sample in the center of the channel at 0.4 to 0.6 depth where the velocity of flow is average or higher than average and chances of solids settling is minimum. This depth avoids bottom sediments and top floating materials such as oils and grease.

3. In a wide channel, divide the channel cross section into different vertical sections so that each vertical is homogeneous. Take a representative sample in each vertical section.
4. In a deep stream or lake collect samples taken at different depths. In those cases of wide and deep streams the samples can be composited or analyzed individually depending upon the program objective.
5. In manual sampling with jars, place the mouth of the collecting container below the water surface and facing flow to avoid an excess of floating material. The hand should be away from the mouth as far as possible.
6. Do not collect large nonhomogeneous particles in the sample (e.g. leaves in a surface water sample, rags in a municipal influent sample).
7. Additional guidelines for manual sampling:
   - Sample facing upstream to avoid contamination.
   - Force sampling vessel through the entire cross section of the stream whenever possible.
   - Drop an inverted bucket and jerk line just before impact with the water surface.
   - Be certain that the sampler closes and opens at the proper time when sampling with a depth integrating sampler; with a point sampler, be certain that sampler opens at a proper depth. If a doubt exists, discard the sample and resample.
8. Do not allow air to enter the sample bottles. Fill the bottles completely if the samples are to be analyzed for purgeables, O_2, CO_2 NH_3, H_2S, free chlorine, pH, hardness, SO_2, NH_4, FE^{++}, acidity or alka-

linity.

9. Collect sufficient volume to allow duplicate analyses and quality assurance testing (split or spiked samples). The required sample volume is a summation of that required for each parameter of interest. Refer to USEPA's "Methods for Chemical Analyses for Water and Wastewater, 1979," for the volume required for analysis of a specific parameter (8).

10. Maintain an up-to-date log book which notes possible interferences, environmental conditions and problem areas.

11. Since mathematical relationship between volumetric flow and height (or depth) of flow is nonlinear, flow proportional samples are composited in relation to the total volume of flow as opposed to gauge height or raw measurement of a secondary device.

12. If samples are taken from a line via a valve or faucet arrangement, allow sufficient flushing time to insure that the sample is representative of the supply, taking into account the diameter, length of the pipe to be flushed and the velocity of the flow.

2.6.3 Sample Preservation, Handling and Chain of Custody Procedures

When immediate analysis of the collected sample is not possible, it will be necessary to take cerain precautions so that the sample characteristics are not altered and representativeness of the sample maintained. Follow these guidelines for sample handling and preservation:

1. Minimize the number of people handling the sample.

2. Follow the guidelines given in Chapters 4 and 5 on sample handling and chain of custody procedures.

3. Store the sample in a manner that insures that the parameters to be analyzed are not altered, and use the preservation methods pertinent to different parameters as per guidelines given in chapter 4.

4. Make sure that the container material does not interfere with the analysis of the specific parameters. Refer to USEPA's "Methods for Chemical Analyses for Water and Wastewaters, 1979" (8)

2.6.4 Field Analysis and Procedures

Appropriate analysis using approved methods and quality control in the field will enhance the efficiency of the sampling program. Approved analytical methods for various parameters are listed in Federal Register vol. 41, No. 232, Title 40, Part 136, pp. 52780-52786. The sampling program should specify the various analyses to be performed in the field and the corresponding analytical methods. Field laboratories must also have standard procedures and methods for handling and analyzing samples such that identification, integrity and representativeness of the samples are maintained at all times.

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CHAPTER 3

FLOW MEASUREMENTS

An overview of different methods of flow measurements is presented in this section. More detailed information can be found in a number of noteworthy publications such as ASME Monograph of Fluid Meters (1), USDI Bureau of Reclamation's Water Measurement Manual (2), many publications of Techniques of Water Resource Investigations, etc. by USDI, U. S. Geological Survey; many texts on hydraulics, and other manuals covering the subject (3-13).

Inaccuracy in flow measurements will eventually be reflected in the results of a sampling program. Inaccurate flow measurements will lead to inaccurate flow proportional composite samples which in turn will lead to inaccurate results. Therefore, due care and effort must be exercised in selecting a flow measurement site. The ideal site gives desired flow measurement to meet program objectives; provides ease of operation and accessibility; personnel and equipment safety; and is free from vandalism.

A flow measurement system usually consists of a primary device having some type of interaction with the fluid and a secondary device which translates this interaction into a desired readout or recording (5).

Flow measurement methods can be broadly grouped into four categories:

1. Closed conduit flow measurement
2. Flow measurement for pipes discharging to atmosphere
3. Open channel flow measurement
4. Miscellaneous methods of flow measurement

Table 3.1 lists different methods of flow measurement and their application to various types of problems.

3.1 CLOSED CONDUIT FLOW MEASUREMENT

Some of the most commonly used devices and methods for closed conduit primary flow measurement are described briefly in this section.

3.1.1 Venturi Meter

The Venturi meter is one of the most accurate primary devices for measuring flow rates in pipes. Basically, the Venturi meter is a pipe segment consisting of an inlet section (a converging section), a throat and an outlet section (a diverging section) as illustrated in Figure 3.1. A portion of potential energy transferred to kinetic energy in the throat section causes a pressure differential which is proportional to the flow rate. One of the advantages of the Venturi meter is that it has a low pressure loss.

Manufacturers of Venturi meters routinely size their meters for a specific use. The accuracy of the Venturi meter is affected by changes in density, temperature, pressure, viscosity and pulsating flow of the fluid.

The following requirements are necessary to obtain accurate flow measurements:

1. Install Venturi meter as per manufacturer's instructions.
2. Install Venturi meter downstream from a straight and uniform section of pipe, at least 5-20 diameters, depending upon the ratio of pipe diameter to throat diameter and whether straightening vanes are installed upstream. Installation of straightening vanes upstream will reduce the upstream piping.
3. For wastewater application, insure that the pressure measuring taps are not plugged.
4. Calibrate Venturi meter in place either by volumetric method (Section

TABLE 3.1 METHODS OF FLOW MEASUREMENT AND THEIR APPLICATION TO VARIOUS TYPES OF PROBLEMS (14,15)

Device or Method	Flow Range Measurement	Applicable to Type of Water and Wastewater	Cost	Ease of Installation	Accuracy* of Data	Pressure Loss Thru the Device	Volumetric Flow Detector	Flow Rate Sensor	Transmitter Available	Application
Mathematical formula	Small to large	All	Low	NA	Fair	NA	NA	NA	NA	Open channel, pipe flow
Water meters	Small to large	All	Low	Fair	Excellent	Medium	NA	NA	NA	Pipe flow
Bucket & stopwatch	Small	All	Low	Fair	Good	NA	NA	NA	NA	Small pipes with ends or joints can be disconnected
Pump capacity & operation	Small to large	All	Low	Fair	Good	NA	NA	NA	NA	Lines where water is being pumped
Floating objects	Small to medium	All	Low	NA	Good	NA	NA	NA	NA	Open channels
Dyes	Small to medium	All	Low	NA	Fairly good	NA	NA	NA	NA	Pipe flow and open channels
Salt Dilution	Small to medium	All	Low	NA	Fair	NA	NA	NA	NA	Pipe flow and open channels
Orifice meter	Small to large	Clean water	Medium	Fair	Excellent 1/4 - 2%	High	Yes	Yes	Yes	Pipe flow
Venturi tubes	Small to large	Clean water, limited for waters with suspended solids	High	Fair	Excellent 1/4 - 3%	Minimal	Yes	Yes	Yes	Pipe flow

* Assumes proper installation and maintenace of primary device

(continued)

TABLE 3.1 (Continued)

Device or Method	Flow Range Measurement	Applicable to Type of Water and Wastewater	Cost	Ease of Installation	Accuracy* of Data	Pressure Loss Thru the Device	Volumetric Flow Detector	Flow Rate Sensor	Transmitter Available	Application
Flow nozzle	Small to large	Clean water	Medium	Fair	Excellent 1/4 - 3%	Minimal	Yes	Yes	Yes	Pipe flow
Pitot tubes	Small to medium	Clean water	Medium	Fair	Good 2 - 5%	Minimal	Yes	Yes	Yes	Pipe flow
Elbow taps	Small to medium	Clean water, limited for water with suspended solids	Medium	Fair	Fair	None	Yes	Yes	Yes	Pipe flow
Rotameters	Small to medium	Clean water, limited for water with suspended solids	Medium	Fair	Excellent	Average	Yes	Yes	Yes	Pipe flow
Magnetic flow-meters	Small to large	All	High	Fair	Excellent 1/2 - 1%	None	Yes	Yes	Yes	Pipe flow
Weirs	Small to large	All	Medium	Difficult	Good to Excellent 2 - 5%	Minimal	Yes	Yes	Yes	Open channel flow
Flumes	Small to large	All	High	Difficult	Good to Excellent 2 - 5%	Minimal	Yes	Yes	Yes	Open channel flow
Acoustic flow-meters	Small to large	All	High	Fair	Excellent 1%	None	Yes	Yes	Yes	Pipe and open channel flow

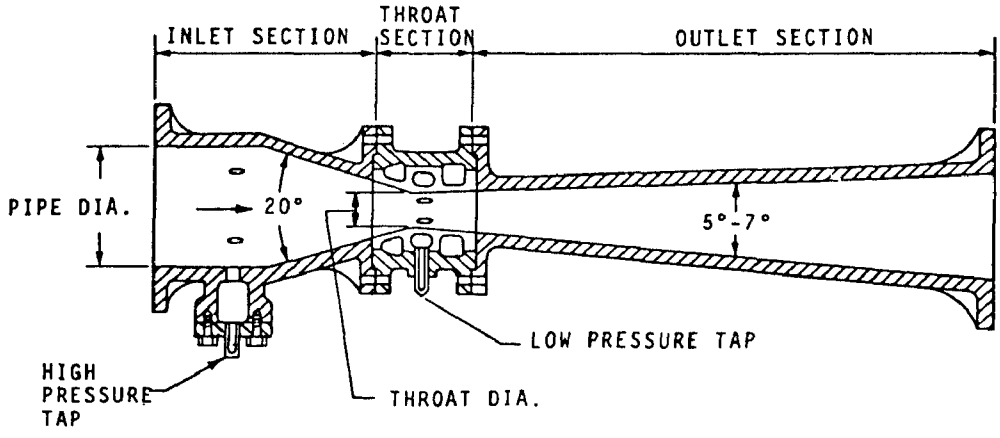


Figure 3.1 Venturi Meter (5)

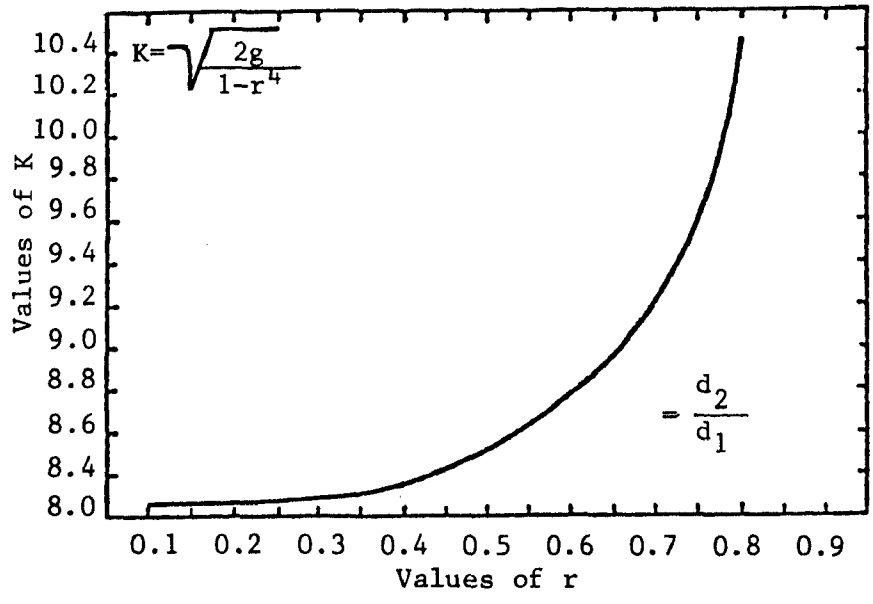


Figure 3.2 Curve for Determining the Values of K used in the Orifice, Venturi, and Flow Nozzle Equations (3)

3.4.5) or comparative salt dilution method (Section 3.3.1.3) to either check the manufacturer's calibration curve or to develop a new calibration curve. (17)

The formula for calculating the flow in a Venturi meter is as follows:

$$Q = CAK\sqrt{H}$$

or $$q = CAK\sqrt{H}\ \ell/s\ (450\ CAK\sqrt{H}\ gpm)$$

where

q = volume of water, in liters per second (gallons per minute).

Q = volume of water, in cubic meters per second (feet per second).

C = discharge coefficient, approximately 0.98. C varies with Reynold's number, meter surfaces and installation.

A = throat area, in square meters (feet) $\frac{\pi}{4} d_2^2$.

H = $H_1 - H_2$, differential head, in meters (feet) of water.

H_1 = pressure head at center of pipe at inlet section, in meters (feet) of water.

H_2 = pressure head at throat, in meters (feet) of water

$$K = \sqrt{\frac{2g}{1-\left(\frac{d_2}{d_1}\right)4}}$$ (Obtain values of K from Figure 3.2)

where

g = acceleration due to gravity, 9.82 m per sec^2 (32.2 ft per sec^2)

d_2 = throat diameter, in meters (feet)

d_1 = diameter of inlet pipe, in meters (feet)

3.1.2 Flow Tubes

Included in the class of flow tubes are Dall tube, "Lo-Loss" tube, and gentle tube.

The Dall tube is a Venturi-type device, wherein the differential pressure results from the streamlined bending as well as the velocity head (Figure 3.3).

The Dall tube is almost as accurate as the standard Venturi and has a higher head recovery, being one of the lowest permanent head loss devices known. It is more sensitive to system disturbances than the Venturi, and straight upstream pipe runs of 40 pipe diameters or more may be required. Installation of straightening vanes upstream will reduce the upstream piping requirement. Although somewhat cheaper than the Venturi, the Dall tube must still be considered expensive. It is much shorter than either long or short tube Venturi meters. Calibration and other installation guidelines for Venturi meters also apply to flow tubes.

3.1.3 Flow Nozzle

A flow nozzle is a measuring device with characteristics between the Venturi meter and an orifice as far as head loss and cost are concerned (Figure 3.4). It operates on the same principles as the Venturi meter. The flow formula for the Venturi tube is also applicable to the nozzle. Flow nozzles can be used in wastewater flows containing moderate amounts of suspended solids. Each manufacturer uses a slightly different nozzle ranging from a Venturi to an orifice. Accuracy, installation and calibration guidelines for Venturi meters also apply to flow nozzles.

3.1.4 Orifice Meter

An orifice meter is a relatively inexpensive, easy to install, and reliable flow measuring device; the thin plate orifice being most commonly used. Basically, an orifice is an obstacle placed in the path of flow in a pipe.

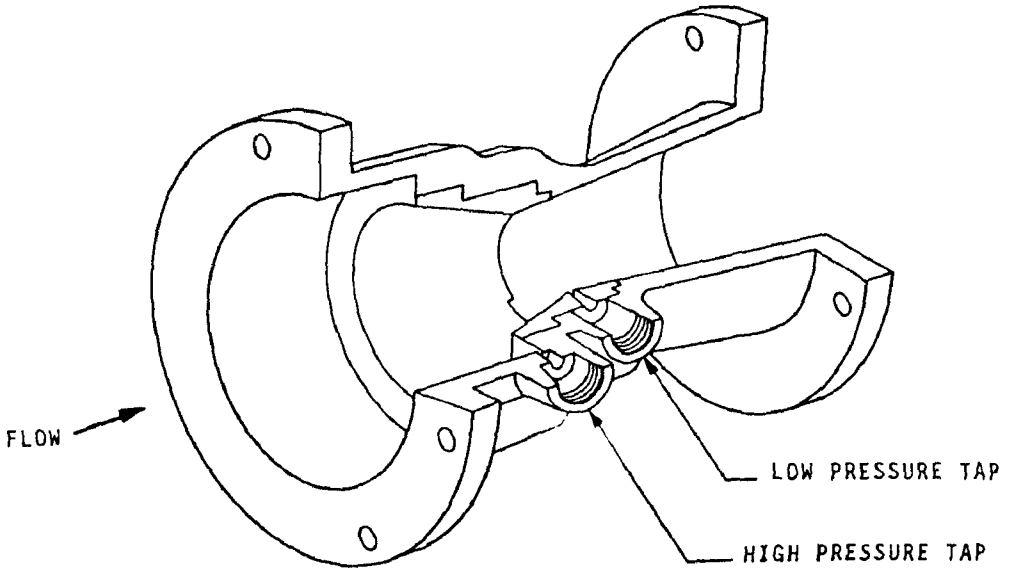


Figure 3.3 Dall Flow Tube (5)

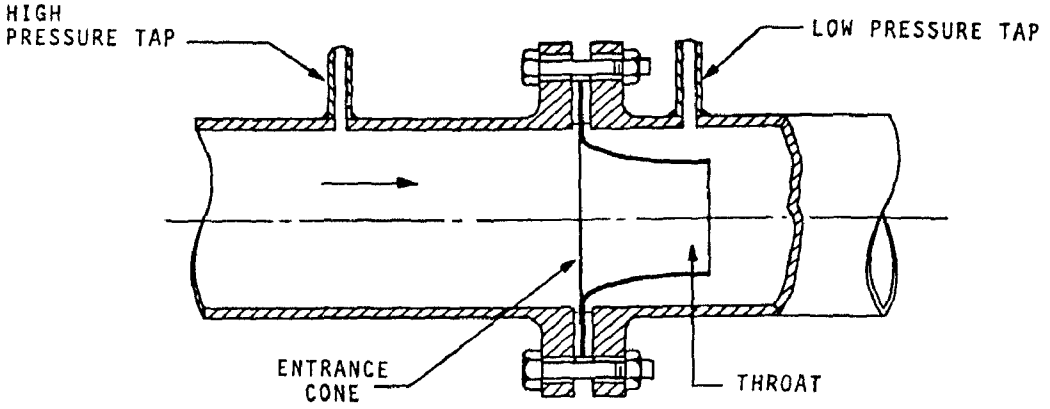


Figure 3.4 Typical Flow Nozzle Installation (5)

The principles of operation of an orifice are the same as for nozzles and Venturi meters, the stream lines of the flow and the basic formula being similar to those of a Venturi meter, i.e.,

$$Q = CAK\sqrt{H} \quad \text{(same as Venturi tube)}$$

The coefficient, C, is illustrated for several forms of orifices in Figure 3.5 and tabulated in Table 3.2. The nominal coefficients are applicable for relatively large orifices operating under comparatively large heads of water.

The orifice is quite useful with variations in flow accommodated by varying the throat width. Orifice plates are the most sensitive of all the differential pressure devices to effects of upstream disturbances, and it is not uncommon to need 40 to 60 pipe diameters of straight run upstream of the installation (3). The main disadvantage to the orifice is the large permanent pressure loss that occurs across the section. The other disadvantage of the orifice is susceptibility to clogging in waters with high suspended solids concentration. The relative permanent pressure losses for the Venturi tube, the nozzle, P/M Lo-Loss tube (Badger Meter Inc.) and the orifice are compared in Figure 3.6.

TABLE 3.2 DISCHARGE COEFFICIENTS FOR PRESSURE TAP, ORIFICES (13)

Orifice Diameter ($\frac{d_2}{d_1}$) / Pipe Diameter	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Coefficient C	---	0.61	0.61	0.61	0.61	0.61	0.64	0.71

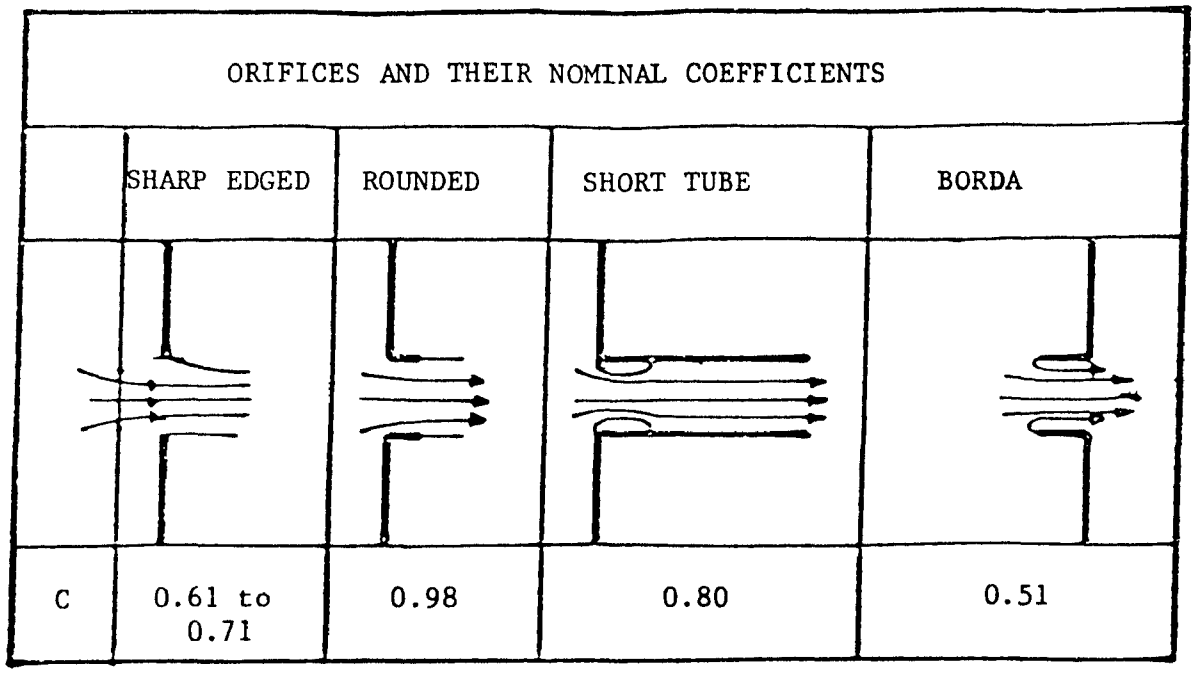


Figure 3.5 Coefficients of Several Types of Orifices (13)

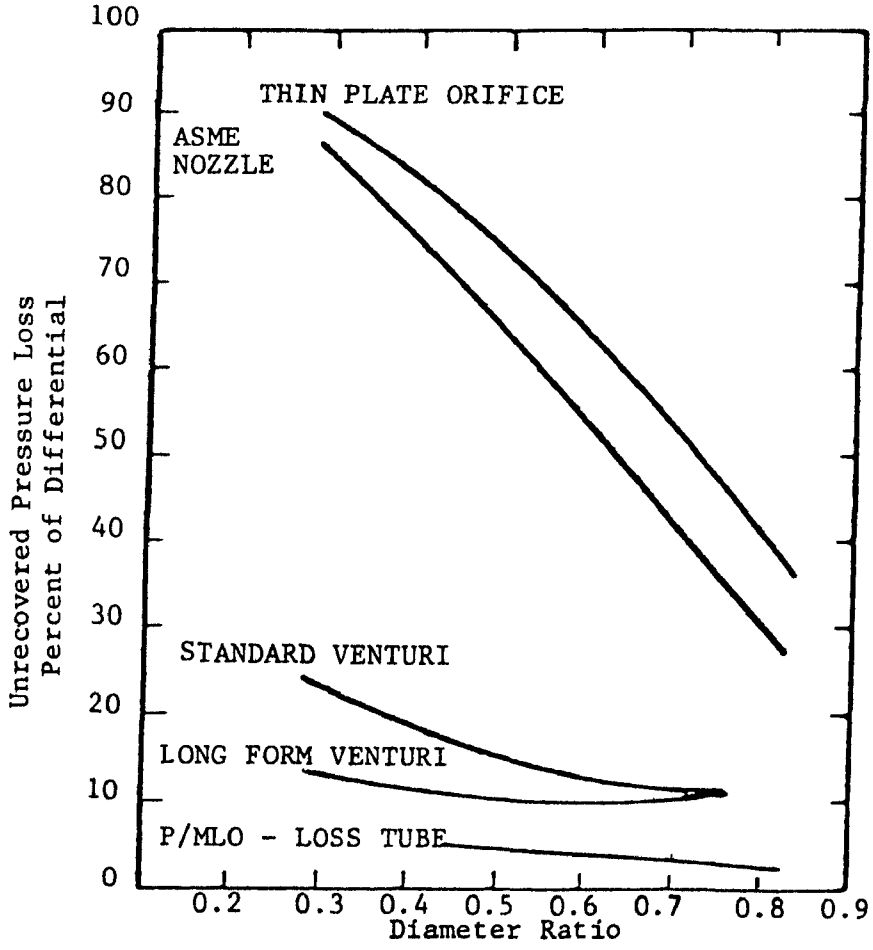


Figure 3.6 Relative Permanent Loss of Primary Elements (3)

3.1.5 Elbow Meters

Flow acceleration induced in a fluid going around a bend (such as an elbow) produces a differential pressure that can be used to indicate flow. The pressure on the outside of an elbow is greater than on the inside, and the pressure taps located midway around the bend (i.e, 45 degrees from either flange) can be connected to a suitable secondary element for indicating or recording.

For accurate flow measurement,straight pipe runs of at least 20 pipe diameters should be provided both upstream and downstream of the elbow. Accuracies of 3 to 10% are generally encountered although accuracies of 1 to 2% or better in some cases may be achieved if calibrated in place (5).

3.1.6 Pitot Tube

A schematic diagram of a simple pitot tube is shown in Figure 3.7. In operation, the velocity of the flow is calculated from the difference in head measured on the manometer. Pitot tubes measure the flow velocity at a point. The basic formula is:

$$V_x = C\sqrt{2gH}$$

V_x = velocity at a point

C = coefficient of discharge obtained by calibration

V_c = velocity at the center

V_m = mean velocity $\simeq 0.83\ V_c$

H = measured pressure differential

Q = discharge volume

A = area of cross section of stream at the point of measurement

$$Q = V_m A$$

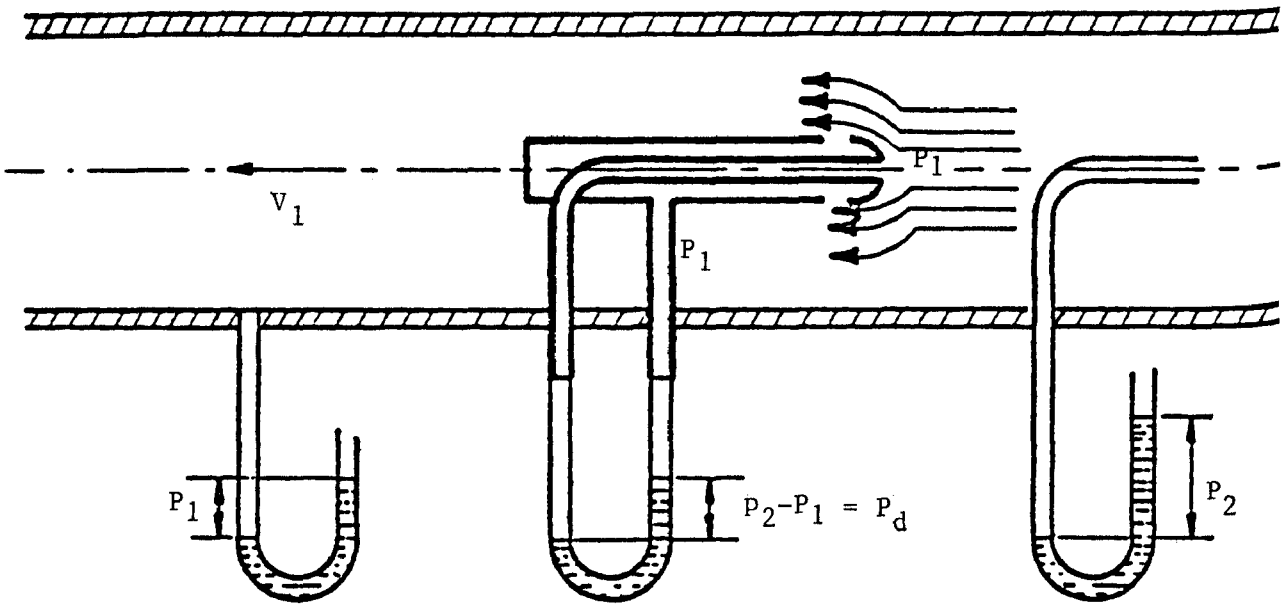


Figure 3.7 Pitot Tube Schematic

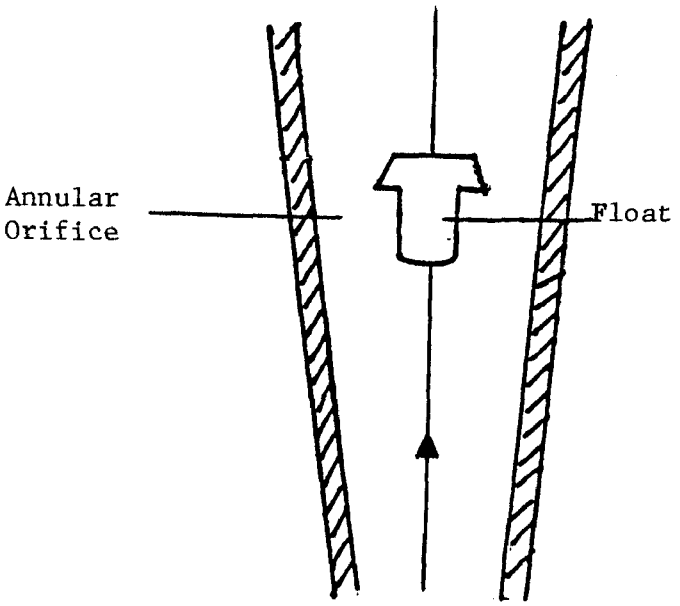


Figure 3.8 Rotameter

commercially available pitot tubes consist of a combined peizometer and total head meter. Pitot tube measurements should be made in a straight section upstream and free of valves, tees, elbows, and other fittings with a minimum distance of 15 to 50 times the pipe diameter. When a straight section is not possible, a velocity profile should be obtained experimentally to determine the point of mean velocity. Pitot tubes are not practical for use with liquids with large amounts of suspended solids because of the possibility of plugging. In large pipes, the pitot tube is one of the most economical means of measuring flows.

3.1.7 Rotameters

Rotameters (Figure 3.8) are tapered tubes in which the fluid flows vertically upward. A metal float in the tube comes to equilibrium at a point where the annular flow area is such that the velocity increase has produced the necessary pressure difference. Rotameters are simple, inexpensive and accurate devices for measuring relatively small rates of flow of clear, clean liquids. For this reason they are often used to measure the water rate into individual processing steps in manufacturing operations. To maintain accuracy in a rotameter, it is absolutely essential that both the tube and float be kept clean.

3.1.8 Electromagnetic Flowmeter

The electromagnetic flowmeter operates according to Faraday's Law of Induction: the voltage induced by a conductor moving at right angles through a magnetic field will be proportional to the velocity of the conductor through the field. In the electromagnetic flowmeter, the conductor is the liquid stream to be measured and the field is produced by a set of electromagnetic coils. A typical electromagnetic flowmeter is shown in Figure 3.9. The

induced voltage is subsequently transmitted to a converter for signal conditioning.

Electromagnetic flowmeters have many advantages: accuracies of ± 1 percent are achievable, a wide flow measurement range, a negligible pressure loss, no moving parts, and rapid response time. However, they are expensive. Build-up of grease deposits or pitting by abrasive wastewaters can cause error. Regular checking and cleaning of the electrodes are necessary.

3.1.9 Acoustic Flowmeters

Acoustic flowmeters, commonly used in water and wastewater flow measurements, operate on the basis of travel time difference method. In the travel time difference method, sound waves are transmitted diagonally across the pipe or channel in opposite directions relative to the flow and the difference in travel times upstream and downstream are measured (Figure 3.10)

Flowmeters must be installed according to manufacturer's instructions and calibrated in place to eliminate errors due to uncertainties in nonlaminar flow profile, error due to accoustic short circuit (where transducers are mounted externally on the pipe), and errors due to mechanical effects or to variations in temperature, pressure or composition of water or wastewater. According to the manufacturers, an accuracy of one percent of full scale is achievable.(2,5)

3.2 FLOW FROM PIPES DISCHARGING TO THE ATMOSPHERE

The common techniques for measuring the flow from open ended pipes either full or partly full are listed below. The orifice and flow nozzle techniques which are not listed here are described in Sections 3.1.3 and 3.1.4 respectively. Rotating element meters are described in Section 3.3.1.1.

3.2.1 Pipes Flowing Full

1. Vertical open end pipe (7)

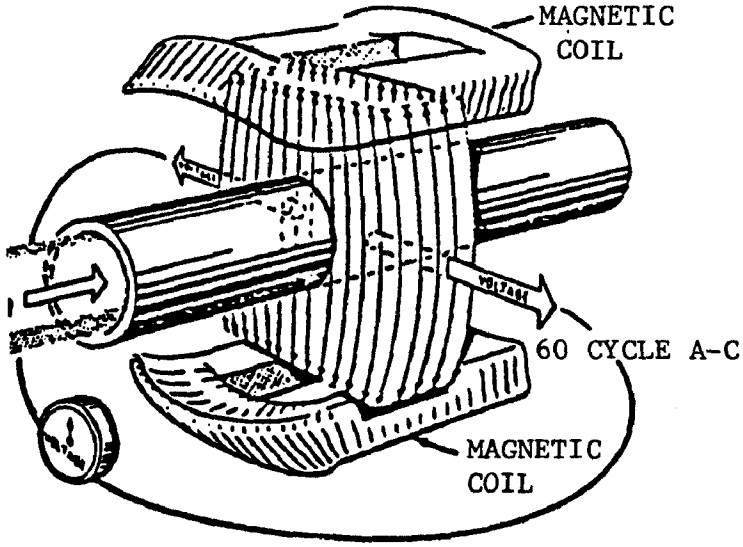


Figure 3.9 Electromagnetic Flowmeter

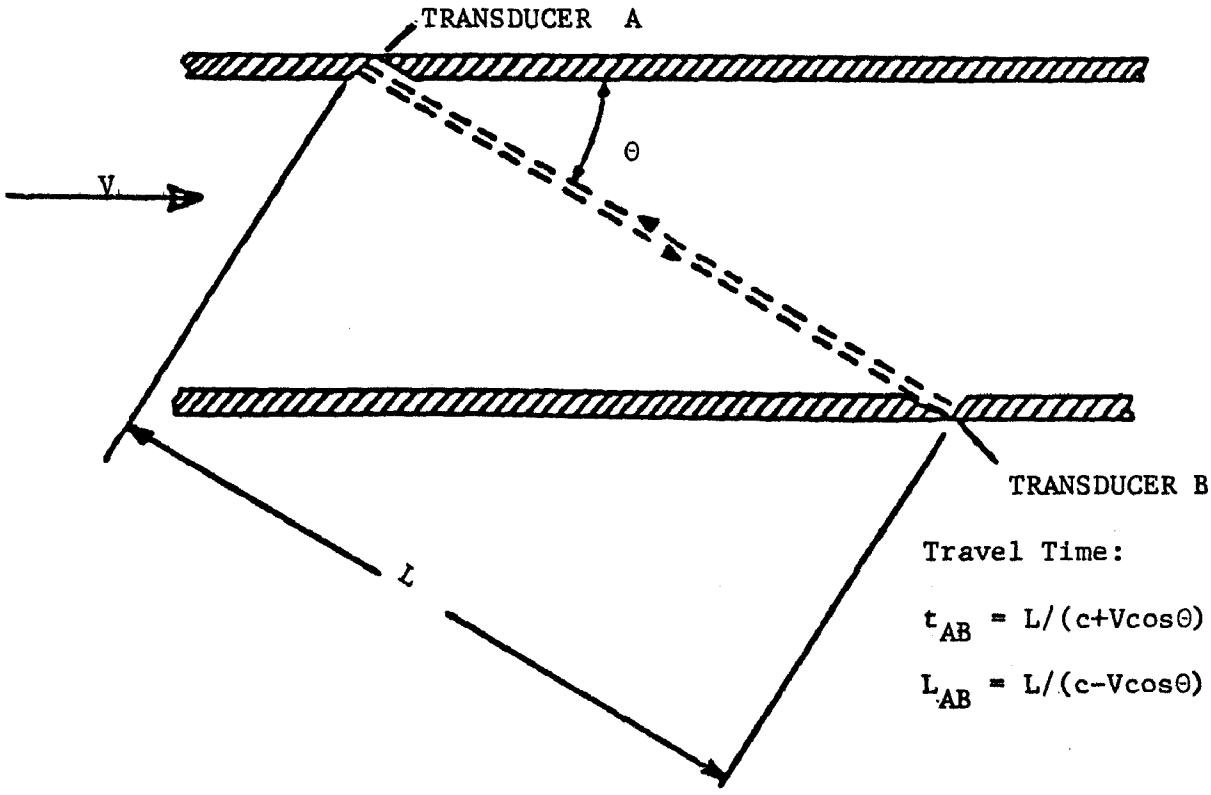


Figure 3.10 Principle of Acoustic Flowmeter (6)

a. Weir flow: $Q = o.249D^{1.20}H^{1.24}$ (Figure 3.11a)

b. Jet flow: $Q = 0.171D^{2.025}H^{0.53}$ (Figure 3.11b)

where, Q = flow m^3/s(cfs = 35.34 m^3/s)

D = internal pipe diameter, meters

H = distance from pipe outlet to top of crest,meters.

2. Horizontal or sloped open end

$$Q = 2.264 \times 10^{-4} \frac{AX}{\sqrt{y}}$$ (Figure 3.11.c and e)

where, Q = flow, m^3/s (cfs = 35.34 m^3/s)

A = cross sectional area of the pipe, m^2

X = distance from the end of the pipe to where Y is measured, m.

Y = vertical distance measured at a distance X from the pipe end, m.

3. Purdue Method (6)

It is similar to the trajectory method for the horizontal open ended pipe, described in (2) above. To obtain the flow, the trajectory measurements X and Y, Figure 3.12 are used in conjunction with curves derived from Purdue University experiments, on pipes 0.05 to 0.15m (2-6 inches) in diameter. Figure 3.13 gives discharge data for Purdue trajectory method for X = 0, 6, 12, and 18 inches and inside pipe diameters of 2,4, and 6 inches.

3.2.2 Pipes Flowing Partially Full

1. Horizontal or sloped open end (7)

$$Q = \frac{2.264 \times 10^{-4} AX\ (CF)}{\sqrt{y}}$$ (Figure 3.11d)

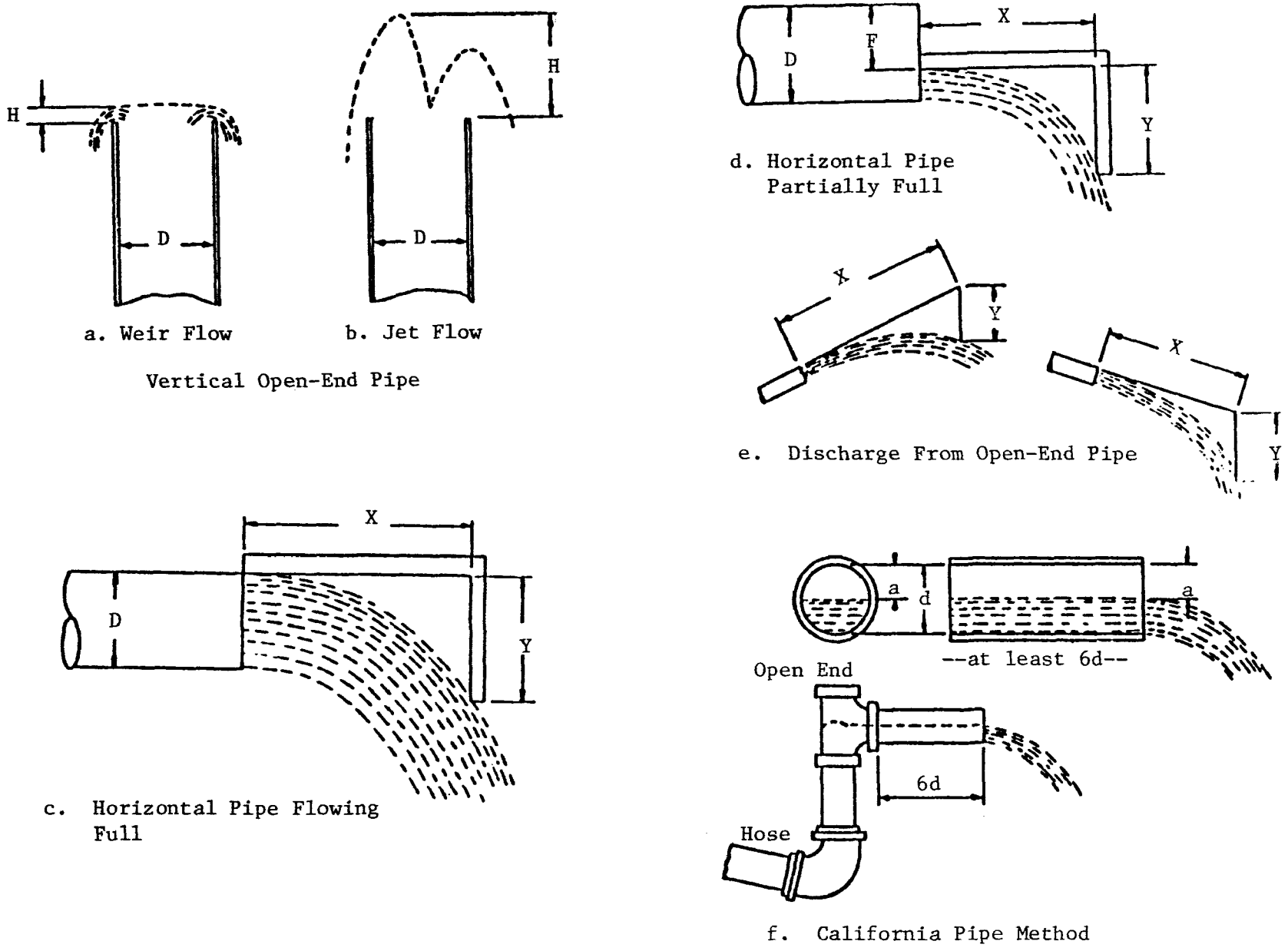


Figure 3.11 Techniques for Pipes Discharging to the Atmosphere (7)

where,

Q = flow, m^3/s (cfs = 35.34 m^3/s)

A = cross-sectional area of the pipe, m^2

X = distance from end of pipe to where Y is measured, m

Y = vertical distance measured at a distance X from the pipe end, m

CF = correction factors which are given in Table 3.3

2. Purdue Method (6)

This method can be used for partially full pipe discharging to atmosphere using the curves (Figure 3.12) for X = 0, provided the brink depth is less than 0.8 diameter.

3. California Pipe Method (6,7)

$$Q = TW, \text{(Figure 3.11f)}$$

where,

Q = flow, m^3/s (cfs = 35.34 m^3/s)

$T = 8.69\ (1 - \frac{a}{d})^{1.88}$

$W = d^{2.48}$

d = pipe diameter, m

a = distance from top of pipe to flow, m

The empirical equation is derived from experiments performed on steel pipes from 3 to 10 inches in diameter and it is imperative that a/d should be less than 0.5 and the straight pipe length to the end of pipe should be at least 6d.

TABLE 3.3 CORRECTION FACTORS FOR DISCHARGE FROM PIPES PARTLY FULL (7)

R*	Correction Factor	R*	Correction Factor	R*	Correction Factor
0.10	0.948	0.37	0.664	0.64	0.324
0.11	0.939	0.38	0.651	0.65	0.312
0.12	0.931	0.39	0.639	0.66	0.300
0.13	0.922	0.40	0.627	0.67	0.288
0.14	0.914	0.41	0.614	0.68	0.276
0.15	0.905	0.42	0.602	0.69	0.265
0.16	0.896	0.43	0.589	0.70	0.253
0.17	0.886	0.44	0.577	0.71	0.241
0.18	0.877	0.45	0.564	0.72	0.230
0.19	0.867	0.46	0.551	0.73	0.218
0.20	0.858	0.47	0.538	0.74	0.207
0.21	0.847	0.48	0.526	0.75	0.195
0.22	0.837	0.49	0.513	0.76	0.184
0.23	0.826	0.50	0.500	0.77	0.174
0.24	0.816	0.51	0.487	0.78	0.163
0.25	0.805	0.52	0.474	0.79	0.153
0.26	0.793	0.53	0.464	0.80	0.142
0.27	0.782	0.54	0.449	0.81	0.133
0.28	0.770	0.55	0.436	0.82	0.123
0.29	0.759	0.56	0.423	0.83	0.114
0.30	0.747	0.57	0.411	0.84	0.104
0.31	0.735	0.58	0.398	0.85	0.095
0.32	0.723	0.59	0.386	0.86	0.086
0.33	0.712	0.60	0.373	0.87	0.078
0.34	0.700	0.61	0.361	0.88	0.069
0.35	0.688	0.62	0.349	0.89	0.061
0.36	0.676	0.63	0.336	0.90	0.052

* R = F/D (Free board in pipe/inside pipe diameter)

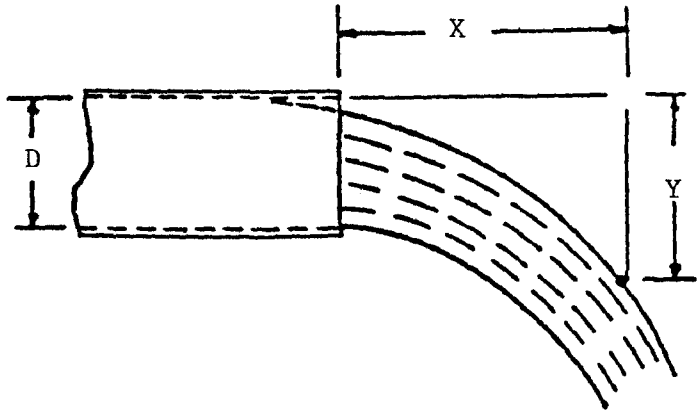


Figure 3.12 Trajectory Measurements, Purdue Method

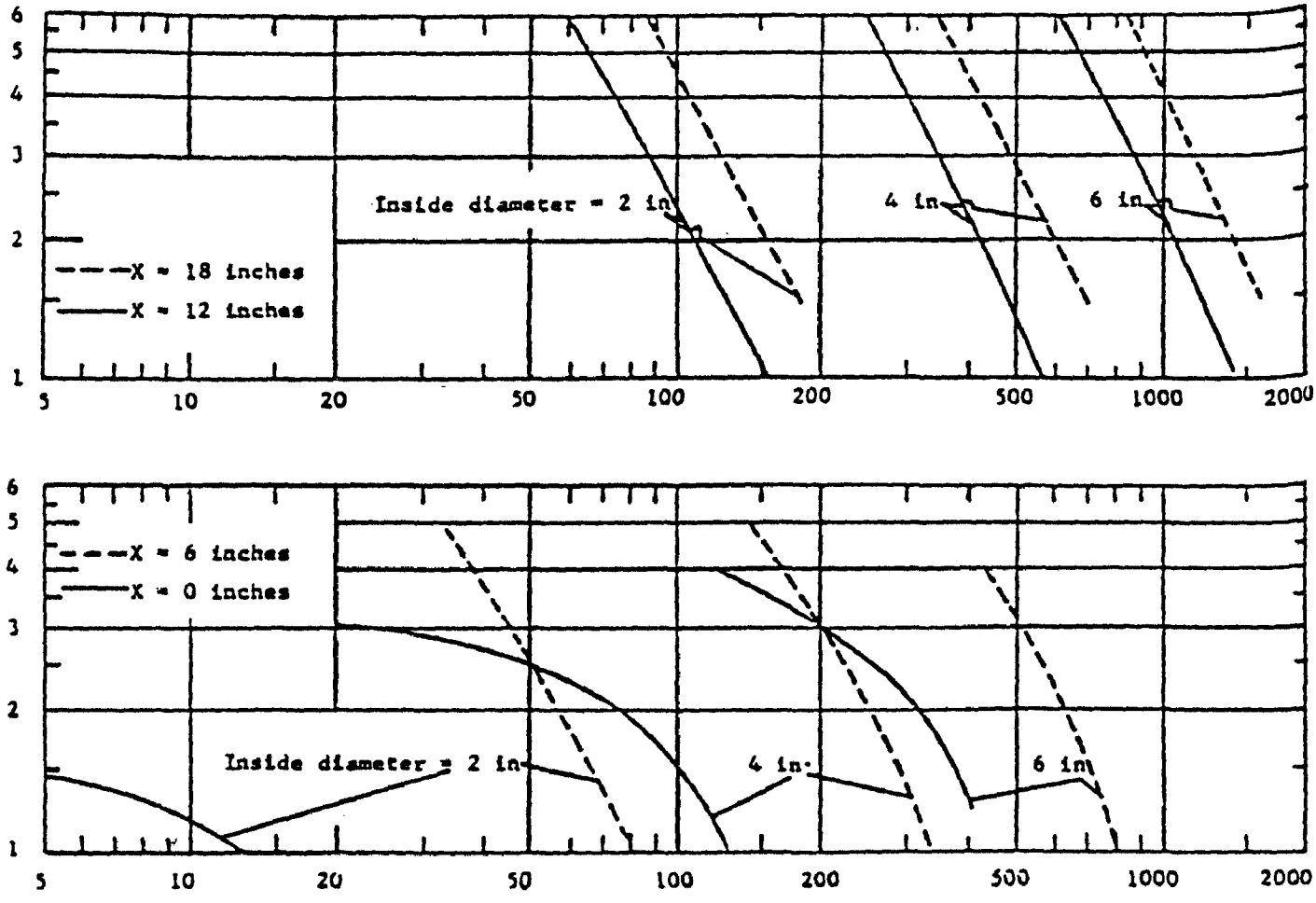


Figure 3.13 Discharge Data, Purdue Method

3.3 OPEN CHANNEL FLOW MEASUREMENTS

Methods of flow measurements for open channels can be applied to flows in non-pressure sewers since both have the same hydraulic characteristics. Different methods in use can be grouped into the following broad classification:

1. Velocity methods
2. Head-Discharge Methods
3. Miscellaneous Techniques

3.3.1 Velocity Methods

Velocity of flow can be measured using different devices; namely, various drag body current meters, eddy-shredding current meter, acoustic velocity meter, doppler-shift velocity meter, electromagnetic current meter, rotating element current meters. Various drag body current meters are compared in Table 3.4. Pitot tubes are described in Section 3.1.6.

3.3.1.1 Rotating Element Current Meters

Of the rotating element current meters, Price and Pigmy meters are quite commonly used. The principle of operation is based on the proportionality between the velocity of water and resulting angular velocity of the meter rotor. In conventional current meters there is a wheel which rotates when immersed in flowing water and a device which determines the number of revolutions of the wheel. The general relation between the velocity of the water and number of revolutions of the wheel is given by: (1,2,4,5,6,16):

$V = a+bN$, where

V = velocity of water meters per second

a and b are constants

N = no. of revolutions per second

TABLE 3.4 COMPARISON OF DRAGBODY CURRENT METERS (16)

Factor	Dragbody Current Meter Type				
	Vertical Axis Deflection Vane	Horizontal Axis Pendulum Type Deflection Vane	Pendulum Current Meter	Inclinometer	Drag Sphere
Velocity Range	Wide range but not suitable for low velocities	Wide range	Wide range	Suitable for low velocities-only single velocity range	Single velocity range
Submerged Installation	No	Possible	Pendulum ball is submerged	Possible	Possible
Debris	Problem	Not a Problem	Affects drag on line and hence accuracy of velocity measurement	Not a problem	Not a problem
Output Recording	Mechanical output	Electrical output	No, manual operation	No, data manually processed	Electrical output
Readout of Deflection	Visual	No visual readout	-	-	Deflection can be resolved-no visual readout
Simplicity	Simple	Simple	Complex		

These current meters can be grouped into two broad classes: 1) vertical-axis rotor with cups or vanes and 2) horizontal-axis with vanes. A number of refrences give the details on different current meters. Figure 3.14 shows the propeller current meter which is typical of a horizontal-axis current meter with vanes. Figure 3.15 shows the Price current meter which is typical of a vertical-axis rotor current meter with cups.

Practical considerations usually limit the ratings of these meters to velocities ranging from 0.030 m/s (0.1 fps) to about 4.57 m/s (15 fps). The comparative characteristics of these two types are summarized below (4):

1. Vertical-axis rotor with cups or vanes
    a. Operates in lower velocities than do horizontal-axis meters.
    b. Bearings are well protected from silty water.
    c. Rotor is repairable in the field without adversely affecting the rating.
    d. Single rotor serves for the entire range of velocities.
2. Horizontal-axis rotor with vanes
    a. Rotor disturbs flow less than do vertical-axis rotors because of axial symmetry with flow direction.
    b. Rotor is less likely to be entangled by debris than are vertical-axis rotors.
    c. Bearings friction is less than for vertical-axis rotors because bending moments on the rotor are eliminated.
    d. Vertical currents will not be indicated as positive velocities as they are with vertical-axis current meters.
    e. They have a higher frequency of mechanical problems.

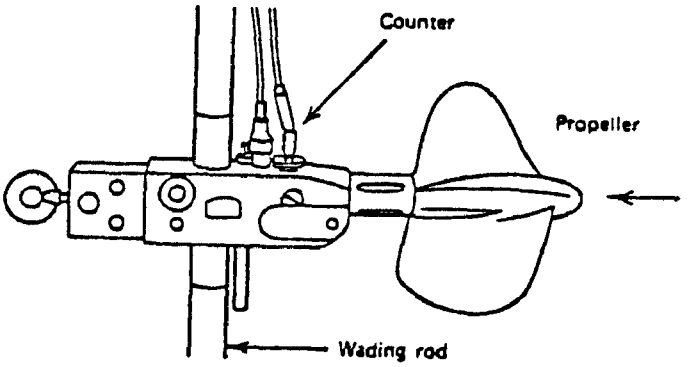


Figure 3.14 Propeller Meter(17)

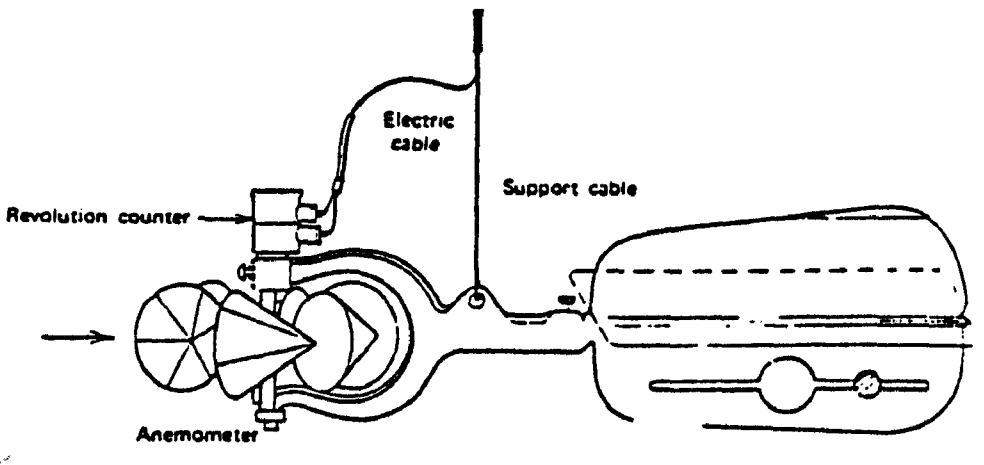


Figure 3.15 Price Meter (17)

To determine the discharge (flow volume), in addition to velocity of flow it is necessary to determine the area of flowing water or wastewaters. This holds especially for large flows in rivers, lakes, and wide and deep channels. A depth sounding is necessary at each vertical and width measurement of the cross-section of flow to determine the area of flowing water or wastewater. Sounding rods, sound weights and reels, handlines, and sonic sounders are common equipment used for depth determinations. Marked cableways and bridges, steel or metallic taps or tag lines are used for width determinations. For details or procedures for depth and width determinations, see reference (4).

3.3.1.2 Measurement of Velocity

To determine the discharge at a particular cross-section, it is necessary to determine the mean velocity of flow at that section. In drag body current meters such as vertical-axis deflection vane, horizontal-axis pendulum type deflection vane and pendulum current meters, it is possible to integrate velocities at different depths in a particular section to obtain the mean velocity of flow, whereas inclinometer, drag sphere, rotating element current meters and pitot tubes measure velocity at a point. Therefore, to obtain the mean velocity of flow at a particular vertical section, it is necessary to take velocity measurements at different depths. The various methods of obtaining mean velocities are:

1. Vertical-velocity curve
2. Two-point
3. Six-tenths-depth
4. Two-tenths-depth
5. Three point
6. Subsurface

Table 3.5 compares these methods in relation to application, flow depth, velocity measuring point(s), and accuracy.

3.3.1.3 Time of Travel-Velocity Methods

a. Salt Velocity Method (1,2,5,6)

The method is based on the principle that salt in solution increases the conductivity of water. This method is suitable for open channels of constant cross-section and for flow in pipes. Sodium chloride and lithium chloride are commonly used. The basic procedure is as follows:

1. Install two pairs of conductivity electrodes down stream from the salt injection point at known distances and sufficiently far apart in the stretch of the channel.
2. Connect the recording galvanometer to the electrodes.
3. Inject the slug of salt solution.
4. The time for salt solution to pass from the upstream to the down-stream electrodes, in seconds, is determined by the distance on the graph between the centers of the gravity of the peak areas.
5. Calculate the discharge, using the formula $Q = \frac{AL}{T}$, where,

   Q = discharge in cubic meters (cubic feet).

   A = cross-sectional area of flow, square meters (square feet).

   L = distance between the electrodes, meters (feet).

   T = recorded time for salt solution to travel the distance between the electrodes, seconds.

B. Color Velocity Method

The color velocity method is used for measuring high velocit flows in open channels. It consists of determining the velocity of a slug of dye between two stations in the channel. This velocity, taken as the mean

TABLE 3.5 COMPARISON OF VARIOUS METHODS TO OBTAIN MEAN VELOCITY

Methods Considerations	Vertical-Velocity Curve Method	Two-point Method	Six-tenth depth Method	Two-tenth Depth Method	Three point Method	Subsurface Method
Application	Not for routine discharge and measurements	Generally used	Primarily used for depths less than 2.5 feet	During times of high velocities when measurements at 0.6 and 0.8 depth are not possible	When velocities in a vertical are abnormally distributed	When it is impossible to obtain soundings and the depth cannot be estimated to an approximate 0.2 depth setting
	To determine coefficients for application to the results obtained by other methods				When more weight to 0.2 and 0.8 depth observations is desired	
Flow depth requirement	Greater than 2.5 feet	Greater than 2.5 feet	0.3 foot to 2.5 feet	No depth constraint	Greater than 2.5 feet	Greater than 2.5 feet
Velocity measuring point(s)	At 0.1 depth increments between 0.1 and 0.9 depth	0.2 and 0.8 depth below the water surface	0.6 depth below the water surface	0.2 depth below the water surface	0.2, 0.6 and 0.8 depth below the water surface	At least 2 feet below the water surface
Mean velocity	From vertical-velocity curve	$\frac{V_{0.2} + V_{0.8}}{2}$	Observed velocity is the mean velocity	$V_{mean} = C \times V_{0.2}$ C=Coefficient obtained from vertical-velocity curve. At that vertical for the particular depth of flow	$V_{mean} = \frac{V_{0.2}+V_{0.8}+V_{0.6}}{4}$	V_{mean} = C x V observed C=Coefficient obtained from vertical-velocity curve at that vertical for the particular depth of flow
Accuracy	Most Accurate	Gives consistent and accurate results	Gives reliable results	If C is accurately known can give fairly reliable results	Gives reliable results	Gives rough estimate as C is difficult to determine accurately

$V_{0.2}$ = Velocity at 0.2 depth from water surface

$V_{0.8}$ = Velocity at 0.8 depth from water surface

$V_{0.6}$ = Velocity at 0.6 depth from water surface

V_{mean} = Mean velocity

velocity, multiplied by the cross-sectional area of flow gives the discharge. Commercial fluorescein or potassium permanganate may be used as the coloring matter. The color velocity is computed from the observations of the time of travel of the center of the mass of colored liquid from the instant the slug of dye is poured at the upstream station to the instant it passes the downstream station, which is at a known distance from the upstream station.

With fluorescent dyes, the use of fluorometer to detect the center of the colored mass will enhance the accuracy of the results.

c. Floats

There are three types of float methods used for flow measurements, namely, surface floats, subsurface floats and integrating floats. To determine the flow velocity one or more floats are placed in the stream and their time to travel a measured distance is determined. These methods are simple, but from an accuracy standpoint, they should only be used for estimating the discharge.

Various surface floats like corks, stoppered bottles etc. and submerged floats like oranges measure the surface velocity. The mean velocity of flow is obtained by multiplying with a coefficient which varies from 0.66 to 0.80 (2). A more sophisticated version is the rod-floats, which are usually round or square wooden rods. These rods have a weighted end so that they float in vertical position with the immersed length extending about nine-tenth of the flow depth. Velocity measured by the time of travel by these rods is taken as the mean velocity of flow. These floats are used in open channels and sewers.

To obtain better results, the velocity measurements should be made on

a calm (winds are very minimal) day in a sufficiently long and straight stretch of channel or sewer of uniform cross-section and grade with a minimum of surface waves. Choose a float which will submerge at least one-fourth the flow depth.

A more accurate velocity measurement is obtained by using integrating float measurements. The method is simple and consists of the release of buoyant spheres (like ping pong balls) from the channel floor. As these spheres rise they are carried downstream by the flow velocity. The time from the moment of release to the moment when they surface, and the distance traveled downstream are measured. The discharge is measured using the following relationships:

$$Q = DV \qquad \text{and} \qquad V = \frac{L}{t}$$

where Q = discharge in cubic meters/sec. (cubic feet/sec.) per unit width of channel

D = flow depth, meters (feet)

V = terminal velocity of the float, meters/sec. (ft./sec.)

L = distance traveled downstream by float, meters (feet)

t = time of rise of float, sec.

In flows of large depth and velocity, integrating float methods with two floats of different velocities of rise are used (18,19). The discharge is calculated, using the relationship:

$$Q = \frac{D(L_2 - L_1)}{t_2 - t_1}$$

where, L_2 and L_1 are distances traveled downstream by float (2) and

float (1), respectively; and t_2 and t_1 are times of rise of float (2) and float (1), respectively.

The integrating float method is simple and does not require any laboratory calibration. It integrates the vertical velocity profile and yields the mean velocity or discharge per unit width of the section. The method is suited to low velocities and is especially useful for flows having abnormal velocity profiles, and it has practically no lower velocity limit. To get better accuracy, the reach of the stream to be measured should be sufficiently long and straight and the bed fairly uniform. Use a fast rising float so that distance travelled downstream is of short length. The shape of the float should be spherical (18).

3.3.2 Head Discharge Methods

This technique takes advantage of the head discharge relationship that exists when a liquid flows over an obstruction or through a specific (convergent-straight-divergent) channel section.

3.3.2.1 Weirs

A weir may be defined as an overflow structure built across as open channel, usually to measure the rate of flow of liquid.

Depending upon the shape of the opening, weirs may be termed rectangular, trapezoidal, triangular, etc. When the water level in the downstream channel is sufficiently below the crest to allow free access of air to the area beneath the nappe, the flow is said to be free. When the water level under the nappe rises above the crest elevation the flow may be considered submerged; the degree of submergence depends upon the ratio of upstream and downstream head (height of water above crest elevation). The effect of submergence is to cause large inaccuracies in the flow mesurements. Therefore, the use of submerged weirs as the

flow measuring device is avoided.

In a sharp crested weir, flowing liquid does not contact the bulk head but springs past it. If the bulk head is too thick for the liquid to spring past, the weir is classed as broad crested.

Weirs may be contracted or suppressed. When the distances from the sides of the weir notch to the sides of the channel (weir pool) are great enough (at least two or three times the head on the crest) to allow the liquid a free, unconstrained lateral approach to the crest, the liquid will flow uniformly and relatively slowly toward the weir sides. As the flow nears the notch it accelerates, and as it turns to pass through the opening, it springs free laterally with a contraction that results in a jet narrower than the weir opening. If a rectangular weir is placed in a channel whose sides also act as the sides of the weir, there is no lateral contraction, and the weir is called a suppressed weir. Various types of weirs are shown in Figure 3.16.

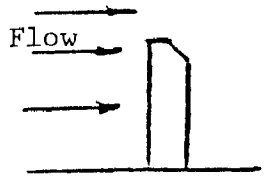
Most of the flow measurements are conducted on sharp crested weirs without submergence and the subsequent discussion is limited to this type. For information on sharp crested weirs with submergence and broad crested weirs, refer to reference (2) and other books on hydraulics.

A typical sharp crested weir is shown in Figure 3.17. Figures 3.18 a,b, and c, show the various dimensions required for fully contracted rectangular Cipolletti and V-notch weirs.

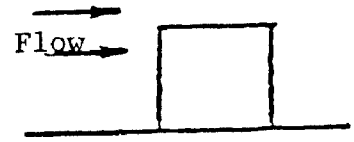
The relationship between head and discharge for different weirs is given in Table 3.6. For rectangular weirs, the Francis formula is widely used for flow measurements. However, it should be born in mind that it is applicable and accurate only for sharp crested fully contracted or suppressed weirs. On the other hand Kindsvater-Carter formula is applicable to any type of sharp crested rectangular weir. It gives accurate results and is being increasingly

SHAPE OF THE WEIR CREST

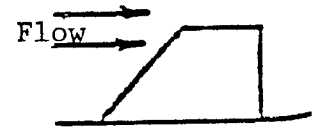
SHARP CRESTED



BROAD CRESTED WEIR



a.

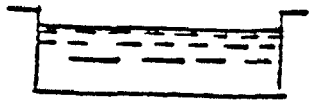


b.

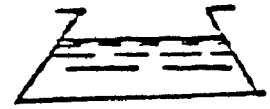
c.

d.

SHAPE OF THE NOTCH



RECTANGULAR



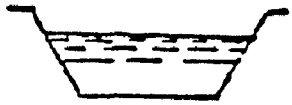
INVERTED TRAPEZOIDAL

POEBING

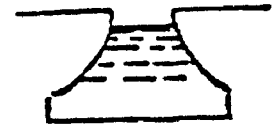
V-NOTCH

COMPOUND

APPROXIMATE LINEAR



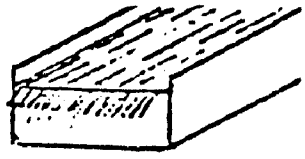
TRAPEZOIDAL



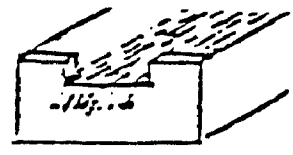
PROPORTIONAL

APPROXIMATE EXPONENTIAL

FLOW CONTRACTION



SUPPRESSED



CONTRACTED

Figure 3.16 Types of Weirs

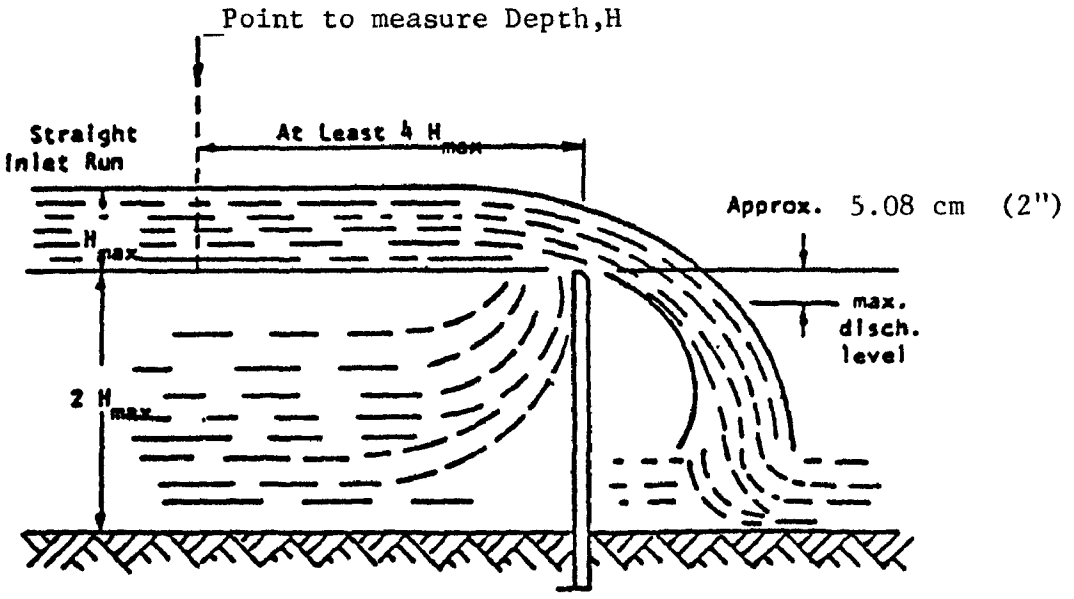
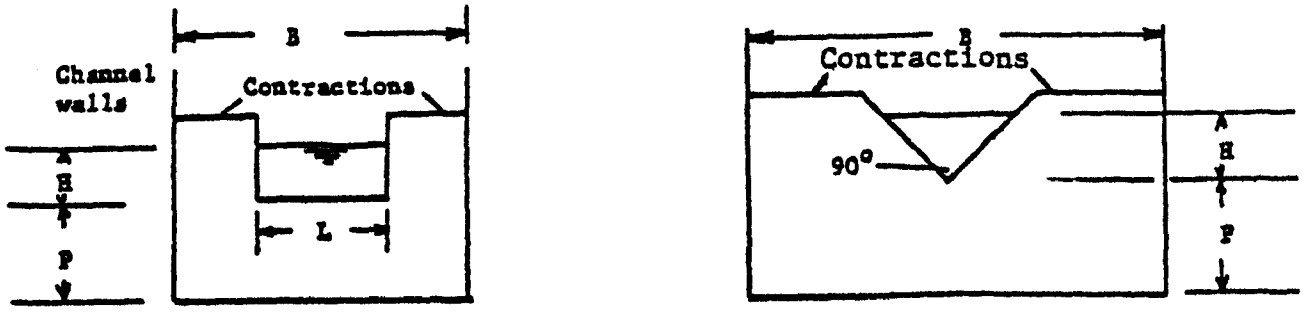
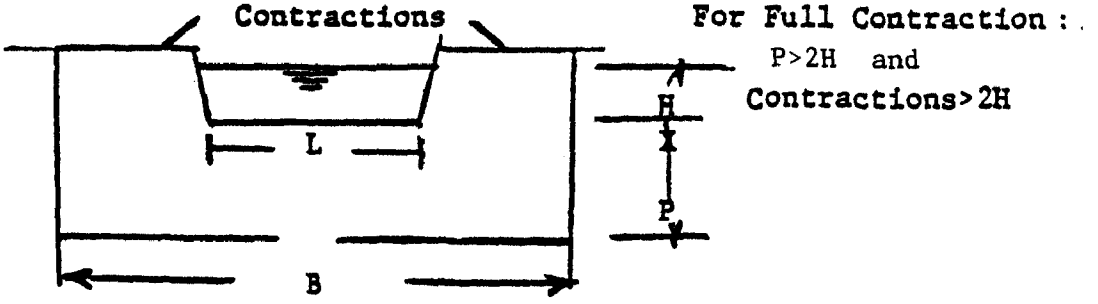


Figure 3.17 Typical Sharp Crested Weir (3)



a. Contracted Rectangular Weir

b. Contracted V - Notch Weir



c. Contracted Cipolletti Weir

Figure 3.18 Various Dimensions for Fully Contracted Rectangular, Cipolletti and V-Notch Weirs (6)

TABLE 3.6 HEAD-DISCHARGE RELATIONSHIP FORMULAS

Weir Type	Contracted	Suppressed	Remarks
Rectangular			
Francis Formulas	$Q^* = 3.33(L-0.2H^{3/2})$	$Q = 3.33LH^{3/2}$	Approach velocity neglected
	$Q = 3.33\left\{(H+h)^{3/2}-h^{3/2}\right\}$ $(L-0.2H)$	$Q = 3.33L\left\{(H+h)^{3/2}-h^{3/2}\right\}$	Approach velocity taken into consideration
Kindsvater-Carter formula	$Q = C_e L_e H_e^{1.5}$	$Q = C_e L_e H_e^{1.5}$	
Cipolletti	$Q = 3.367\ LH^{3/2}$	NA	Approach velocity neglected
	$Q = 3.367L(H+1.5h)^{3/2}$	NA	Approach velocity taken into consideration
V-Notch			
Cone formula for 90° V-Notch only	$Q = 2.49\ H^{2.48}$	NA	V-Notch weirs are not appreciably affected by approach velocity
Kindsvater-shen formula	$Q = \frac{8}{15}\ C_e \tan(\frac{\theta}{2})\ (2gH_e^5)^{1/2}$	NA	

Q = discharge in cubic feet per second L = crest length in feet
H = head in feet h = head in feet due to the approach velocity (V), = $62/2g$
C_e = coefficient, $L_e = L+k_b$, where k_b = ratio of crest (L) to channel width (B), $k_b = L/B$
$H_e = H+0.003$ NA = Not applicable
θ = Angle of the notch $H_e = H+k_h$

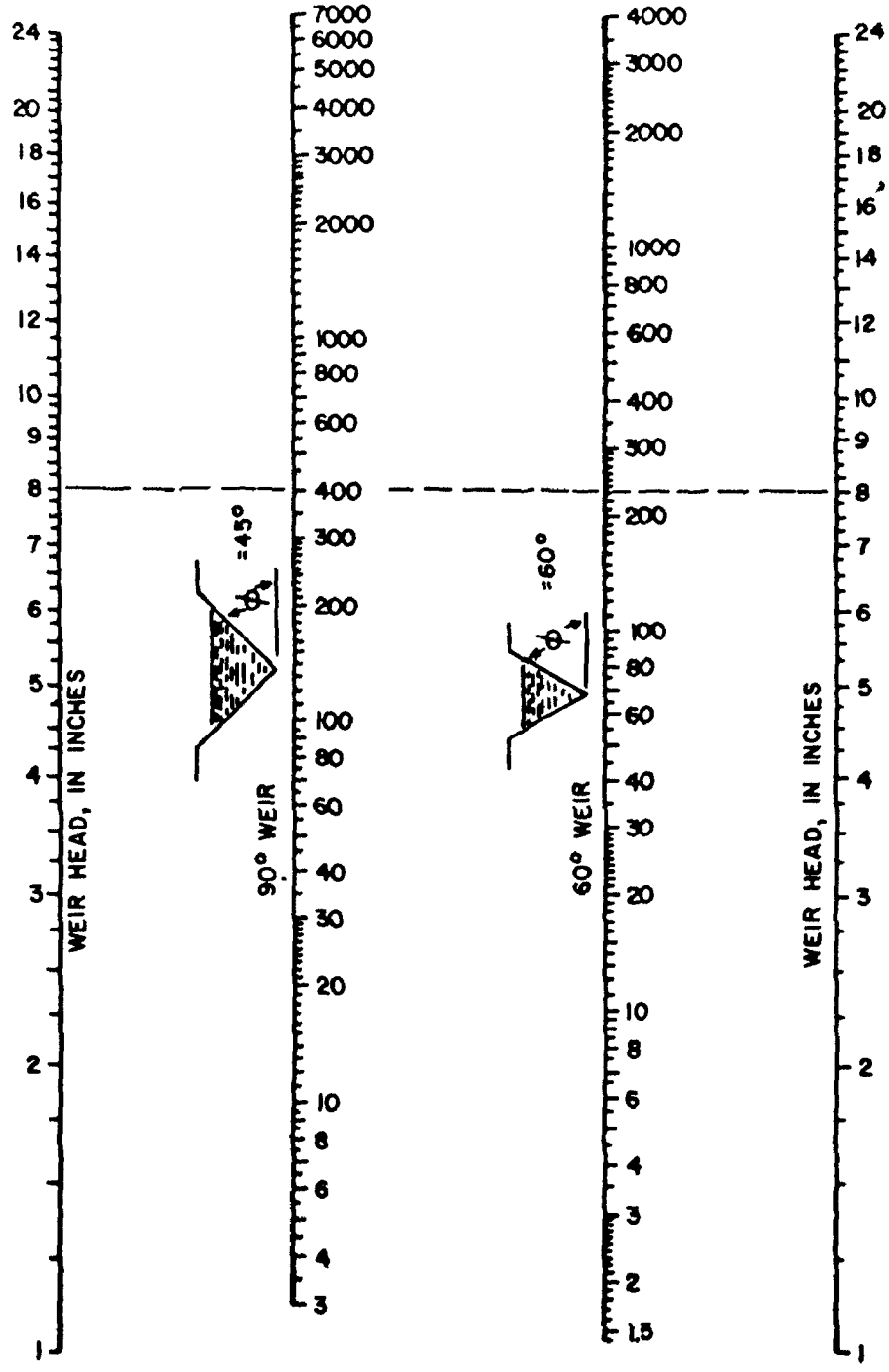
used.

The rate of flow determines the type of weir to use. A rectangular weir is preferable for flows greater than 3.4 cubic meters/min. (2 cubic feet/sec.) V-notch weirs are used for flows of less than 0.17 cubic meters/min. (1.0 to 10 cubic feet/sec.) (2). The Cipolletti weir is also used in the same range as the rectangular weir. The accuracy of measurements obtained by the use of Cipolletti weirs, based on the formulas given in Table 3.6 is inherently not as great as that obtained with suppressed rectangular and V-notch weirs (2).

With these ranges in mind, the minimum head should be at least 5 cm (0.2 ft.) to prevent nappe from clinging to the crest, and because at smaller depths it is difficult to get sufficiently accurate gauge readings. The crest should be placed high enough so that the water flowing over will fall freely, leaving an air space under and around the jets. Requirements for standard weir installations are shown in Figures 3.18 a,b, and c for rectangular, Cipolletti and V-notch weirs, respectively.

For shapes other than those mentioned above, head-discharge relationship must be established through field calibration using the salt-dilution (Section 3.4.3) or other methods.

Flow rates for 60^{o} and 90^{o} V-notch weirs can be determined from the nomographs in Figure 3.19. Figures 3.20a and 3.20b should be used for flow rates of V-notch weirs in conjuction with the Kindsvater-shen formula (6); the cone formula should be used only with fully contracted V-notch weirs. Flow rates for Cipolletti weirs can be obtained from Figure 3.21. Figure 3.22 is a nomograph for flow rates for rectangular weirs using Francis formula; whereas Figure 3.23a and 3.23b should be used in conjunction with Kindsvater-Carter formula.



$$\frac{90^{\circ}\text{V-Notch}}{Q = 2.49H^{2.48}} \qquad \frac{60^{\circ}\text{V-Notch}}{Q = 1.443_{H}^{2.50}}$$

Where Q = discharge in cubic feet per second H = head in feet

Figure 3.19 Nomograph for Capacity of 60° and 90° V-Notch Weirs (16)

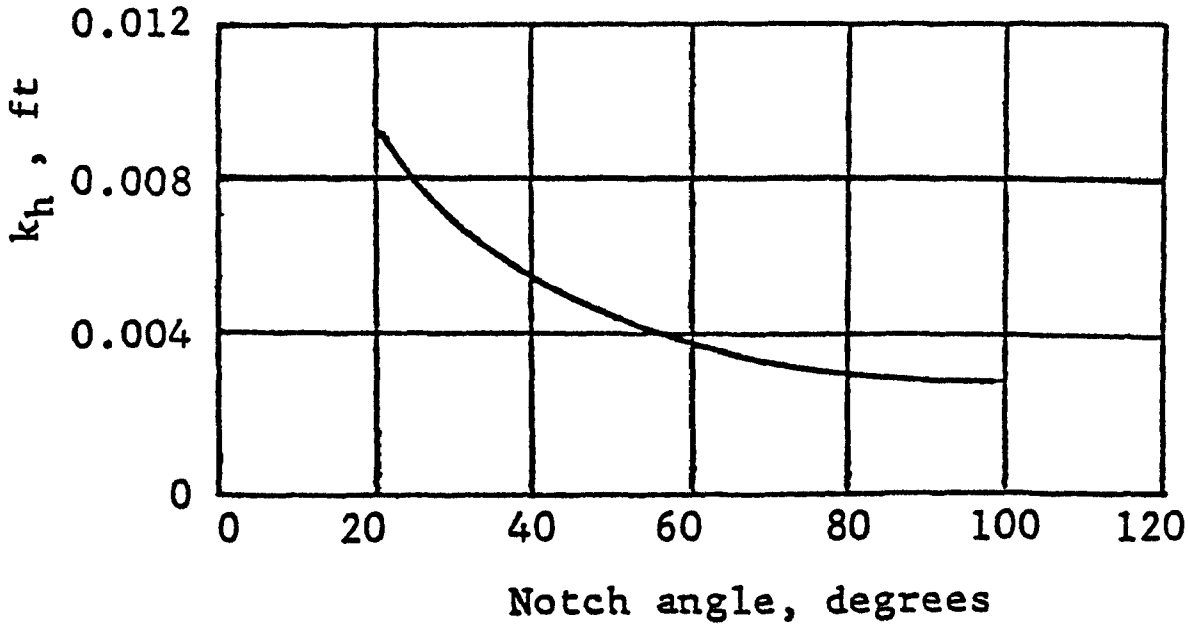


Figure 3.20a Value of K_h Kindsvater-shen Formula for V-Notch Weir

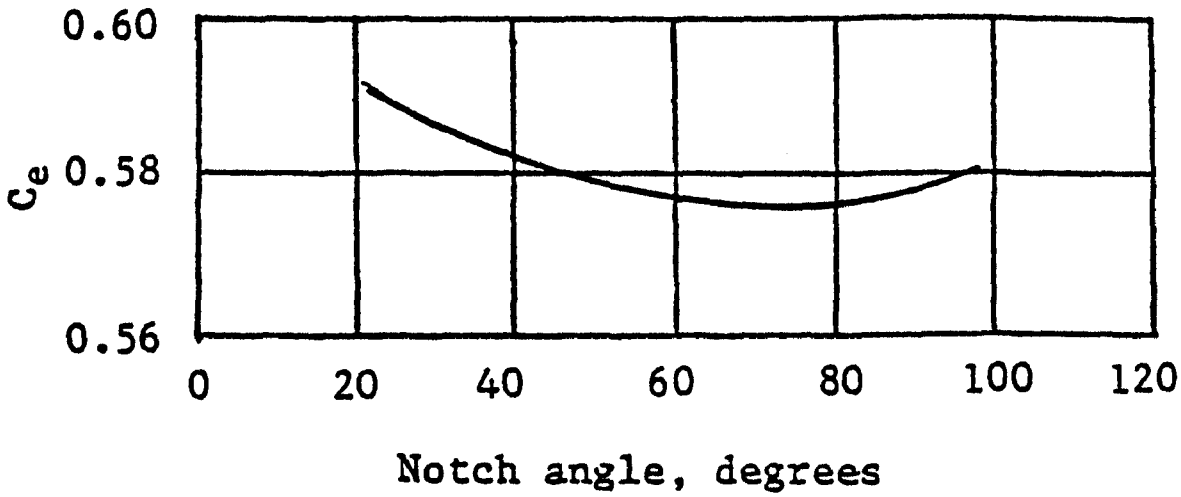


Figure 3.20b Value Of C_e For Kindsvater-Shen Formula For V-Notch Weirs (20)

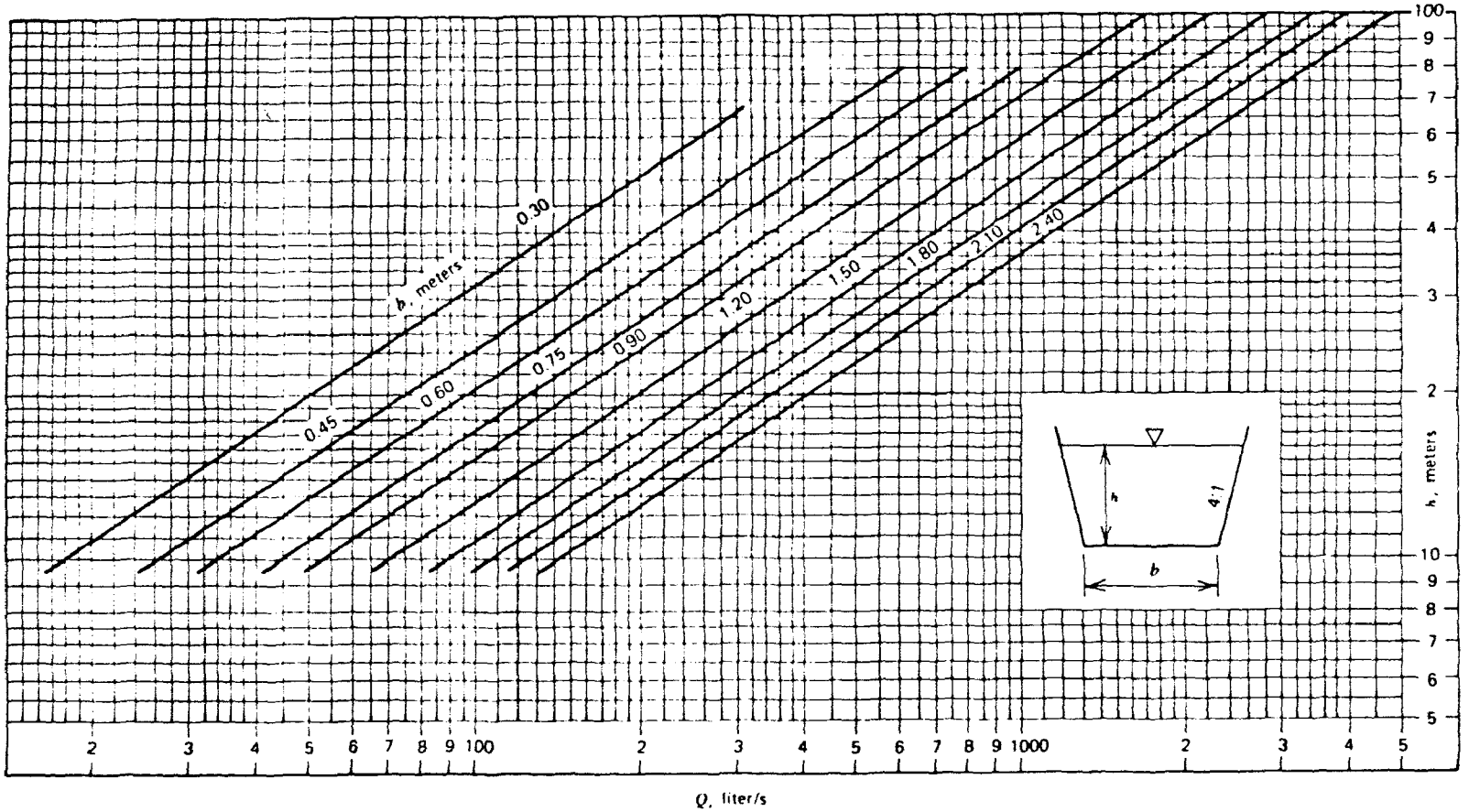
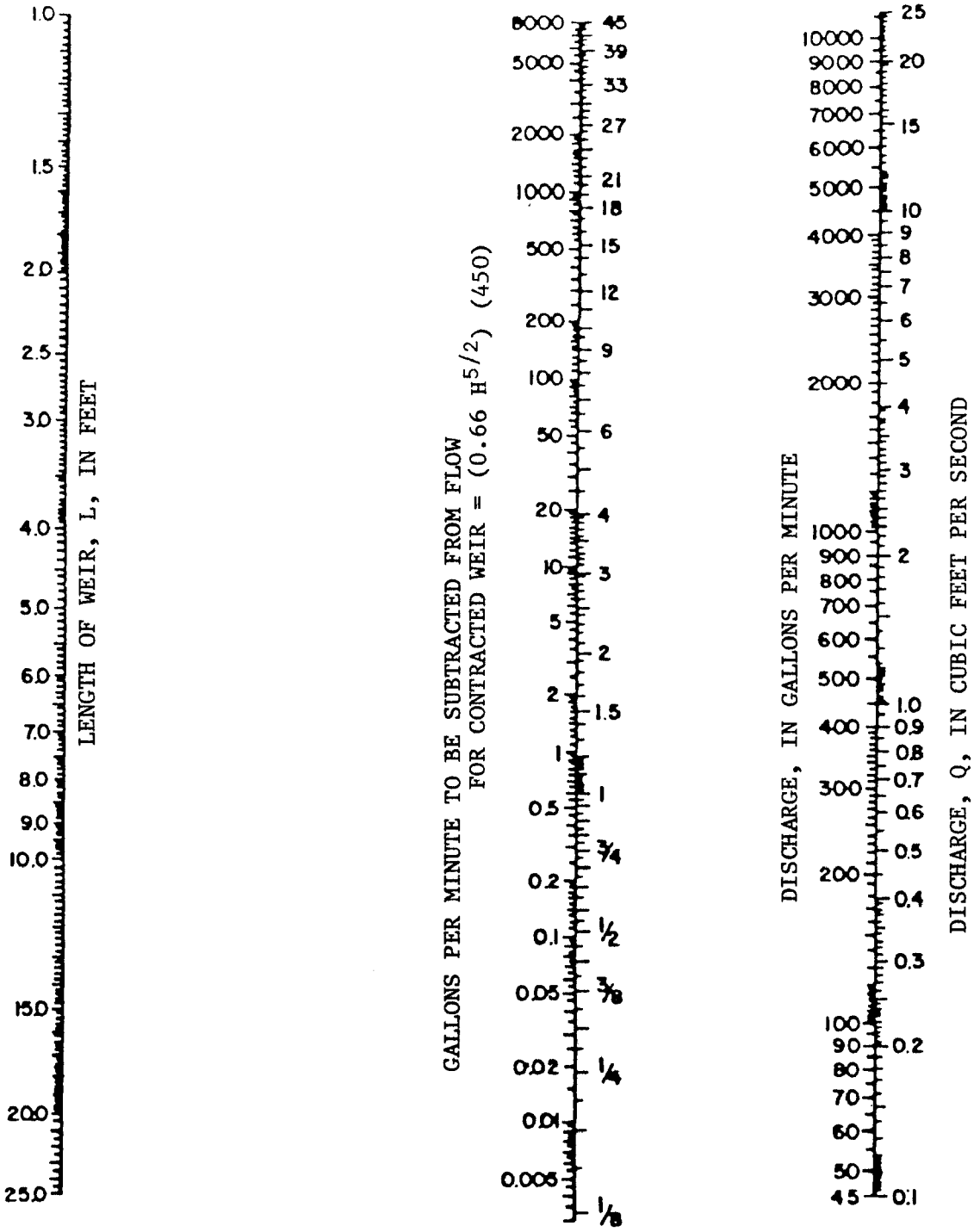


Figure 3.21 Flow Rates for Cipolletti Weirs (17)



Note: Based on Francis weir formula as follows:

$Q = 3.33LH^{3/2}$ (for suppressed weir)

or

$Q = 3.33(L-0.2H)H^{3/2}$
$= 3.33LH^{3/2}-0.66H^{5/2}$ (for contracted weir with two end contractions)

Where:

Q = discharge, in cubic feet per second
L = length of weir, in feet
H = head, in feet.

Figure 3.22 Nomograph for Capacity of Rectangular Weirs (7)

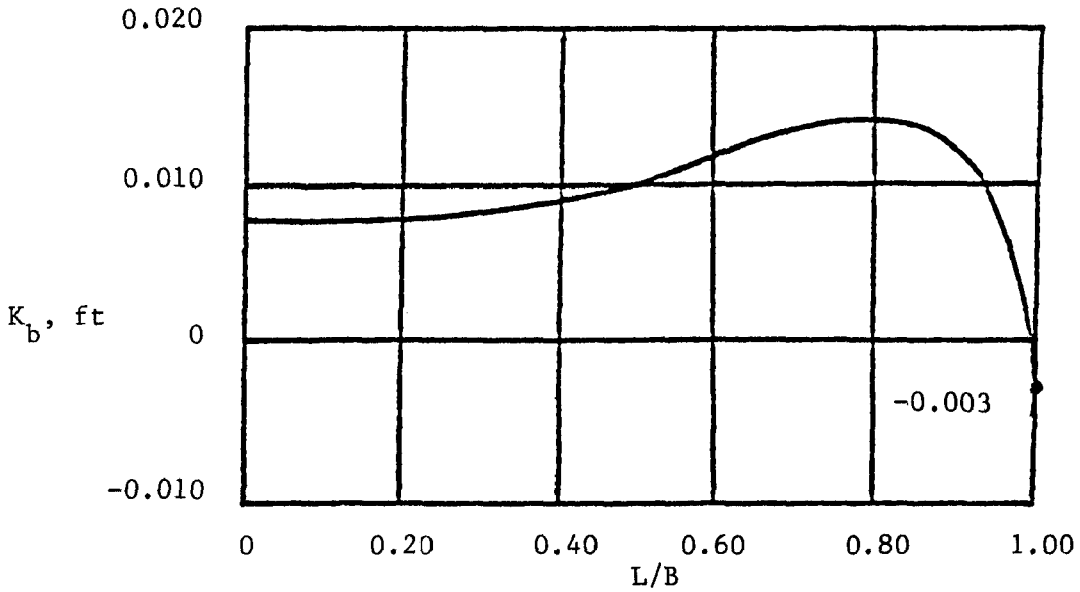


Figure 3.23a Value of K_b for L/B Ratio Kindsvater-Carter Formula for Rectangular Weirs (31)

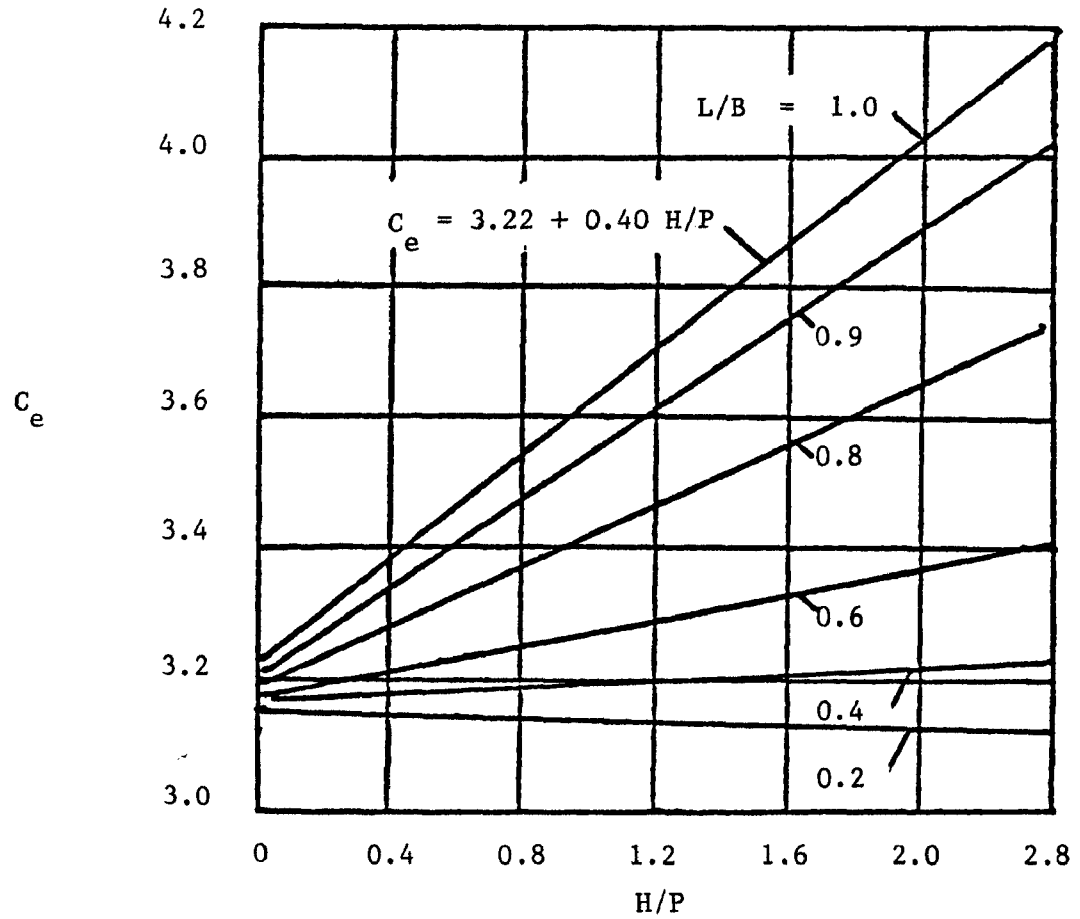


Figure 3.23b Value of C_e for H/P Ratio Kindsvater-Carter Formula for Rectangular Weirs (21)

3.3.2.1.1 Criteria for Installing Standard Weirs

To achieve the best accuracy in flow measurement the following criteria should be met in installing standard weirs (2):

1. The upstream face of the bulkhead should be smooth and in a vertical plane perpendicular to the axis of the channel.
2. The upstream face of the weir plate should be smooth, straight, and flush with the upstream face of the bulkhead.
3. The entire crest should be a level, plane surface which forms a sharp, right-angled edge where it intersects the upstream face. The thickness of the crest, measured in the direction of flow should be between 1 and 2 mm (about 0.03 to 0.08 in.) Both side edges of rectangular weirs should be truly vertical and of the same thickness as the crest.
4. The upstream corners of the notch must be sharp. They should be machined or filed perpendicular to the upstream face, free of burrs or scratches, and not smoothed off with abrasive cloth or paper. Knife edges should be avoided because they are difficult to maintain.
5. The downstream edges of the notch should be relieved by chamfering if the plate is thicker than the prescribed crest width. This chamfer should be at an angle of 45° or more to the surface of the crest.
6. The distance of the crest from the bottom of the approach channel (weir pool) should preferably be not less than twice the depth of the water above the crest and in no case less than 4.72 cm (1 foot).

7. The distance from the sides of the weir to the sides of approach channel should preferably be no less than twice the depth of water above the crest and never less than 4.72 cm (1 foot). (Exception: suppressed rectangular weir for which sides of the notch should be coincident with the sides of the approach channel).
8. The overflow sheet (nappe) should touch only the upstream edges of the crest and sides.
9. Air should circulate freely both under and on the sides of the nappe.
10. The measurement of head on the weir should be taken as the difference in elevation between the crest and the water surface at a point upstream from the weir a distance of four times the maximum head on the crest.
11. The cross-sectional area of the approach channel should be at least 8 times that of the overflow sheet at the crest for a distance upstream from 15 to 20 times the depth of the sheet.
12. If the weir pool is smaller than defined by the above criteria, the velocity of approach may be too high and the staff gauge reading too low, and the head discharge relationship given in Section 3.3.1.1 will not hold good.

3.3.2.2 Flumes

In contrast to weirs which have a tendency to settle the suspended particles near their upstream side, most of the flumes have a self cleansing feature which makes them a preferred flow measuring device where sediment is a factor in the stability of the stage (head) discharge relation.

Flumes are comprised of three sections: a converging upstream section, a throat or contracted section, and a diverging downstream section. The size

of flume is the width of the throat section.

The following factors must be considered in the location of flume (2):

1. Do not install flume too close to turbulent flow, surging or unbalanced flow or poorly distributed velocity pattern.
2. Locate flume in a straight channel section having no bends upstream of the flume.
3. For convenience install flume at a location which is readily accessible, near the diversion point, and near the devices installed to control the discharge.

Some of the flumes commonly used as flow measurement devices are described below.

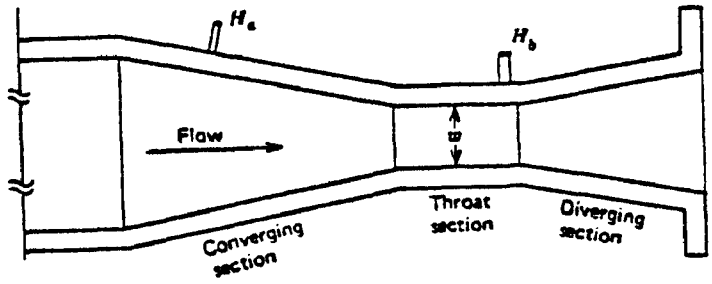
a. Parshall Flumes

Parshall flumes have been developed in various sizes (throat width) from 2.50 mm (1 inch) to 15.24 m (50 feet). The configuration and standard nomenclature for Parshall flumes is given in Figure 3.24. Strict adherence to all dimensions is necessary to achieve accurate flow measurement.

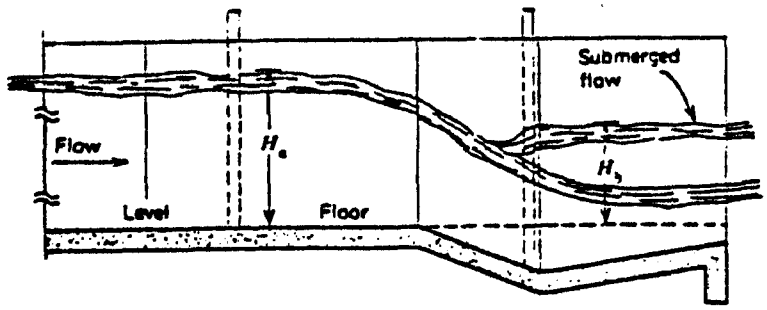
Flow through a Parshall flume may be either free or submerged. The degree of submergence is indicated by the ratio of the downstream head to the upstream head (H_b/H_a) - submergence ratio. The flow is submerged if the submergence ratio is:

- greater than 0.5 for flumes under 0.076 m (3 in.) size
- greater than 0.6 for flumes 0.15 m -0.23 m (6 in. - 9 in.) size
- greater than 0.7 for flumes 0.3 m - 2.44 m (1 to 8 ft.) size
- greater than 0.8 for flumes bigger than 2.44 m (8 ft.) size

For a free flow in a Parshall flume of size (W), the upstream head (H_a) and discharge (Q) relationship is given by the general equation $Q = CWH^n$.



a) Plan



b) Section

Figure 3.24 Parshall Flume Configuration and Nomenclature (17)

Table 3.7 gives the values of c, n, and Q, for different sizes (W) of the Parshall flume. Nomographs, curves or tables are readily available to determine the discharge from head observations. Flow curves are shown in Figure 3.25 to determine free flow through 0.07 m to 15.24 m (3 in. to 50 ft.) Parshall flumes (4).

For submerged conditions, correction factor should be applied to the free flow determined using the relationship $Q = CWH^n$. These correction factors are given in Figure 3.26 for different sizes of the Parshall flume.

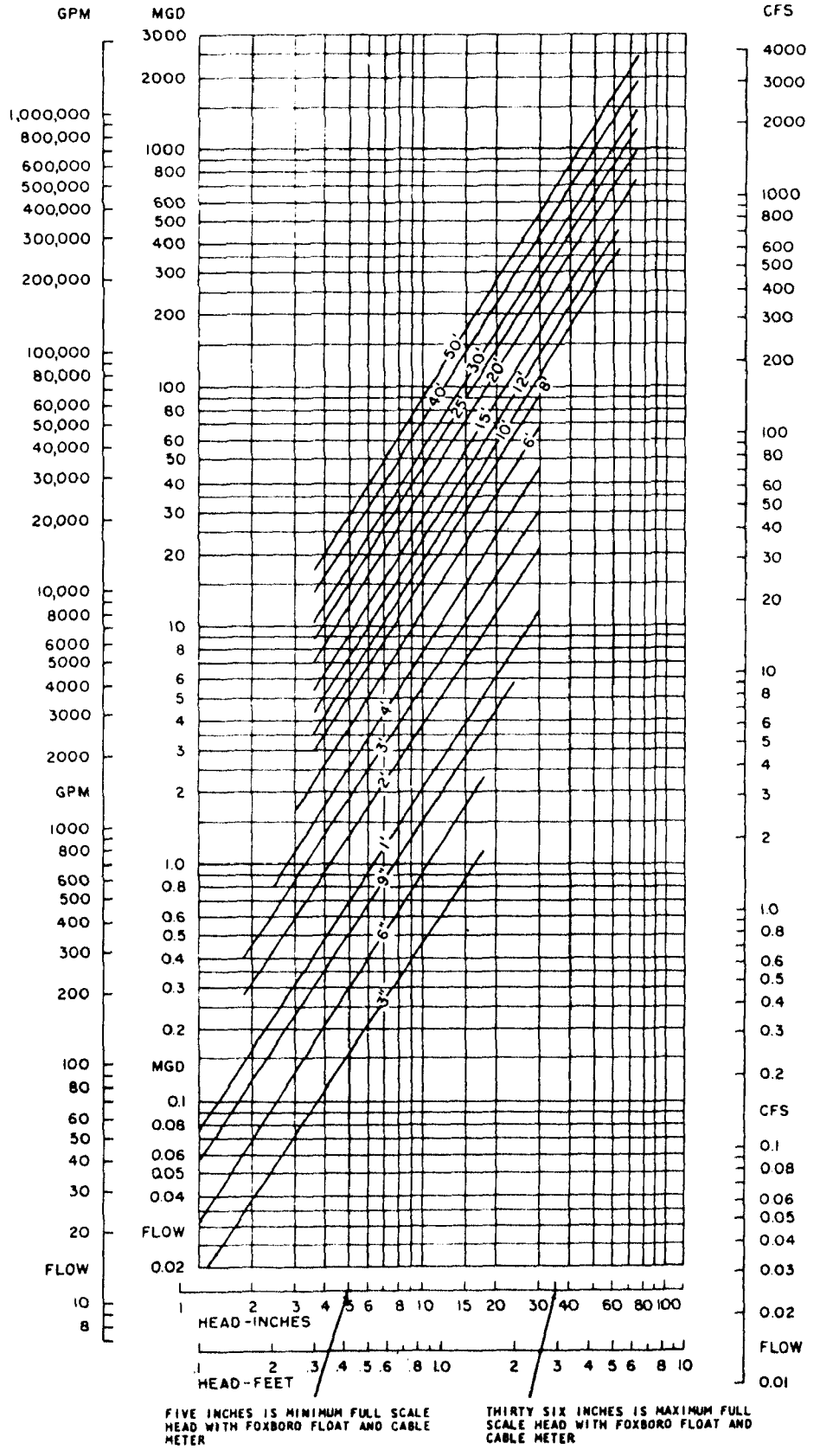


Figure 3.25 Flow Curves for Parshall Flumes (3)

TABLE 3.7 FREE FLOW VALUES OF C AND N FOR PARSHALL FLUME BASED ON THE RELATIONSHIP $Q = CWH^n$ (7)

Flume Throat, W	C	n	Max. Q, cfs
1 in	0.338	1.55	0.2
2 in	0.676	1.55	0.5
3 in	0.992	1.55	1.1
6 in	2.06	1.58	3.9
9 in	3.07	1.53	8.9
1 ft	4W(*)	$1.522W^{0.026}$	16.1
1.5 ft	"	"	24.6
2 ft	"	"	33.1
3 ft	"	"	50.4
4 ft	"	"	67.9
5 ft	"	"	85.6
6 ft	"	"	103.5
7 ft	"	"	121.4
8 ft	"	"	139.5
10 ft	39.38	1.6	200
12 ft	46.75	1.6	350
15 ft	57.81	1.6	600
20 ft	76.25	1.6	1000
25 ft	94.69	1.6	1200
30 ft	113.13	1.6	1500
40 ft	150.00	1.6	2000
50 ft	186.88	1.6	3000

(*)W in feet

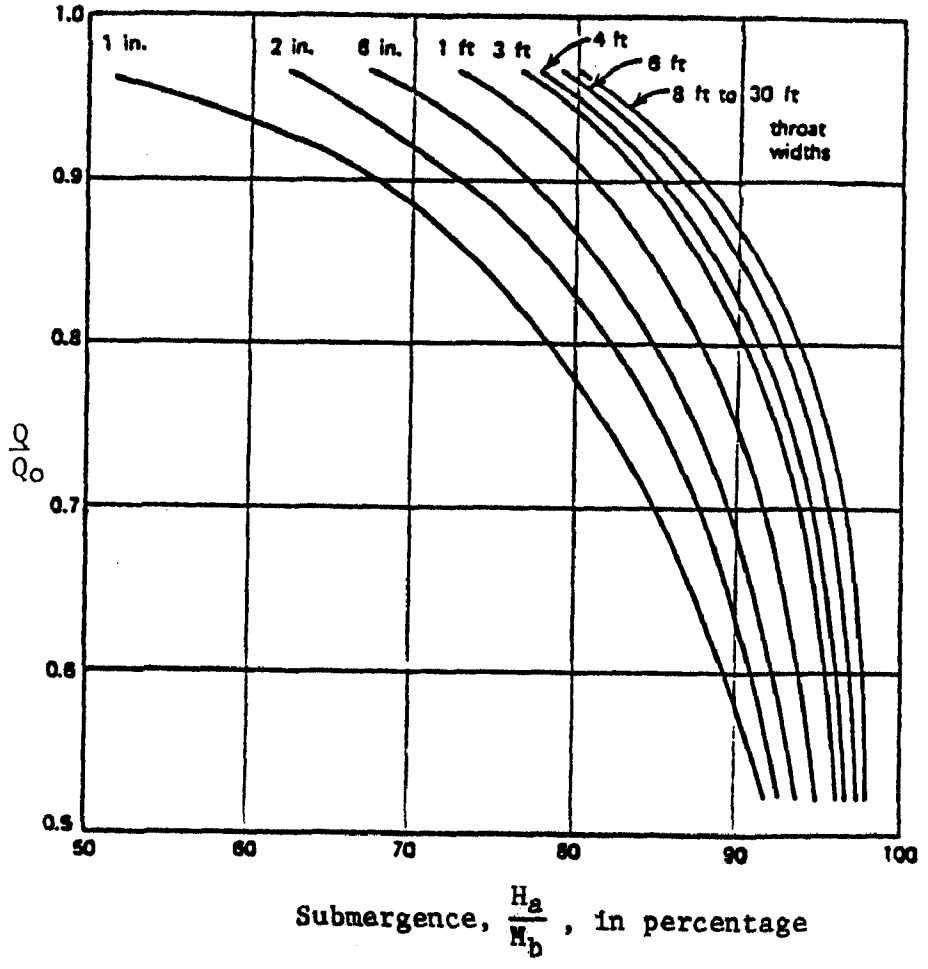


Figure 3.26 Correction Factor for Flow Discharge Determination for Parshall Flumes(22)

b. Palmer Bowlus Flumes

Palmer Bowlus flumes are venturi flumes of a super-critical flow type designed as a device to be inserted into an existing conduit with minimal site requirements other than sufficient slope. Figure 3.27 shows various types of Palmer Bowlus flumes. A laboratory study indicates that accuracies within ± 3% of the theoretical rating curve could be obtained at depths as great as 90% of the pipe diameter (23). The chief advantage of Palmer Bowlus flumes

over Parshall flumes is their ease of installation in existing conduits, sewers, etc. Standard Palmer Bowlus flumes are available to fit pipe sizes 15.2 cm (6 in.) to 2.4 meters (8 ft.). A disadvantage of Palmer Bowlus flumes is that they have a small range of flow, about 20:1.

Diskin flumes (24), an unconventional type of Palmer Bowlus flume, are portable devices but have limiting submergence, (H_b/H_a), between 0.75 and 0.85, and are not suited to trashy or debris laden flows.

c. Cut-throat Flumes

These are in a way modified Parshall flumes without throat section and flat bottom. (Figure 3.28). They are suitable for flat gradient channels; level flow and every flume size having same wall lengths makes construction easy and less costly. Analytical and experimental background on these flumes can be found in reference (24).

d. Type HS, H, HL Flumes

These flumes are primarily used in irrigation channels and small water sheds. Figure 3.29 illustrates these flumes. Their main advantage is simplicity of construction, and they have a wide range of flow. Details on discharge ratings can be found in references (2,25). Their design incorporates the sensitivity of a sharp crested weir and the self cleansing feature of a Parshall flume.

e. Other Flumes

Trapezoidal flumes (Figure 3.30) have much larger capacities than rectangular flumes of the same bottom width. Two common types of flumes are: 1) Tapezoidal flumes with bottom slope, 2) Trapezoidal critical depth flume. Accuracy of ±2 percent is claimed for trapezoidal critical depth flumes.

The San Dimas flume (Figure 3.31) was developed specifically to pass

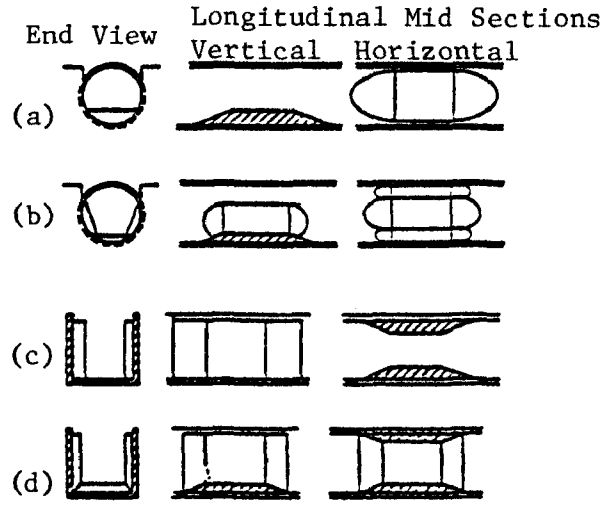


Figure 3.27 Palmer Bowlus Flumes (3)

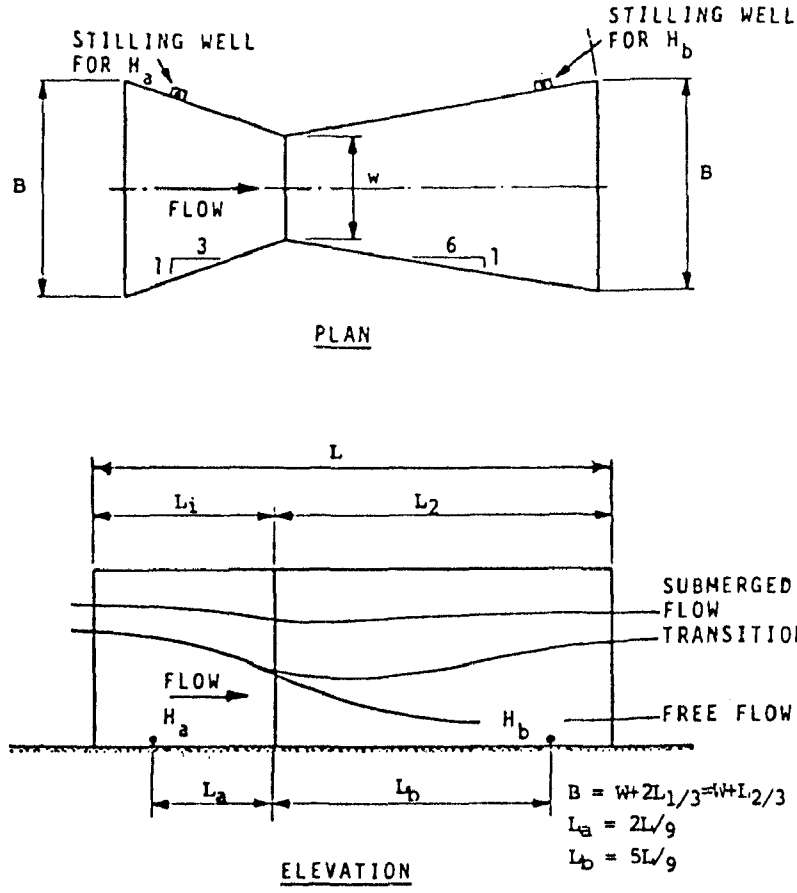


Figure 3.28 Rectangular Cut throat Flumes (5)

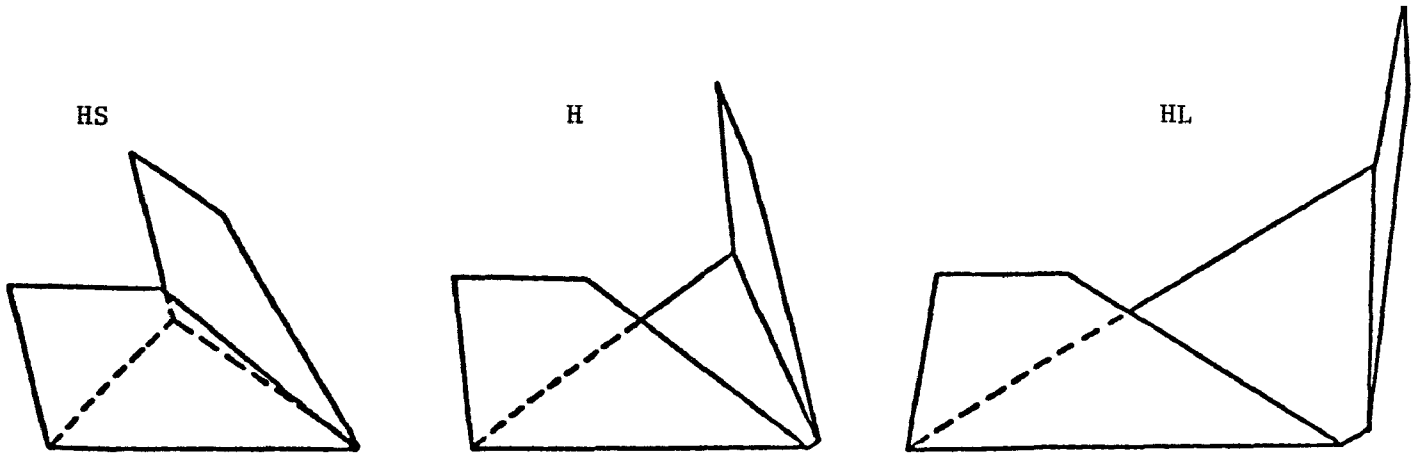


Figure 3.29 Type HS, H and HL Flumes (5)

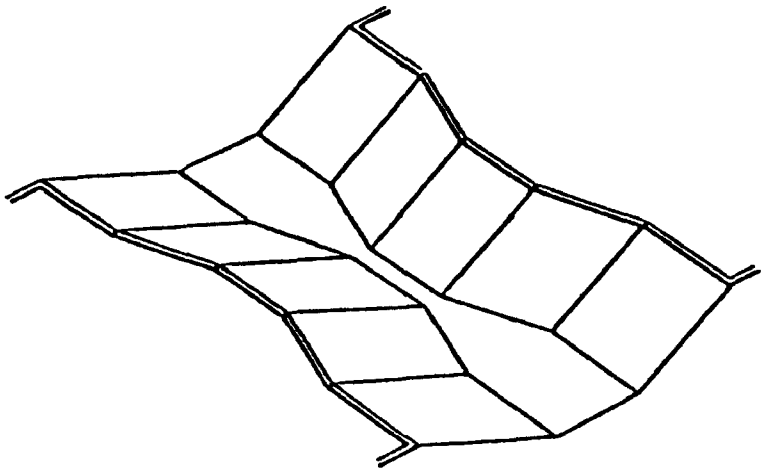


Figure 3.30 Trapezoidal Flume (5)

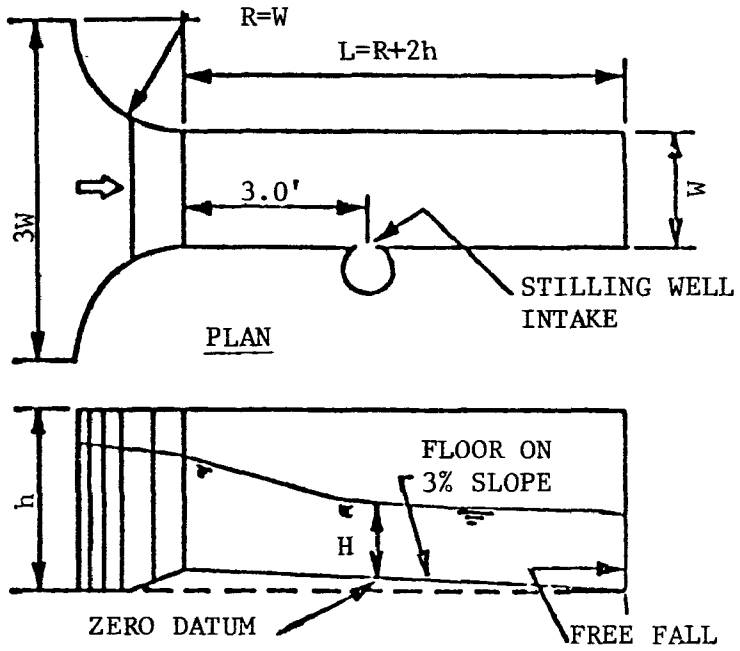


Figure 3.31 San Dimas Flume (5)

large amounts of sediment and debris. These flumes have the advantage that neither approach conditions nor disturbances upstream or downstream have an effect on their discharge ratings. Their rectangular cross-section makes them less sensitive or accurate at low flows.

3.4 MISCELLANEOUS FLOW MEASUREMENT METHODS

3.4.1 Friction Formula

Measurements of channel or sewer bottom slope, depth of flow and flow velocity can be used to only rough estimate the flow. The Manning formula is commonly used for estimating a flow:

$$V = \frac{0.453}{n} R^{2/3} S^{1/2}$$

V = average velocity, m/s (fps = 3.28 m/s)

n = coefficient of roughness

R = hydraulic radius, m $\left(\frac{\text{cross sectional area of flow}}{\text{wetted perimeter}}\right)$

s = slope of energy grade line.

The Manning formula is widely used for the engineering design of sewers and channels. However, for flow measurement,its usefulness is limited for a number of reasons. It is difficult to assign an appropriate value to the roughness coefficient which varies with the channel or sewer material (concrete, brick, etc.), and the surface of the channel or sewer (new, old, etc). For sewers, it varies also with the ratio of depth of flow to the depth when flowing full. The other inaccuaracy that may enter into the flow measurement is due to the slope of the energy grade line which is taken as the slope of the channel or sewer. However, these two slopes may or may not be identical. For various charts, tables and nomographs on the use of the Manning formula refer to reference (26)

3.4.2 Radioactive Tracer Techniques (7)

Radioactive tracer techniques measure the flow rate at the time of the measurement. These techniques are simple and relatively inexpensive and the equipment is portable. Successful use of these techniques requires a section of the pipe or channel free of branch connections and requires turbulence at the injection point for thorough mixing of the tracer. The tracer used must be a gamma-ray emitter, must be compatible with the flowing liquid, and must have a half-life longer than the duration of the test. Tracers generally used are salts of cesium-134, iodine-131, sodium 24, or gold-198. There are two methods of flow measurements by the radioactive tracers: 1) Two-Point Method and 2) Total-Count Method. Accuracies within 2% to 5% of the actual flow can be achieved using these methods.

a. Two-Point Method

This method uses the time interval for the surge of tracer to pass between two points separated by a determinable volume of the liquid. This time interval is determined by peaks on the chronological chart of a common amplifier-recorder connected to two G-M counters separated by a known or determinable volume of a section of a pipe. The schematics of the arrangement of the test is shown in Figure 3.32.

b. Total-Count Method

The basic principle of the total-count method is that a well mixed finite quantity of radiotracer, A, passing through a measurement point will produce a total number of N counts on a Scaler connected to a Geiger counter fixed in or near the stream some distance downstream. The value of N is inversely proportional to the flow rate q and is directly proportional to A, the quantity of the tracer mixed:

$N = \frac{A\ F}{q}$, where F is a proportionality factor which is characteristic of the isotope, the counter, and geometrical relationship of the stream . Note that q is the flow rate at the tracer injection point.

The total-count method gains versatility through the divided-stream principle: The same number of counts is obtained on the fraction or split flow as is obtained on the total flow. This allows one to measure a small fraction or bypass of the total flow.

To obtain accurate results, the numerical value of F must be determined in the laboratory by exposing the counter to a tracer solution in the same geometrical arrangement as in the field test, to find the counting rate that corresponds to a certain concentration of the tracer.

For example, if one desires to measure the flow of water/wastewater through a 30.4 cm (12 in.) pipe, take a 60.8 cm (2 ft.) length of 30.4 cm (12 in.) pipe closed at one end, and fill it up with water/wastewater containing a known concentration of the radioactive tracer C to obtain millicuries per cubic meter (gallon). Strap the Geiger counter to the pipe and connect it to a scaler. Determine the number of counts per minute, n. Then the factor, F, for cubic meters per minute (gallons per min.) is:

$$F\ m^3/min = \frac{n\ \text{Counts per minute}}{C\ \text{millicuries per cubic meter}}$$

Arrangement for the field measurement is schematically shown in Figure 3.33, upper post. To place the measurement, inject a known amount of tracer, A, either in a slug or gradually and record the total number of counts, N. Calculate, the flow using the formula

$Q = \frac{A}{N} F$ substituting these values, and value of

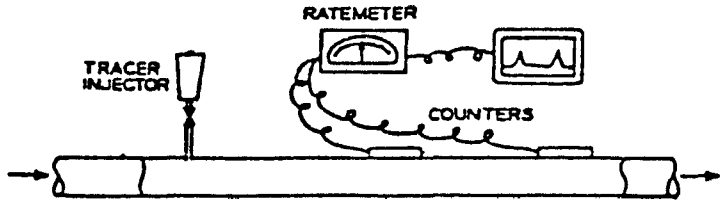


Figure 3.32 Schematic of Two Point Method (7)

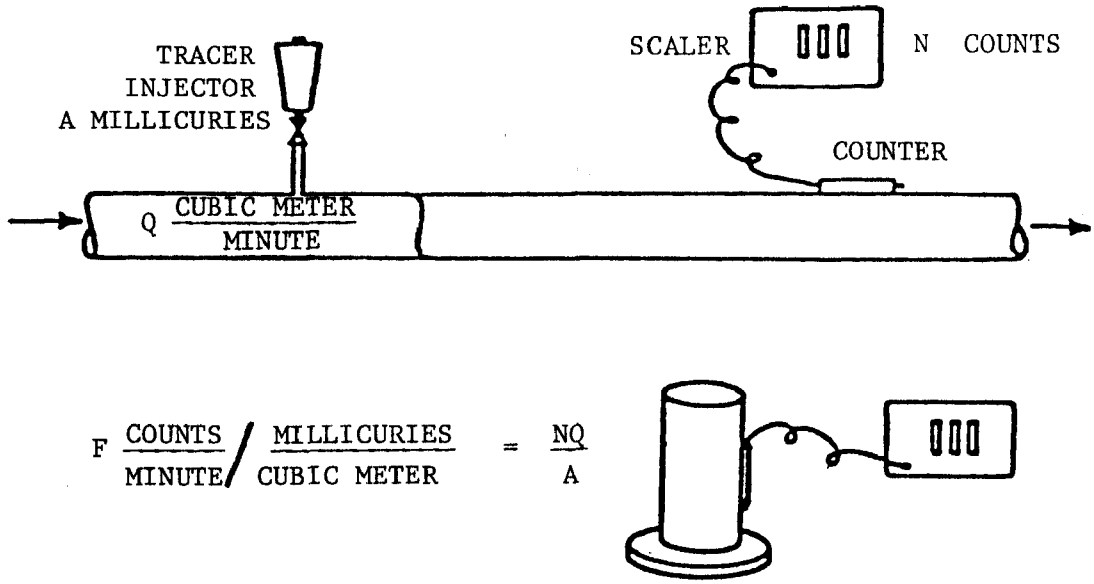


Figure 3.33 Schematic of Total Count Method (Upper Post) and arrangement for the Determination of F-Factor (Lower Post) (7)

F m^3/min. obtained above.

The divided-stream principle is used in a modified technique, the sample-bucket technique, in which a fraction of total flow is passed through a bucket containing the counter. The factor F is determined with the actual bucket and the counter.

The procedure for measuring flow of a large open stream, such as a river, is accomplished by floating the counter any place in the flow downstream from the injection point. The value of F, is predetermined by submerging the counter at least 15.2 cm (6 in.) under the surface of liquid in a tank at least 1.2 m (4 ft.) in diameter.

For better sensitivity a bundle of four counters connected in parallel and enclosed in lucite pipe is used.

3.4.3 Chemical Dilution (2,6,7,27)

Chemical dilution technique often known as the salt dilution technique, is applicable to both the open channel and pipe flow. This technique does not require the stream dimensions or the measurements of fluid levels or pressures. The flow is determined by measuring the concentration of the chemical at two points downstream from the injection point. The following should be considered when using this technique for flow measurements in waters and wastewaters:

- Turbulence at the point of injection of the chemical should assure thorough mixing (especially the lateral mixing) of the chemical in the field.
- Flow in the channel or pipe should be steady.
- Chemical used should meet the following requirements:
  - Compatible with the fluid; no loss or deterioration of the chemical in the fluid.

. Nontoxic to plant and animal life.

. Easy and accurate quantitative detection at low concentration.

. Low cost of the chemical and the equipment.

Chemicals commonly used are lithium chloride (atomic adsorption analysis of lithium) and fluorescent dyes (fluorometer measurement) such as sodium fluorescein, Rhodamine B, Pontacyl Brilliant Pink B, and Rhodamine WT. However, use of sodium fluorescein is not recommended as it is easily affected by light and bacterial action. In waters/wastewaters with high suspended solids, there will be pronounced loss of Rhodamine B dye. Pontacyl Brilliant Pink B and Rhodamine WT dyes are compared in Table 3.8.

The chemical dilution technique is used in two ways: 1) continuous addition or 2) slug injection.

a. Continuous-Addition-of-Chemical Method

In this technique the chemical of known concentration is added at a uniform rate to the stream and the dilution is determined after it has traveled downstream at least a distance 100 times the width at the surface of the fluid. The relationship to determine the flow is

$$A = q \frac{C_1 - C_2}{C_2 - C_0}$$ where,

A = stream discharge

C_0 = natural (or background) concentration of the chemical in the stream

C_1 = concentration of the chemical injected

C_2 = final concentration of the chemical at downstream sampling point

q = rate of injection of the chemical

TABLE 3.8 COMPARISON OF RHODAMINE B, RHODAMINE WT AND PONTACYL BRILLIANT PINK B DYES (27)

Factors	Rhodamine B	Rhodamine WT	Pontacyl Brilliant (Pink B)
pH 5-10	Stable	Stable	Stable
Absorption peak-visible light range	550 mu	556 mu	560 mu
Fluorescence peaks	570 mu	580 mu	578 mu
Suspended solids	Pronounced absorption	Low absorption	Low absorption

b. Slug Injection Method

In this method a known amount, S, of the chemical is added to the stream. At a point sufficiently downstream (minimum 100 times the width at the surface of the flow), the concentration, $\bar{C}$, of the chemical during its time of travel, Δt, is determined by continuously sampling from the stream during the passage of the chemical wave and mixing this constant continuous sample into a single container to obtain an "integrated sample". The flow is determined by the relationship $Q = \frac{S}{\bar{C}\Delta t}$ where,

Q = stream discharge

S = amount of chemical injected

$\bar{C}$ = average concentration of chemical during its passage over a downstream point during time interval Δt.

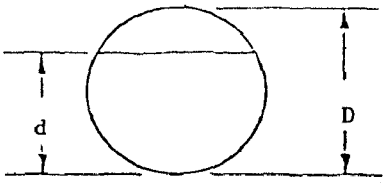
3.4.4 Water Meters

An estimate of the flow can be obtained from water meter readings when an instantaneous flow rate is not critical. This technique is used in a confined area, such as the industrial plant. Water meters should be certified periodically. When using the incoming and outgoing flow for an initial estimate of the flow rate, all changes in the water quantity that occur in various processes must not be overlooked. These changes may be due to water actually consumed in the process, e.g., cement manufacturer, conversion of quick lime to slaked lime, or the change of phase: water changing to steam, etc.

3.4.5 Measuring Level Change in Tank

In some instances the level change in a tank can be used to estimate flow. To accomplish this, the volume of the tank related to depth must be established; then the flow is allowed to enter and the level change with time is recorded. Figure 3.34 gives the relationship of depth to volume for various shapes of the

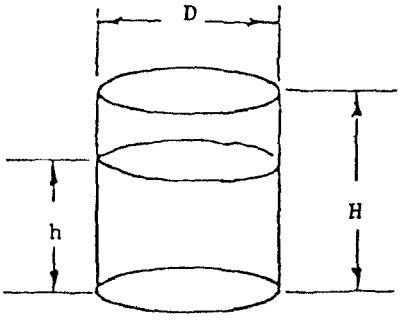
SPHERE



Total Volume
$V = 1/6\ \pi D^3 = 0.523498 D^3$

Partial Volume
$V = 1/3\ \pi d^2\ (3/2\ D-d)$

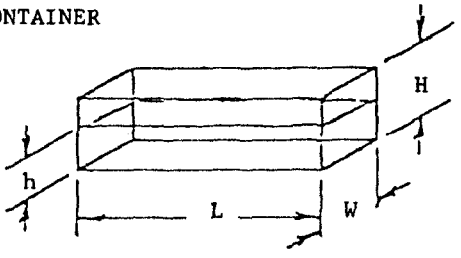
RIGHT CYLINDER



Total Volume
$V = 1/4\ \pi D^2 H$

Partial Volume
$V = 1/4\ \pi D^2 h$

ANY RECTANGULAR CONTAINER

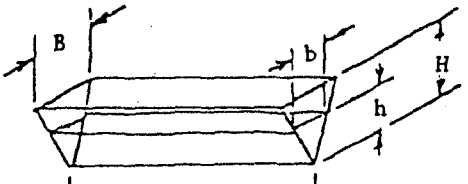


Total Volume
$V = HLW$

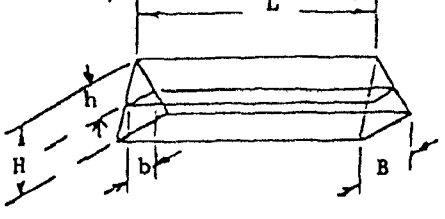
Partial Volume
$V = hLW$

TRIANGULAR CONTAINER

Case 1



Case 2

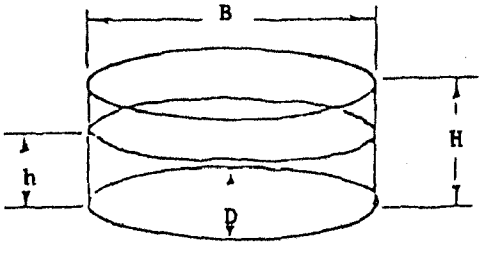


Partial Volume (Case 1)
$V = 1/2\ hBL$

Total Volume
$V = 1/2\ HBL$

Partial Volume (Case 2)
$V = 1/2\ L\ (HB - hB)$

ELLIPTICAL CONTAINER



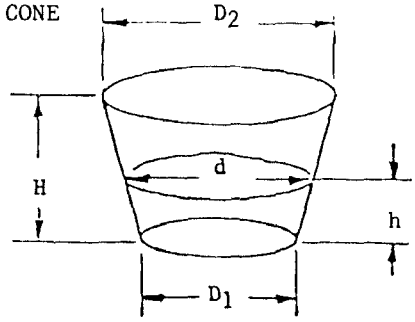
Total Volume
$V = \pi BDH$

Partial Volume
$V = \pi BDh$

Figure 3.34 Equations for Container Volumes

FRUSTUM OF A CONE

Case 1



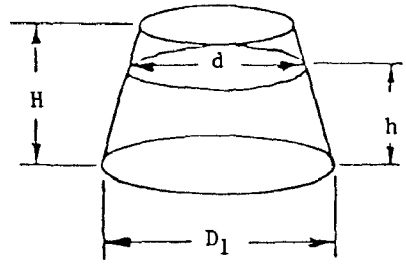
Total Volume

$V = \pi/12\ H(D_1^2 + D_1\ D_2 + D_2^2)$

Partial Volume

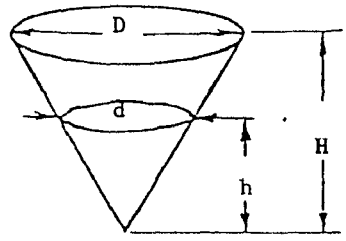
$V = \pi/12\ h(D_1^2 + D_1\ d + d^2)$

Case 2



CONE

Case 1



Partial Volume (Case 1)

$V = 1/12\ \pi\ d^2h$

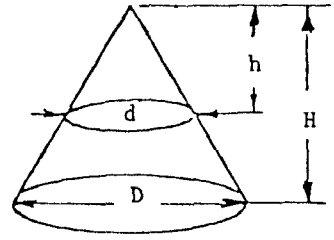
Total Volume

$V = 1/12\ \pi\ D^2H$

Partial Volume (Case 2)

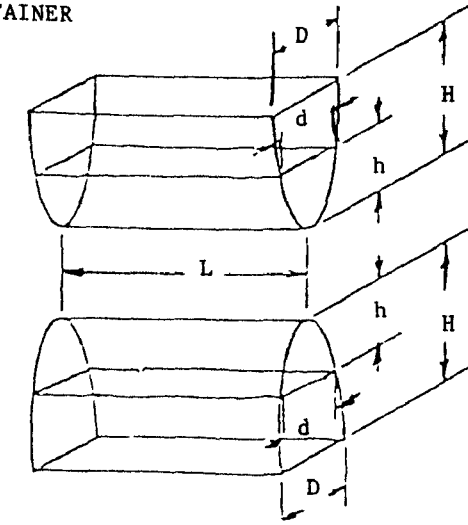
$V = 1/12\ \pi(D^2H - d^2h)$

Case 2



PARABOLIC CONTAINER

Case 1



Partial Volume

$V = 2/3\ hdL$

Total Volume

$V = 2/3\ HDL$

Partial Volume

$V = 2/3\ (HD - hd)\ L$

Case 2

Figure 3.34 (Continued)

tank.

3.4.6 Pump Rates

When other methods are not available for flow measurement and a pump is used in the system, the operating characteristics of the pump can be used to estimate flow. One method is to multiply the pumping time and the pump capacity at the discharge pressure as obtained from manufacturer's head curves vs. flow (28).

Another technique is to establish the pump's horsepower and determine the capacity from the manufacturer's curves. However, these techniques should be used only for estimates of flows.

3.4.7 Calibrated Vessels

Another technique useful for free falling water is to capture a known volume of water over a recorded time interval. The flow rate is then established for a specific time. More than one measurement is necessary to allow accurate estimates; the volume chosen should allow time of collection to be more than 10 sec. (29).

3.5 SECONDARY DEVICES

Secondary devices are the devices in the flow measurement system which translate the interaction of primary devices in contact with the fluid into the desired read-out or records.

These devices can be classified into two broad classes:

1. Non-recording type with
    a. Direct read-out such as a staff gauge
    b. Indirect read-out from fixed points as in a chain, wire weight and float type.
2. Recording type, where the recorders may be graphic or digital. Examples of recording type devices are: float in well, float in flow, bubbler, electrical and acoustic.

The advantages and disadvantages of the various secondary devices are given in Table 3.9 and relative comparison of primary and secondary open channel flow measurement devices is shown in Table 3.10. Table 3.11 compares various recording type secondary devices.

3.5.1 Non-recording Type Secondary Devices

3.5.1.1 Staff Gauge

A staff gauge, shown in Figure 3.35a, is usually a graduated enameled steel plate bolted to a staff. Care must be taken to install the gauges solidly to prevent errors caused by change in elevation of the supporting structure.

3.5.1.2 Hook Gauge

A hook gauge, shown in Figure 3.35b, is a modification to a staff gauge. The gauge (hook) is manually brought to the water surface and the water elevation read.

3.5.1.3 Chain Gauge

The chain gauge, shown in Figure 3.35c, is a substitute for the staff gauge and consists of a horizontal seal and a chain that passes over a pulley to fasten a hanging weight. Water level is indicated by raising or lowering the weight until it just touches the water surface. Sources of errors in the measurement are,settling of supporting structure, temperature changes, changes in length due to wear, and wind action.

3.5.1.4 Wire Weight Gauge

Wire weight gauge, shown in Figure 3.35d, is a modification of the chain gauge and uses a wire or small cable wound on a reel. The reel is graduated or a counter is used to give readings from a reference check bar of the water elevations to the tenths and hundredths of a foot.

TABLE 3.9 ADVANTAGES AND DISADVANTAGES OF SECONDARY DEVICES

Device	Advantages	Disadvantages
Hook gauge or stage board	Common, accurate	Manual only, stilling well may be needed
Differential Pressure Measurement		
a. Pressure bulb	No compressed air source, can be directly linked to sampler	Can clog openeings, expensive
b. Bubbler tube	Self-cleaning, less expensive; reliable	Need compressed air or other air source; can't stand much abuse
Surface float	Inexpensive, reliable	In-stream float catches debris
Dipper	Quite reliable, easy to operate	Oil and grease will foul probe, expensive, possible sensor loss
Ultrasonic	No electrical or mechanical contact	Air bubbles may cause echo rebounding

TABLE 3.10 RELATIVE COMPARISON OF PRIMARY AND SECONDARY OPEN CHANNEL FLOW MEASUREMENT DEVICES (a)

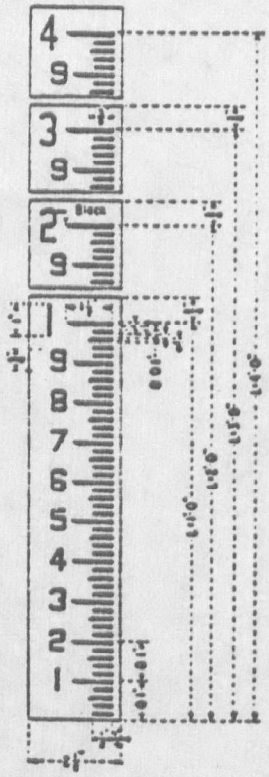
	Primary devices			Secondary devices				
Characteristic	Channel-char's only (Manning formula)	Weir	Flume	Hook gauge stage board	Differential pressure	Float Device	Dipper	Ultra-sonic
Suitable for continuous measurement	+	+	+	-	+	+	+	+
Capability for sending signal to sample (flow-proportional sampling)	na	na	na	-	+	+	+	+
Need for stilling well	na	na	na	+	-	+	-	-
Low initial cost	3	2	1	3	2	3	1	1
Easy to install	na	2	1	3	2	1	2	2
High accuracy of measurement	1	2	3	2	3	3	3	3
Low maintenance (incl. cleaning)	3	1	3	3	2	2	3	3
Suitable for high solids wastewater	3	2	3	3	3	2	2	3
Low susceptibility to fouling (rags, debris, grease)	3	1	3	3	2	1	1	3
Wide flow range	3	2	3	+	+	+	+	+
Low headloss	3	1	3	+	+	+	+	+
Low auxiliary requirements (manpower, compressed air, AC power)	na	na	na	1	2	3	3	1

(a) na = not applicable
- = no or not suitable
+ = yes or suitable

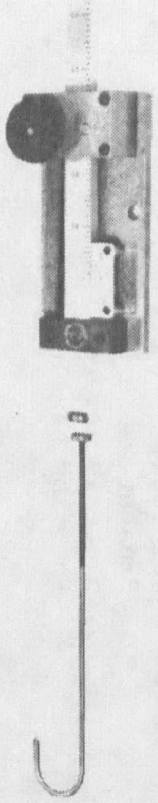
1 = fair frequently a problem
2 = good, sometimes a problem
3 = excellent, seldom or never a problem

TABLE 3.11 COMPARISON OF RECORDING TYPE SECONDARY DEVICES

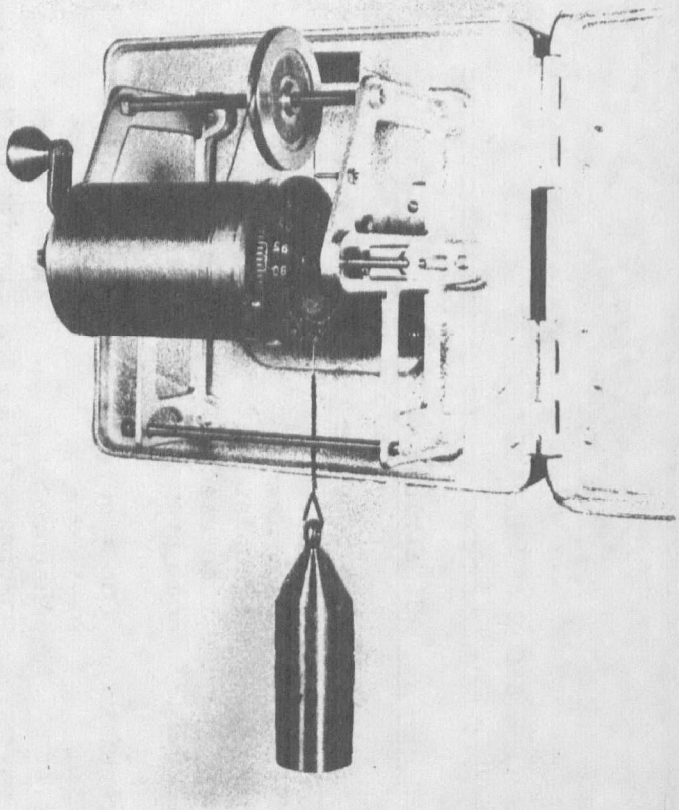
Features	Floating in Well	Float in Flow	Bubbler	Electrical	Acoustic
Stilling Well	Necessary	Not necessary	Not necessary	Not necessary	Not necessary
Sensing Flow Level	Indirectly	Directly	Flow level translated into air back pressure	Flow level translated into electrical property	Flow level translated into acoustic response
Purge System	Not required	Not required	Maybe required	Not required	Not required
Moving Parts	Presence of moving parts	Presence of moving parts	Absence of moving part	Absence of moving part where sensing element is physically in the flow. Present where probe is lowered for flow sensing.	Absence of moving parts



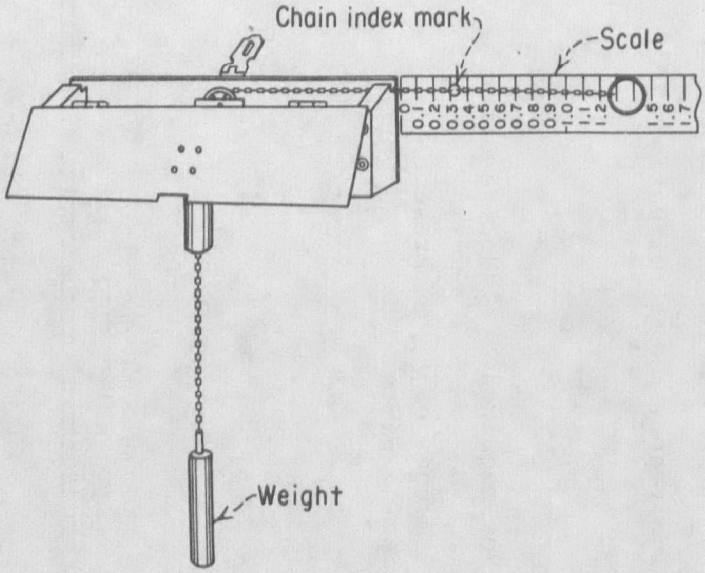
a) Staff gauge



b) Hook gauge



d) Wire Weight gauge



c) Chain gauge

Figure 3.35 Various Non-recording Type Secondary Devices

3.5.2 Recording Type Secondary Devices

3.5.2.1 Float in Well

It essentially consists of a float (sensor weight) and a counter weight connected via a cable to a wheel which rotates as the float rises or falls with changes in the water level. The wheel is connected mechanically or electronically to the read-out, recorder, etc. The float is installed in a stilling well.

3.5.2.2 Bubbler

In a bubbler, Figure 3.36, a pressure transducer senses the back pressure experienced by a gas which is bubbled at a constant flow rate through a tube anchored at an approximate point with respect to a primary device. This back pressure can be translated into water depth and subsequently related to discharge.

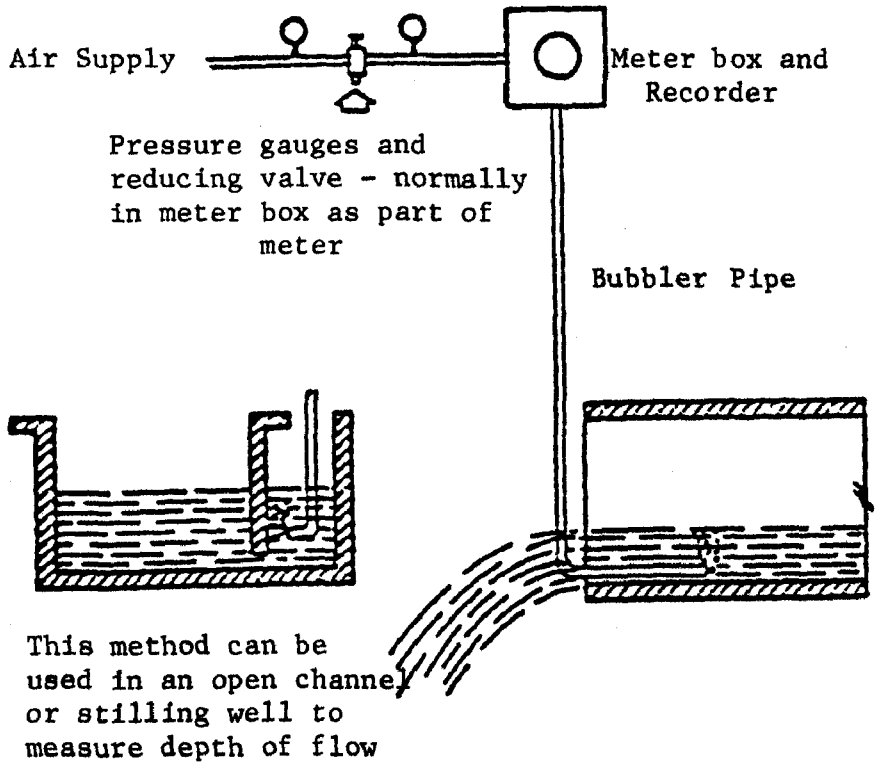


Figure 3.36 Bubbler

3.5.2.3 Electrical

These devices use the change in an electrical property (capacitance, resistance, etc.) to sense liquid depth. The probe or sensor is a part of an electrical circuit, and its behavior in a circuit is a function of its degree of immersion.

3.5.2.4 Acoustic

With acoustic devices, continuous measurement of liquid depth is accomplished by measuring the time required for an acoustic pulse to travel to the liquid-air interface and return. Of the two physical arrangements, liquid path and air path measurement, the air path arrangement is commonly used since installation is simplified, is independent of fluid velocity, and avoids any contact with the fluid.

3.5.3 Errors in Flow Measurement (20,30)

The final measurement accuracy of a system (primary and secondary devices included) depends on many factors.

3.5.3.1 Sources of Errors Related to the Primary Devices

Sources of errors described here are in relation to weirs and flumes, but similar arguments can be developed for other devices. The following are the main sources of errors:

- Basic errors in the discharge/head tables or formulas. In many instances, the discharge tables, charts or formulas have been developed empirically. They show experimental relationship. Therefore, extrapolation beyond the range of observations from which they were developed can lead to serious errors.
- Faulty fabrication or construction. Erroneous Length: An error of 0.1 foot in the length of a rectangular or Cipolletti weir will cause

an error of 1% in the flow measurement of a one foot weir. A corresponding error in 0.30 meter (one foot throat-width) flume will be 0.86% and that in a four foot flume 0.23%.

- Error due to transverse slope of weir crest. When the crest of the rectangular or Cippoletti weir is sloped, the common practice is to measure the head at the center of the crest. This leads to an error of $\frac{100S^2L^2}{32H^2}$ % where:

  S = Slope of the weir crest

  L = Length of the weir

  H = Head at the center of the weir crest.

  This error can be reduced to an insignificant amount if the discharge is calculated as the difference of the discharges based on higher and lower heads on the weir crest.

- Stilling well not at a proper location. The head of the weir must be measured beyond the effect of the drawdown. For standard weirs the stilling well for the head measurement should be placed at a distance upstream of four times the maximum head on the weir. For Parshall flumes the locations of stilling wells for the head measurement bear a definite relationship with the throat width. Substantial errors in the field measurements have been traced to changes in the location or design of the stilling well entrance.

- Errors due to neglecting velocity of approach to weir. When the velocity of approach is greater than 0.5 fps it should be considered in the discharge formula. For a 0.2 ft head on the weir, this error for approach velocities of 0.15 m/s, 0.30 m/s, and 0.46 m/s (0.5 fps, 1.0 fps, and 1.5 fps) is 2.7, 9.8, and 20.8 percent respectively. This

error is less when the head on the weir is greater. For a 0.30 m (1 ft) head, corresponding figures are 0.6, 2.2, and 4.7 percent. Use of the Kindsvater-Carter formula will help alleviate this error.

- The error due to the reduction of depth of the weir pool. The height of the weir, when less than twice the head on the weir, will introduce an error of 5.6, 2.7, and 1.5 percent for).06 meter (0.2 ft) head and 0.15, 0.30, and 0.61 meter (0.5, 1.0, 2.0 ft) height of the weir. A corresponding error of a 0.5 foot head will be 13.1, 6.4, and 3.4 percent respectively. This error can be corrected by using Rehbock's formula, $Q = \frac{2}{3}\sqrt{2g}\, LH^{3/2}\left(0.605 + \frac{1}{320H-3} + 0.08\ \frac{H}{P}\right)$ or the Kindsvater-Carter formula. In a standard sized weir pool, this error can be minimized or eliminated by proper maintenance and cleaning.
- Weir blade sloping upstream or downstream. The error introduced is normally small. It becomes significant, however, if the face goes out of plumb by a few degrees.
- Roughness of upstream face of weir or bulkhead. The roughness of the upstream face of weir or bulkhead can cause an increase in the discharge. The discharge is observed to increase by changing the roughness of the upstream face of the weir bulkhead from that of a polished brass plate to that of a coarse file for a distance of 30.48 cm (12 in) below the crest. The increase ranges from 2 percent for 0.15 meters (0.50 ft) head to about 1 percent for 0.412 meter (1.35 ft) head (30).
- Aeration of the nappe. Insufficient aeration of the nappe will increase the discharge over the weir. It has been observed that for a drop in pressure under the nappe by 20.32 mm (0.8 in) of water below atmospher-

pressure, the discharge increased by 3.5 percent at 0.15 meter(0.5 ft) head and about 2.0 percent at 0.30 meter(1.0 ft) head (30).

- Other errors may be due to submergence of the weir. Obstructions in the measuring section, changes in the viscosity and surface tension, unstable flow at very low heads, etc.

3.5.3.2 Errors in the Secondary Devices

- One of the most common errors is the incorrect zero setting of the head gauge. This error is of the same magnitude as the error for misreading the head.
- Error due to misreading the head is another common error. Common causes of this error are incorrect location of the gauge, the dirty head gauge, not using the stilling well, considerable fluctuations of the water surface and carelessness on the part of the reader. For 30.48 cm - 12.19 m (12-48 in) Cipolletti and 90° V-notch weirs, a small error of 3.05 cm (0.01 ft) in reading will introduce an error approximately 7.5 percent in discharge results for the lower heads. For greater heads, the error is less.
- The chart related errors are common to all the recording type devices. These errors are the result of the variations in the chart due to humidity, paper expansion and shrinkage.
- The error common to the totalizers is the variation in the speed of totalizer drive motors.
- Other errors which are characteristics of particular secondary devices are:

  Float Devices (12)

  The error due to a float lag which is similar to the "play" be-

tween gears. Once the index is set to the true water level while the water is rising, it will thereafter show the correct water level. For a falling water level however, the index will be above the true water level by the amount of the float lag as shown in Figure 3.37a. If the index is set at true water level at some intermediate point between rising and falling water levels, the index will be proportionately low by the amount of the float lag for rising water levels and high a similar amount on the falling water level, as shown in Figure 3.37b.

For recorders and indicators,

float lag = $0.37 \frac{F}{D2}$, where F = force required to move the mechanism, ounces. D = diameter of the float, inches, and float lag in feet.

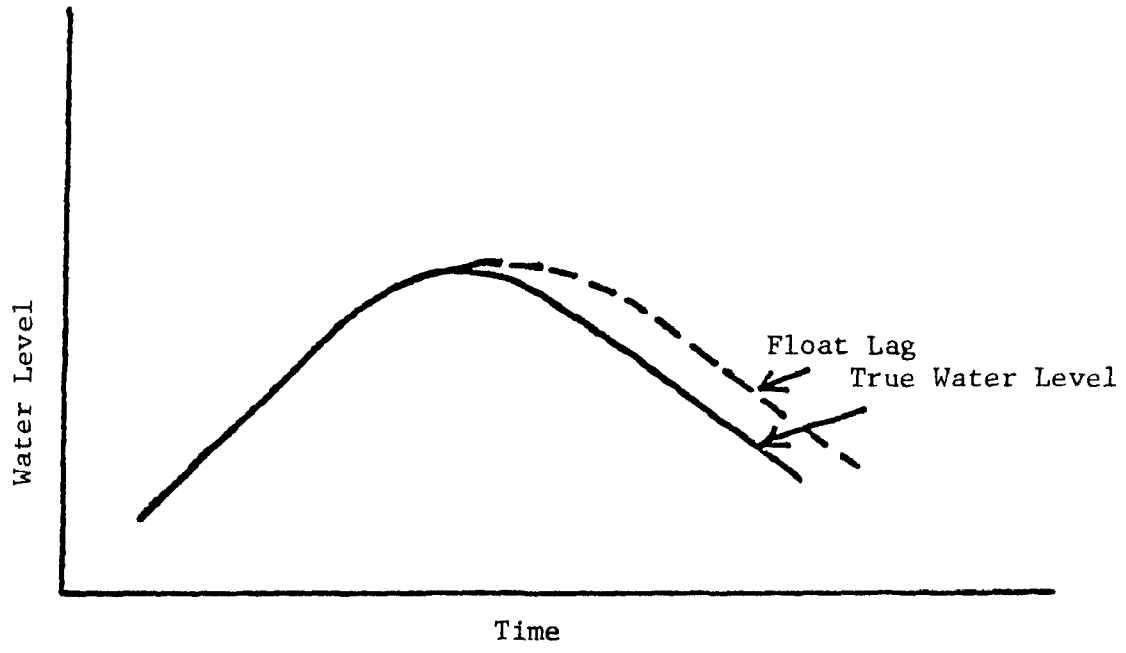
The error due to line shift. For every change in the water level, there is a movement of float line from one side of the float pulley to the other. This change of weight changes the depth of floatation of the float, consequently the stylus deviates from the true water height by a small amount. This is dependent on the change in the water level since the last correct setting, and the weight of the line used between the float and the counter weight.

Error from live shift = $0.37 \frac{P}{D2} \Delta H$ where

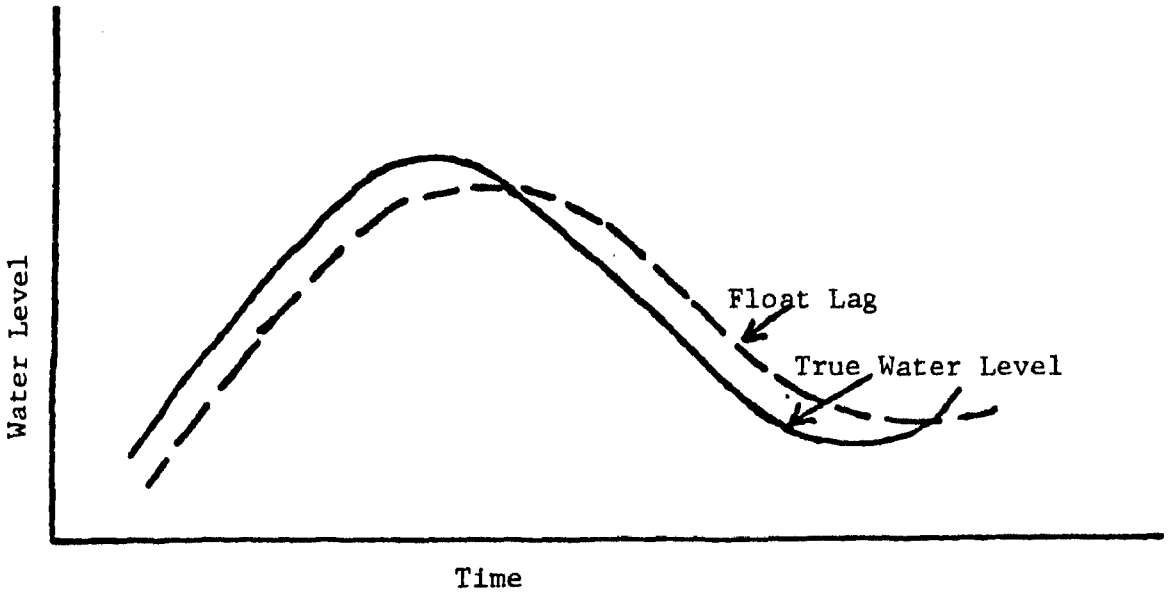
P = weight per unit length of the line ounces

D = diameter of the float, inches

ΔH = change in water level, feet and error from line shift shift in feet.



a) Showing float lag when index is set to True Water Level while the water is rising



b) Showing float lag when index is set at some intermediate point between rising and falling water levels.

Figure 3.37 Float Lag (12)

If the error from line shift occurs when the counter weight is submerged, the error = $0.34 \frac{P}{D^2} \Delta H$

The error for the submergence of the counter weight, is the result of the reduced pull on the float which leads to the increased depth of floatation. The error for the submergence is given by ΔX.

$$\Delta X = \frac{C}{S_c WA} - \frac{P(L-2\ell)}{WA} \left(2 - \frac{1}{S_1}\right)$$

where,

C = the counter weight

S_c = specific gravity of the counter weight

W = weight of the float

P = weight per unit length of the float line

L = total length of the float line from float to counter weight

ℓ = length of the float line, on the counter weight side

A = area of the float

S_1 = specific gravity of the float line.

- The error due to fouling by trash or debris.

- Bubbler

  . clogging of the exit and base of the bubble tube

  . aspiration effects due to velocity of flow

  . Errors due to temperature and aging

  . Errors due to hysteresis (lag effect)

Electrical

Main error is due to foam, floating oil or grease in the

liquid

Acoustic

The main errors are due to foam, highly turbulent-flow and false echo in restricted sites like manholes, meter vaults, etc.

3.5.3.3 Total Error in the Flow Measurement

Often the total error in the flow measurement in a system is wrongfully taken as the sum of the errors in the primary and the secondary devices. However, the total error in the flow measurement is the square root of the sum of the squares of the individual errors (31). Illustrative example is given below:

In the flow measurements through a 30.48 cm (12 in) Parshall flume, the flow was 0.21 m^3/s (7.41 cfs) at 457.20 mm (18 in) of head. It was observed that there was a 3 percent error in the flow measurement for the Parshall flume. The error introduced by the use of a flow measurement formula was 1.5 percent. There was an error of 6.350 mm (1/4 in) in the measurement of the throat. The error due to incorrect setting of zero was 3.175 mm (1/8 in) and the error in the reading of the head was 3.18 mm (1/8 in).Calculate the total percentage error.

Percentage error in the head measurement (secondary device) $= X_n(e) = 100 \times \sqrt{\frac{\left(\text{error zero setting}\right)^2 + \left(\text{error head-reading}\right)}{(\text{Head})^2}}$

$$X_n(e) = 100 \sqrt{\frac{(3.175)^2 + (3.175)^2}{(457.20)^2}} = .982 = 1 \text{ percent approximately}$$

Pecentage error in the primary device dimensions $X_b(e) = 100 \times \frac{6.350}{304.80} = 2\%$ approximately

Percent total error in the system

$$= X = \sqrt{\left(\begin{matrix}\text{Percent}\\ \text{error of}\\ \text{the flow}\end{matrix}\right)^2 + \left(\begin{matrix}\text{Percent}\\ \text{error of}\\ \text{the formula}\end{matrix}\right)^2 + \left(\begin{matrix}\text{Percent}\\ \text{error of}\\ \text{primary}\\ \text{device}\end{matrix}\right)^2 + \left(\begin{matrix}\text{Percent}\\ \text{error of}\\ \text{secondary}\\ \text{device}\end{matrix}\right)^2}$$

$$= 3^2 + 1.5^2 + 2^2 + 1^2$$

= 4 percent approximately

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CHAPTER 4

STATISTICAL APPROACH TO SAMPLING

For every sampling program four factors must be established:

1. Number of samples
2. Sampling frequency
3. Parameters to be measured
4. Location(s) of sampling

These variables are usually established in varying degrees by the discharge permit requirements which may or may not be scientifically sound. In those cases where a new program is being initiated or where the permit requirements need review, statistical methods and scientific judgment should be used to establish the best procedures.

This chapter explains various statistical terms and techniques and their applications to sampling. Each new concept is introduced with an example to illustrate its use. After the basic terms are defined and illustrated, statistical methods are introduced for analyzing data and determining the above four factors. These methods are also illustrated with examples.

4.1 BASIC STATISTICS AND STATISTICAL RELATIONSHIPS

Data representing a physical phenomenon are broadly classified as continuous (such as temperatures measured constantly and recorded as a continuous curve) or discrete (such as temperatures recorded hourly), and as deterministic (able to be described by an explicit mathematical relationship or formula) or nondeterministic (random). Due to the nature of water quality

changes and the complexity of the processes affecting the water or wastewater characteristics, there is no way to predict an exact value for a datum at a future instant in time. Such data are random in character and are conveniently described in terms of probability statements and statistical averages rather than by explicit equations. However, long-term changes in water quality tend to have a functional character with random fluctuation components. Statistical evaluation techniques provide a tool with which to detect and quantify both the deterministic and random components of a water or wastewater quality record.

4.1.1 Statistical Sample Parameters - Definitions and Examples (1)

A wastewater stream was sampled once a week for a period of one year and the concentration of a cerain parameter recorded. (See Table 4.1)

These data don't give much information as presented, so certain operations are performed on them to give them some meaning. Two things that give useful information about a set of data are measures of location (such as arithmetic mean and median) and measures of spread (such as range, variance and standard deviation).

4.1.1.1 The Arithmetic Mean

The arithmetic mean or simply the mean is one statistic used to locate the "center" of a data set. It is defined to be the sum of all the observations divided by the number of observations (N) or, in symbols:

$$\bar{X} = \frac{\sum_{i=1}^{N} x_i}{N}$$

TABLE 4.1 WASTEWATER PARAMETER DATA

Week	Concentration	Week	Concentration
1	35.8	27	31.1
2	33.0	28	33.6
3	33.6	29	28.9
4	35.0	30	35.6
5	33.5	31	32.9
6	34.7	32	31.8
7	33.6	33	37.4
8	36.9	34	32.0
9	38.8	35	34.8
10	35.5	36	31.7
11	32.2	37	32.7
12	32.2	38	36.0
13	33.3	39	34.2
14	33.5	40	30.3
15	33.0	41	39.6
16	33.1	42	34.6
17	33.5	43	31.7
18	31.9	44	30.3
19	31.7	45	34.4
20	32.4	46	32.4
21	34.8	47	31.1
22	33.5	48	36.5
23	33.9	49	33.2
24	32.0	50	34.3
25	34.2	51	35.8
26	33.4	52	32.4

TABLE 4.2 WASTEWATER PARAMETER DATA IN NUMERICAL ORDER

Observation #	Concentration	Observation #	Concentration
1	39.6	27	33.5
2	38.8	28	33.4
3	37.4	29	33.3
4	36.9	30	33.2
5	36.5	31	33.1
6	36.0	32	33.0
7	35.8	33	33.0
8	35.8	34	32.9
9	35.6	35	32.7
10	35.5	36	32.4
11	35.0	37	32.4
12	34.8	38	32.4
13	34.8	39	32.2
14	34.7	40	32.2
15	34.6	41	32.0
16	34.4	42	32.0
17	34.3	43	31.9
18	34.2	44	31.8
19	34.2	45	31.7
20	33.9	46	31.7
21	33.6	47	31.7
22	33.6	48	31.1
23	33.6	49	31.1
24	33.5	50	30.3
25	33.5	51	30.3
26	33.5	52	28.9

where: X_i are the observations, with i ranging from 1 to N

N is the number of observations

$\sum_{i=1}^{N}$ is the operator "sum" meaning to add together all the values of the variable following it (in this case X_i) as i covers the integers from 1 to N.

$$\left[\sum_{i=1}^{N} X_i = X_1 + X_2 + X_3 + \ldots + X_N \right]$$

In the above example (from Table 4.1), $X_1 = 35.8$, $X_2 = 33.0$, $\ldots, X_N = X_{52} = 32.4$;

$\sum_{i=1}^{N} X_i = 35.8 + 33.0 + 33.6 + \ldots + 35.8 + 32.4 = 1748.3$; and so the mean, which is denoted $\bar{X}$ (read "X-bar") is:

$$\bar{X} = \frac{\sum_{i=1}^{N} X_i}{N} = \frac{1748.3}{52} = 33.6$$

The mean, unlike the median, uses all the data, and is therefore more representative of the whole set. Unfortunately, it is affected by extreme values. If in Table 4.2 the first observation is replaced by 396.0 the median is still 33.5, but the mean becomes:

$$\bar{X} = \frac{396.0 + 38.8 + 37.4 + \ldots + 28.9}{52} = \frac{2104.7}{52} = 40.5$$

which is considerably greater than the former value of 33.6.

The mean, since it makes use of all the data, is the most often used measure of the "center" of a data set.

4.1.1.2 The Median

The median of a set of data is the observation in the middle, that is, the number that is located such that half of the observations are less than it and half are greater. To find the median of a set of observations, the data must first be arranged in numerical order as in Table 4.2.

If N is the number of observations in the ordered data set (in this case, N, is 52), then the median is defined to be the mean of the $\frac{N}{2}$ th and $\frac{N}{2}$ + 1st observations if N is even (between the 26th and 27th here, which would be 33.5) or the $\frac{N+1}{2}$th observation if N is odd (i.e. with 15 ordered observations, the median is the 8th value).

The median is a good measure of the location of the center of a set of data because it is unaffected by extreme values (i.e. if the largest observation were 396.0 instead of 39.6, the median would still be 33.5). It's fault is that it doesn't make use of all the information contained in the data, but rather uses only the relative sizes of the observations.

4.1.1.3 The Range

In addition to knowing where the "center" of a data set is, it is useful to know how spread out the data set is. One indicator of the spread of a data set is the range, which is defined as the difference between the largest and the smallest values in the set. For example, in Table 4.2, the largest is 39.6 (#1) and the smallest is 28.9 (#52) and so the range is R = 39.6 - 28.9 = 10.7.

Like the median, the range is simple to compute, once the data are arranged in decreasing or increasing order, but doesn't use all the data, and therefore does not carry much information.

4.1.1.4 The Variance

The variance, which could be called the average of the squares of the deviations of the data from their mean, is another indicator of how spread out the observations are. To find the variance, you subtract the mean from each observation, square each of these differences, sum the squared terms, then divide the sum by one less than the number of observations, or, in symbols;

$$S_X^2 = \frac{\sum_{i=1}^{N} (X_i - \bar{X})^2}{N - 1}$$

Table 4.3 shows how this is done; i is the week and X_i is the corresponding concentration.

$$\sum_{i=1}^{52} (X_i - \bar{X})^2 = \sum_{i=1}^{26} (X_i - \bar{X})^2 + \sum_{i=27}^{52} (X_i - \bar{X})^2 = 67.00 + 151.11 = 218.11$$

$$\text{Variance} = S_X^2 = \frac{\sum_{i=1}^{N} (X_i - \bar{X})^2}{N - 1} = \frac{\sum_{i=1}^{52} (X_i - 33.6)^2}{51} = \frac{218.11}{51} = 4.28$$

There is another formula for computing S_X^2 which will be given here without an example:

$$S_X^2 = \frac{\sum_{i=1}^{N} (X_i^2) - N(\bar{X}^2)}{N - 1}$$

This formula says to square each observation and sum the squares. Then multiply the square of the mean (found earlier) by the number of observations (N), subtract this from the sum of squares just computed, then divide by N-1. This formula involves fewer steps since there is only one subtraction, as opposed

TABLE 4.3 COMPUTATION OF THE VARIANCE

i	X_i	$(X_i-\bar{X})$	$(X_i-\bar{X})^2$	i	X_i	$(X_i-\bar{X})$	$(X_i-\bar{X})^2$
1	35.8	2.2	4.84	27	31.1	-2.5	6.25
2	33.0	-0.6	0.36	28	33.6	0.0	0.00
3	33.6	0.0	0.00	29	28.9	-4.7	22.09
4	35.0	1.4	1.96	30	35.6	2.0	4.00
5	33.5	-0.1	0.01	31	32.9	-0.7	0.49
6	34.7	1.1	1.21	32	31.8	-1.8	3.24
7	33.6	0.0	0.00	33	37.4	3.8	14.44
8	36.9	3.3	10.89	34	32.0	-1.6	2.56
9	38.8	5.2	27.04	35	34.8	1.2	1.44
10	35.5	1.9	3.61	36	31.7	-1.9	3.61
11	32.2	-1.4	1.96	37	32.7	-0.9	0.81
12	32.2	-1.4	1.96	38	36.0	2.4	5.76
13	33.3	-0.3	0.09	39	34.2	0.6	0.36
14	33.5	-0.1	0.01	40	30.3	-3.3	10.89
15	33.0	-0.6	0.36	41	39.6	6.0	36.00
16	33.1	-0.5	0.25	42	34.6	1.0	1.00
17	33.5	-0.1	0.01	43	31.7	-1.9	3.61
18	31.9	-1.7	2.89	44	30.3	-3.3	10.89
19	31.7	-1.9	3.61	45	34.4	0.8	0.64
20	32.4	-1.2	1.44	46	32.4	-1.2	1.44
21	34.8	1.2	1.44	47	31.1	-2.5	6.25
22	33.5	-0.1	0.01	48	36.5	2.9	8.41
23	33.9	0.3	0.09	49	33.2	-0.4	0.16
24	32.0	-1.6	2.56	50	34.3	0.7	0.49
25	34.2	0.6	0.36	51	35.8	2.2	4.84
26	33.4	-0.2	0.04	52	32.4	-1.2	1.44

$$\sum_{i=1}^{26} (X_i - \bar{X})^2 = 67.00 \qquad \sum_{i=27}^{52} (X_i - \bar{X})^2 = 151.11$$

to N subtractions using the other method.

4.1.1.5 The Standard Deviation

The units of the variance are the square of the units of the mean (and the original data), i.e. if the data are expressed in mg/l, the variance is in mg^2/l^2. Because of this, the standard deviation, which is the square root of the variance, is more commonly used as a measure of dispersion. In our example the variance, S_x^2, is 4.28, and so the standard deviation is:

$$S_x = \sqrt{S_x^2} = \sqrt{4.28} = 2.07.$$

Since the data are expressed as mg/l, the standard deviation is also in mg/l.

The mean ($\bar{X}$) and standard deviation (S_x) are actually only estimates of parameters known as the population mean (μ_x) and population standard deviation (σ_x), which are discussed in Appendix A.

An interesting and useful fact about these two numbers is that in a normal population (which is discussed later and is a phenomenon which occurs quite frequently), 68.3% of the observations will fall within $\mu_x \pm \sigma_x$, 95.5% will be found within $\mu_x \pm 2\sigma_x$, and 99.7% within $\mu_x \pm 3\sigma_x$. Since $\bar{X}$ approximates μ_x and S_x approximates σ_x, these percentages will hold approximately for $\bar{X} \pm S_x$, $\bar{X} \pm 2S_x$ and $\bar{X} \pm 3S_x$.

4.1.1.6 Coefficient of Variation

This statistic provides a measure of the dispersion relative to the location of the data set, so that the spread of the data in sets with different means can be compared.

$$\text{Coefficient of Variation} = CV = \frac{S_x}{\bar{X}}$$

4.1.1.7 The coefficient of Skewness

The coefficient of skewness is a measure of the degree of assymetry of the data about its mean:

$$\text{Coefficient of Skewness} = k = \frac{N \sum_{i=1}^{N} (X_i - \bar{X})^3}{(N-1)\ (N-2)\ S_x^3}$$

In our example, $k = \frac{52\ (272.765)}{51\ (50)\ 8.870} = .63$ (see Table 4.4)

A positive coefficient of skewness indicates high extreme values and, as shown on page (4), leads to a mean greater than the median.

4.1.2 Harmonic Variations (2)

The use of the statistical concepts discussed so far depends on the assumption that the data record is random. The identification and estimation of the transient variations of a wastewater monitoring record is extremely important. It reduces the standard deviation, thereby making estimators more reliable. The techniques used in identifying and evaluating these components are trend removal and time series analysis.

4.1.2.1 Trend Removal

A trend in a wastewater monitoring record can usually be detected visually. Trends can be either linear (increasing or decreasing) or non-linear (e.g. exponential or logarithmic). A trend may be defined as any harmonic component whose period is longer than the record length. Trend removal is an important step in data processing. If trends are not removed, large distortions can occur both in further data processing and in conclusions on the probability distribution of the measured parameter. In many wastewater monitoring programs the evaluation or detection of the trend is a desired result

TABLE 4.4 COMPUTATION OF THE COEFFICIENT OF SKEWNESS

i	$X_i - \bar{X}$	$(X_i - \bar{X})^3$	i	$X_i - \bar{X}$	$(X_i - \bar{X})^3$
1	2.2	10.648	27	-2.5	-15.625
2	-0.6	-0.216	28	0.0	0.000
3	0.0	0.000	29	-4.7	-103.823
4	1.4	2.744	30	2.0	8.000
5	-0.1	-0.001	31	-0.7	-0.343
6	1.1	1.331	32	-1.8	-5.832
7	0.0	0.000	33	3.8	54.872
8	3.3	35.937	34	-1.6	-4.096
9	5.2	140.608	35	1.2	1.728
10	1.9	6.859	36	-1.9	-6.859
11	-1.4	-2.744	37	-0.9	-0.729
12	-1.4	-2.744	38	2.4	13.824
13	-0.3	-0.027	39	0.6	0.216
14	-0.1	-0.001	40	-3.3	-35.937
15	-0.6	-0.216	41	6.0	216.000
16	-0.5	-0.125	42	1.0	1.000
17	-0.1	-0.001	43	-1.9	-6.859
18	-1.7	-4.913	44	-3.3	-35.937
19	-1.9	-6.859	45	0.8	0.512
20	-1.2	1.728	46	-1.2	-1.728
21	1.2	1.728	47	-2.5	-15.625
22	-0.1	-0.001	48	2.9	24.389
23	0.3	0.027	49	-0.4	-0.064
24	-1.6	-4.096	50	0.7	0.343
25	0.6	0.216	51	2.2	10.648
26	-0.2	-0.008	52	-1.2	-1.728

$$\sum_{i=1}^{52} (X_i - \bar{X})^3 = 272.765$$

in itself.

The best method for evaluating a trend is the least-square procedure which can be used if a random or harmonic component is superimposed on a linear trend such that:

$$X(t) = x(t) + X'(t)$$

where $X(t)$ is the data record expressed as a function of time. (In the Table 4.1 data, t is expressed in weeks, and so $X(1) = X_1 = 35.8$, $X(2) = X_2 = 33.0, \ldots, X(52) = X_{52} = 32.4$.

$x(t)$ is the linear trend.

$X'(t)$ is the random component.

In this case, the trend can be approximated by a straight line of the form

$$\hat{X}(t) = a + bt.$$

The coefficients a and b are computed by regression analysis and can be proven to be:

$$a = \frac{\left[2\ (2N + 1) \sum_{t=1}^{N} X(t)\right] - \left[6 \sum_{t=1}^{N} t\ \ X(t)\right]}{N\ (N - 1)}$$

$$b = \frac{\left[12 \sum_{t=1}^{N} t\ X(t)\right] - \left[6(N+1) \sum_{t=1}^{N} X(t)\right]}{(\Delta t)\ (N)\ (N-1)(N+1)}$$

where N is the number of samples.

t is the sampling interval.

After removal of this linear trend, $\hat{X}(t)$, the new time series is:

$$X(t) = X'(t) = X(t) - (a + bt)$$

Table 4.5 contains a data set with a linear trend. There follows an example of identifying and removing this trend.

It can be seen in Figure 4.1 that the data contain an upward trend and also a harmonic component. The trend is identified by finding $\hat{X}(t) = a + bt$.

$$a = \frac{2((2)(34) + 1)(104.1) - 6\ (2133.1)}{(34)\ (33)} = 1.4$$

$$b = \frac{12(2133.1) - 6(35)(104.1)}{(1)(34)(33)(35)} = 0.1$$

Therefore the line $X(t) = 1.4 + 0.1\ t$. Since a linear trend is removed by subtraction, the new time series is:

$$\overline{X}(t) = X(t) - (a + bt) = X(t) - (1.4 + 0.1t)$$

Table 4.6 lists the adjusted data and Figure 4.2 shows the series after the removal of the trend.

4.1.2.2 Time Series Analysis

Time series analysis is the most powerful method of analyzing a large volume of data, such as continuous records with high frequency of data acquisition. Since large amounts of data are required, time series analysis should not be used for short surveys or low frequency monitoring when limited amounts of data are available, or if part of the record is missing.

Auto-Covariance and Auto-Correlation Analysis

These functions describe the dependence of the values of the data at one time on the values at another time. An estimate of the auto-covariance

TABLE 4.5 DATA SET WITH LINEAR TREND

Data		computation	Data		computation
t	X(t)	tX(t)	t	X(t)	tX(t)
1	1.0	1.0	18	3.8	68.4
2	1.4	2.8	19	3.7	70.3
3	1.9	5.7	20	4.8	96.0
4	2.0	8.0	21	4.4	92.4
5	2.5	12.5	22	4.3	94.6
6	2.4	14.4	23	4.6	105.8
7	2.5	17.5	24	4.3	103.2
8	2.8	22.4	25	4.4	110.0
9	2.1	18.9	26	4.3	111.8
10	2.2	22.0	27	3.9	105.3
11	1.7	18.7	28	4.3	120.4
12	1.8	21.6	29	3.6	104.4
13	1.5	19.5	30	3.2	96.0
14	1.8	21.6	31	3.8	117.8
15	1.9	28.5	32	3.4	108.8
16	2.8	44.8	33	4.5	148.5
17	2.7	45.9	34	4.6	156.4

$$\sum_{t=1}^{34} t\,X(t) = 2139.5 \qquad \sum_{t=1}^{34} X(t) = 104.90$$

TABLE 4.6 ADJUSTED DATA SET OF TABLE 4.5

	Computation	Adjusted Data		Computation	Adjusted Data
t	$\hat{X}(t)$	$\bar{X}(t)$	t	$\hat{X}(t)$	$\bar{X}(t)$
1	1.5	-0.5	18	3.2	0.6
2	1.6	-0.2	19	3.3	0.4
3	1.7	0.2	20	3.4	1.4
4	1.8	0.2	21	3.5	0.9
5	1.9	0.6	22	3.6	0.7
6	2.0	0.4	23	3.7	0.9
7	2.1	0.4	24	3,8	0.5
8	2.2	-0.6	25	3.9	0.5
9	2.3	-0.2	26	4.0	0.3
10	2.4	-0.2	27	4.1	-0.2
11	2.5	-0.8	28	4.2	0.1
12	2.6	-0.8	29	4.3	-0.7
13	2.7	-1.2	30	4.4	-1.2
14	2.8	-1.0	31	4.5	-0.7
15	2.9	-1.0	32	4.6	-1.2
16	3.0	-0.2	33	4.7	-0.2
17	3.1	-0.4	34	4.8	-0.2

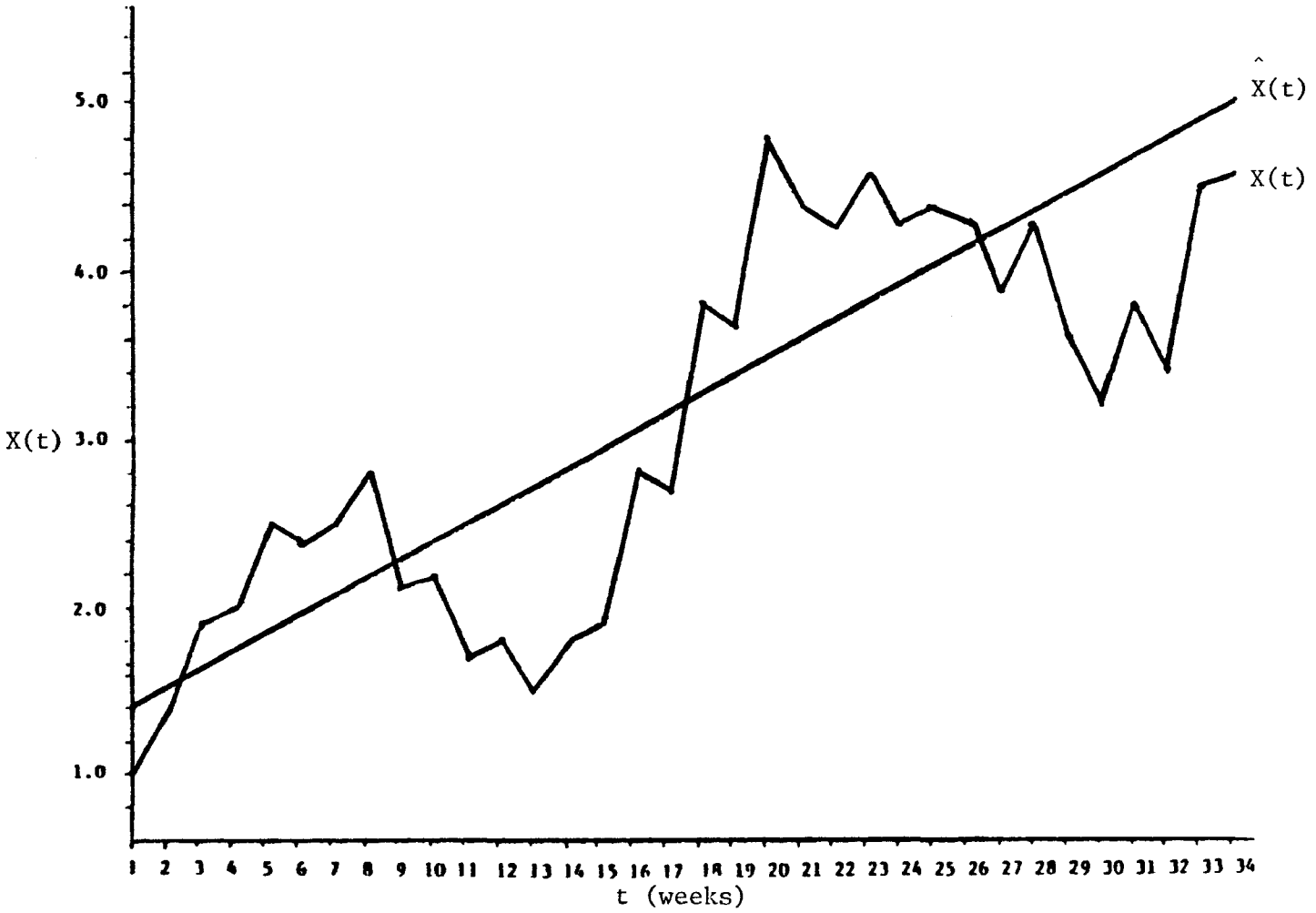


Figure 4.1 Series before removal of trend

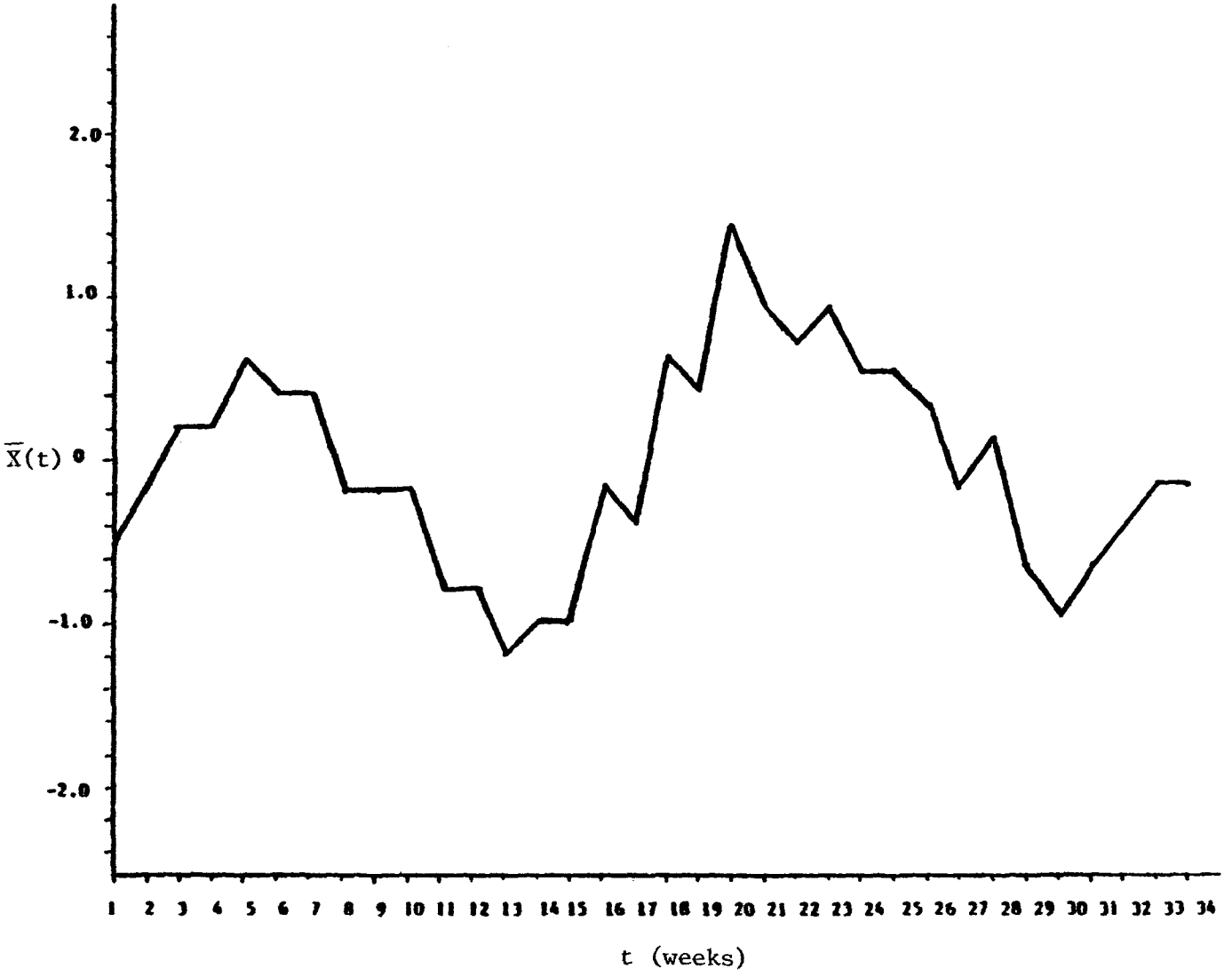


Figure 4.2 Series after removal of trend

function (acvf) between two observations X(t) and X(t + u), separated by a lag time, u, is given by;

$$c(u) = \frac{1}{N} \sum_{t=1}^{N-u} \{(X(t) - \bar{X})(X(t + u) - \bar{X})\}$$

where N is the number of observations in the record.

$\bar{X}$ is the mean of the N observations.

c(u) is called the sample auto-covariance function of the time series, and is a function of the lag time, u.

Using the data in Table 4.5, we find that

$$\bar{X} = \frac{104.1}{34} = 3.1$$

and so, for u = 4,

$$c(4) = \frac{1}{34} \sum \left[X(t) - 3.1\right] \left[X(t + 4) - 3.1\right]$$

$$= \frac{1}{34} (1.0 - 3.1)(2.5 - 3.1) + (1.4 - 3.1)(2.4 - 3.1) +$$

$$\ldots + (3.2 - 3.1)(4.6 - 3.1)$$

$$= \frac{1}{34} (22.19) = .65$$

Since the acvf is a measure of the dependence between values spaced a certain distance apart, looking at c(u) for various values of u will give information on this dependence. For example, in this set of data, c(4) = 0.65, c(1) = 1.06, and c(10) = 0.12. This shows that the auto-correlation decreases with increased lag time and is quite small when u reaches 10.

Notice that, except for N rather than N-1 in the denomenator, c(0) = S_x^2, the sample variance. This says that the variance is just the auto-

covariance of each observation with itself.

When the acvf is normalized by dividing by c(0), it becomes the sample auto-correlation function (acf)

$$r(u) = \frac{c(u)}{c(0)}$$

which is an indicator of how much one observation is dependent on those around it. It gives a visual picture (when plotted against the lag, u, between points) of how the dependence damps out as the lag increases. This graph is called the auto-correlogram. Figure 4.3 is the auto-correlogram for the data in Table 4.5. The fact that the curve in Figure 4.1 is somewhat like a sine wave is reflected in the auto-correlation, which begins to show negative correlation after u passess 11. For purely random data the acf would approach zero as u increases. A periodic component in the record would result in a periodic auto-correlogram with period similar to that of the original data. The principal application of the acf is to establish the influence of values at any time over values at a later time. It provides a tool for detecting deterministic data which might be masked in a random background.

Variance Spectral Analysis

In the analysis of time series, the "variance spectrum" more commonly known as "power spectrum" is a basic tool for determining the mechanism generating an observed series. The power spectrum is just the Fourier Transform of the theoretical acvf, $\gamma(u)$, and so is defined, as a function of frequency f, by

$$\Gamma(f) = \int_{-\infty}^{\infty} \gamma(u) \cos(2\pi f u)\, du$$

where

$$\gamma(u) = E\{ (X(t) - \mu)(X(t+u) - \mu) \}.$$

(The expectation operator E is defined in Appendix A).

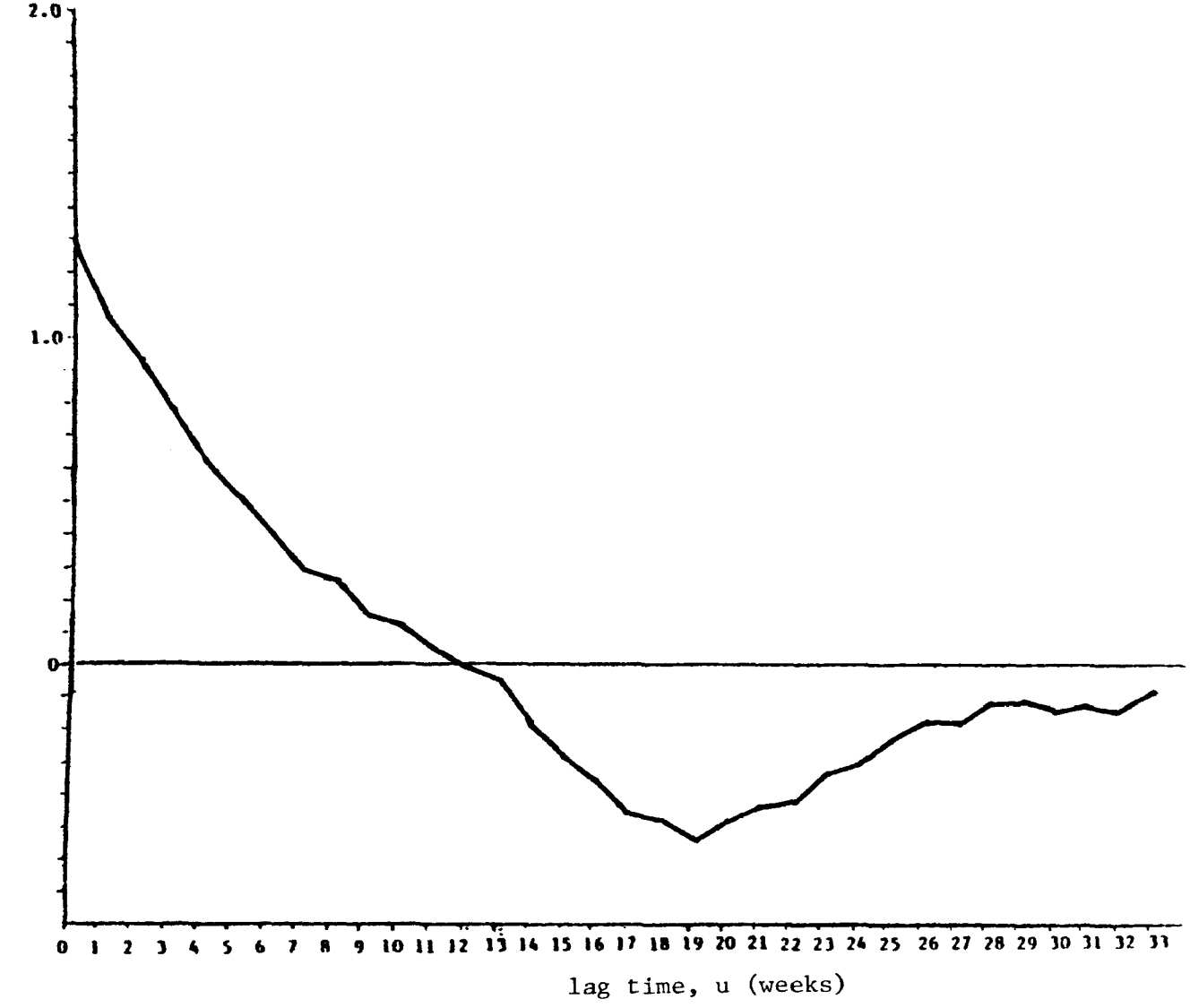


Figure 4.3 Auto-correlogram

By definition (cf. Section 4.1.1) variance is a measure of the dispersion of observations about their mean value. This dispersion may result from purely random fluctuations (noise) in the observed data as well as from deterministic (non random) fluctuations. These deterministic fluctuations may be the result of trends (e.g. linear trends) as well as periodic components in the record. Spectral analysis is a useful tool for the analysis of data records in in which both random and deterministic fluctuations may be present as it allows its user to separate these two types of fluctuations.

In spectral analysis of a data record (which ideally but not necesssarily should be continuous) the power spectrum $\Gamma(f)$ of the series is plotted against frequency f. Figure 4.4 shows six hypothetical data records and their corresponding power spectra.

Figure 4.4a shows a record on which all observed values are equal and therefore equal to their mean. Their variance is zero and therefore the power spectrum plot is zero at all frequencies.

Figure 4.4b shows a record with a linear trend. The variance in this record is a result of the time dependent linear trend in the record. There is no random or periodic dispersion about the mean, consequently all of the variance (or power) spectrum is concentrated at the zero frequency.

Figure 4.4c shows a record exhibiting periodic harmonic fluctuations with frequency f_1. The variance in this record is a result of the harmonic fluctuation of frequency f_1 about the mean. All the power spectrum is concentrated at the f_1 frequency.

Figure 4.4d shows a record with purely random fluctuations (white noise) about a constant mean value. The variance in this record is a result of these purely random fluctuations. There is no trend or harmonic fluctuations. The

power spectrum is uniformly distributed over all frequencies. Figure 4.4e shows a record with purely random fluctuations superimposed on a linear trend. Its power spectrum is the superposition of power spectra corresponding to the linear trend record and the purely random record.

Figure 4.4f shows a record with purely random fluctuation superimposed on harmonic variations of frequency f_1 . It's power spectrum is the superposition of power spectra corresponding to the harmonic record and the purely random record.

The power spectra depicted in Figure 4.4 are theoretical power spectra. They are based on infinite continuous records. In practice records will be of finite duration and discrete. When evaluating the power spectrum of a finite duration record it is assumed that this finite record repeats itself periodically at intervals of length equal to the duration of the given record.

When dealing with discrete records (or digital treatments of a continuous record) the frequency of data acquistion is a frequency foreign to the phenomenon under study which would appear in the power spectrum. These two practical limitations on spectral analysis lead to distortion in the low and high frequency regions of the spectrum known as "aliasing". The highest frequency which can be resolved from a discrete record with sampling interval Δt is the "Nyquist frequency"

$$f_{max} = \frac{1}{2 \Delta t}$$

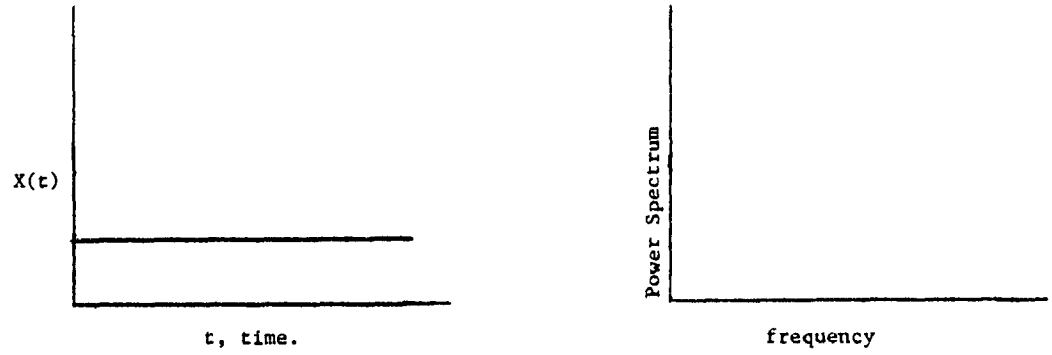
Furthermore, the length of the record should be large enough to resolve its periodic fluctuations. For example, spectral analysis of the portion AB of the record in Figure 4.4f would lead to a power spectrum similar to that of Figure 4.4e and not the actual power spectrum of Figure 4.4f.

Besides, purely random fluctuations (white noise) are never met in practical applications where the theoretical power spectra depicted in Figures 4.4d-f would not be obtained. Rather, spectra similar to those of Figures 4.5 a-c would be encountered. In Figure 4.5a the absence of any significant peak in the spectrum reflects the absence of any significant periodicity in the record of 4.4d. In Figure 4.5b the presence of a significant peak at the low frequency end of the spectrum is indicative of the linear trend in the record of Figure 4.4e. The significant peak at frequency f_1 on the spectrum of Figure 4.5c reflects the presence of the harmonic component of frequency f_1 in the record of Figure 4.4f.

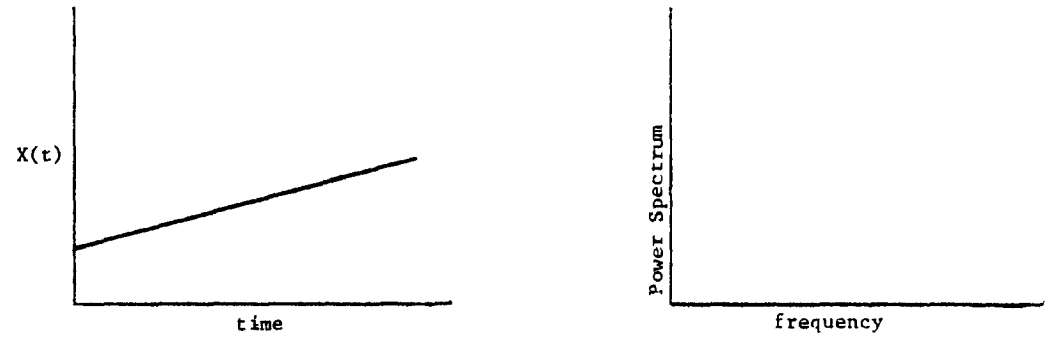
The following rules of thumb should be followed when using spectral analysis:

- The length of the record should be at least 10 times as long as the longest period of interest (e.g. 10 years of data if the annual period is the longest period of interest).
- The sampling interval should be less than half the shortest period of interest (which would then have the Nyquist frequency). A sampling interval of one third or one fourth the length of the shortest period of interest is recommended.

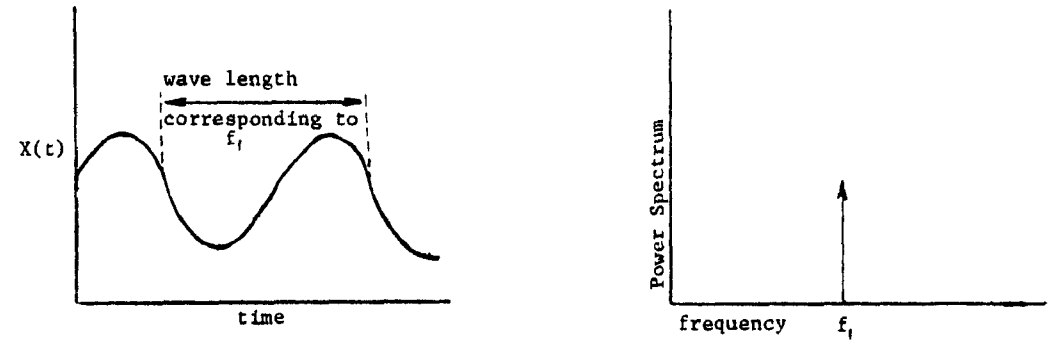
In view of the length of record and the high frequency of data acquisition necessary for accurate spectral analysis, an overwhelming number of calculations will have to be carried out and treatment of the data on a digital computer is necessary. In carrying out spectral analysis with the aid of a digital computer, the practitioner may wish to write his own program or take advantage of existing programs such as BMD02T, BMD03T, BMD04T, or SPECTRA which are described in references (16,17).



(a) Constant record

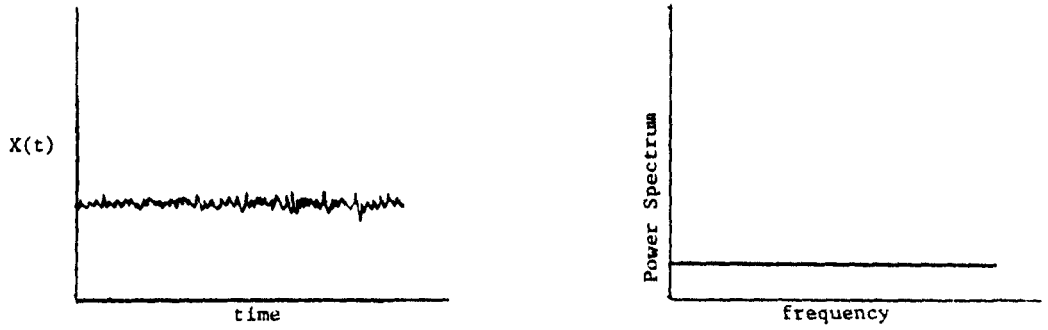


(b) Linear trend record

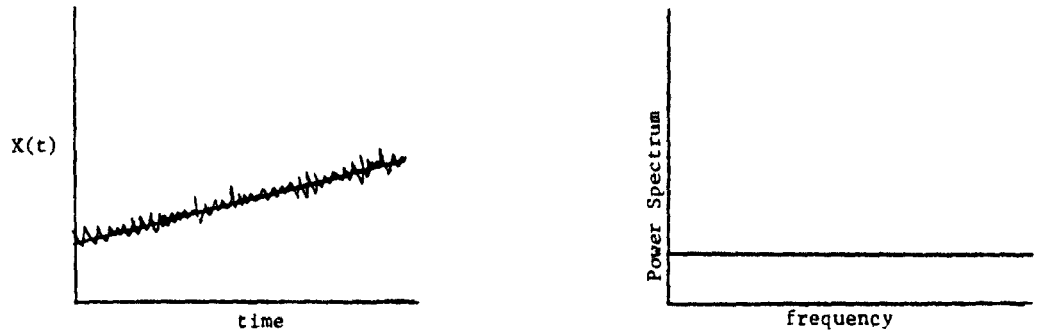


(c) Harmonic record

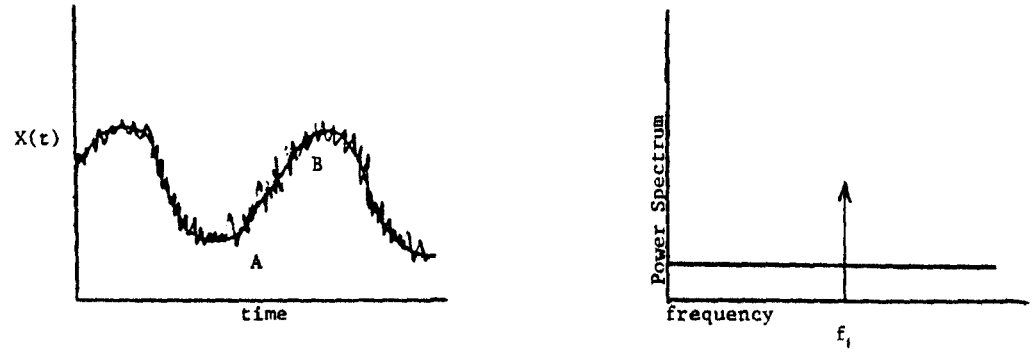
Figure 4.4 Typical theoretical power spectra for several records



(d) Purely random fluctuations

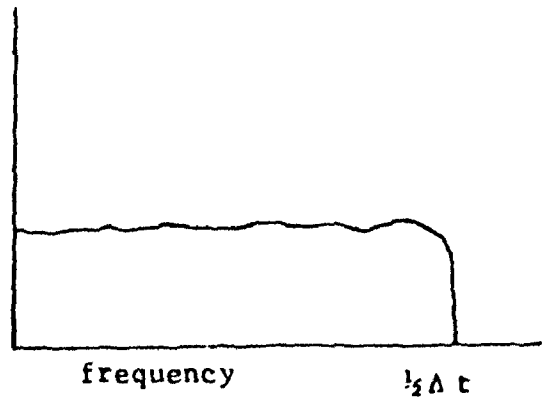


(e) Linear trend with random fluctuations

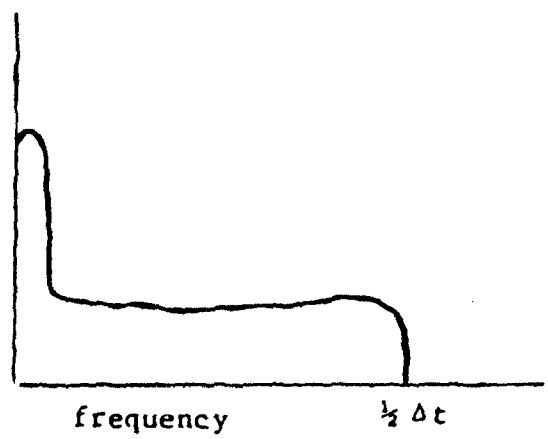


(f) Harmonic record with random fluctuations

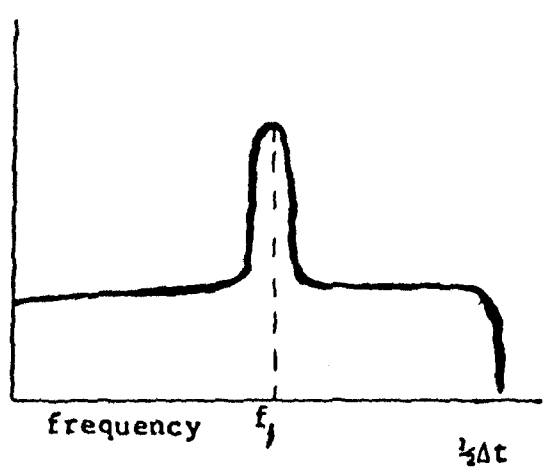
Figure 4.4 (continued)



(a)



(b)



(c)

Figure 4.5 Typical practical power spectra for the records of Figure 4.4 d,e,and f

4.1.3 Probability Density Functions (1,3,4)

When data are not deterministic (i.e. they can't be defined by an explicity function), there are functions, called probability density functions (pdf's) and denoted $f_X(x)$, which describe the probabilistic properties by the formula

$$F_X(x) = \int_{-\infty}^{x} f_X(u)du = P(X \leq x)$$

where $P(X \leq x)$ is read "the probability that X is less than or equal to x".

4.1.3.1 The Gaussian or Normal Distribution

This is the most widely used and frequently found distribution because most natural occurrences tend to behave according to this distribution in the long run (sometimes very long). If X has a normal distribution with mean μ_X and variance $\sigma_X 2$, then

$$f_X(x) = \frac{1}{\sigma_X\sqrt{2\pi}} \exp\left(\frac{-(x-\mu_X)^2}{2\sigma_X^2}\right) \quad \text{and so}$$

$$P(X \leq x) = \int_{-\infty}^{x} \frac{1}{\sigma_X\sqrt{2\pi}} \exp\left(\frac{-(t-\mu_X)^2}{2\sigma_X^2}\right) dt.$$

Using a substitution of $z = \frac{t-\mu_X}{\sigma_X}$ (and so $dz = \frac{dt}{\sigma_X}$), we get

$$P(X \leq x) = P\left(Z \leq \frac{x-\mu_X}{\sigma_X}\right) = \int_{-\infty}^{(x-\mu_X)/\sigma_X} \left(\frac{1}{\sqrt{2\pi}} \exp(-z^2/2)\right) dz.$$

It is easily seen that μ_X and σ_X define the function, so if it is known that data have a normal distribution and the mean and standard deviation are known, the probability distribution is completely defined. Another property of the normal distribution is that if X has a normal distribution with mean μ_X and

variance σ_x^2 (denoted $X \sim N(\mu_x, \sigma_x^2)$),

$$Z = \frac{X-\mu_x}{\sigma_x}$$

has a normal distribution with 0 mean and a variance of 1 (i.e. $Z \sim N(0,1)$) which is called the standard normal distribution.

Another property of the normal distribution is that approximately 68.3% of all the values will fall in the interval $\bar{X} \pm S_x$, 95.5% within the interval $\bar{X} \pm 2S_x$, and 99.7% within the interval $\bar{X} \pm 3S_x$. Figure 4.6 shows a graph of the normal distribution and illustrates this property.

4.1.3.2 The Pearson Type III Distribution

Unlike the normal distribution, which is defined from $-\infty$ to ∞, this distribution is defined only on the range 0 to ∞, and is therefore applicable to water quality situations, where negative values do not occur. The pdf of this distribution is given by

$$f_X(x) = Y_o \exp(-\gamma x) \times \left(1 + \frac{x}{d}\right)^{\gamma d}$$

where

Y_o and γ are constants,

d is the distance between the mode (the value that occurs most often) and the origin, as is shown in Figure 4.7.

4.1.3.3 Chi-Square Distribution

This is the probability distribution of a random variable of the form $X = Z_1^2 + Z_2^2 + \ldots + Z_n^2$ where $Z_1, \ldots, Z_n$ are a set of n independent random variables, each having a standard normal distribution and n is called the degrees of freedom of the distribution. The probability density function for a random

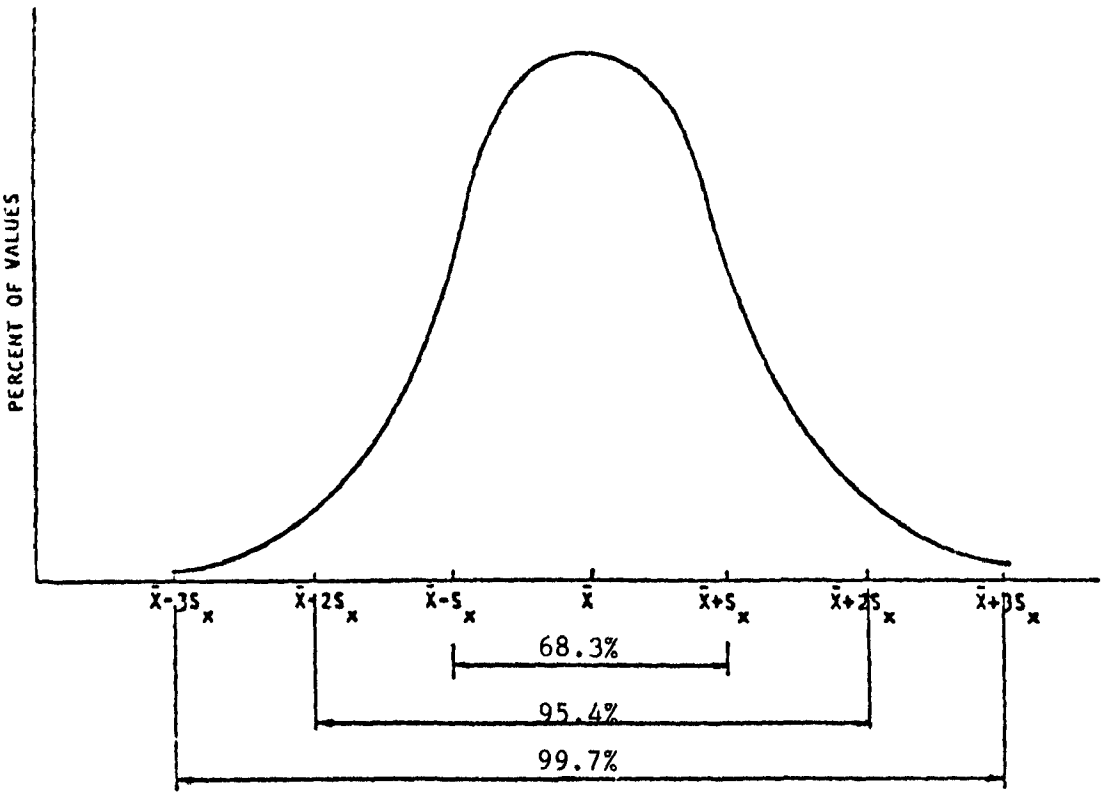


Figure 4.6 Gaussian or normal distribution

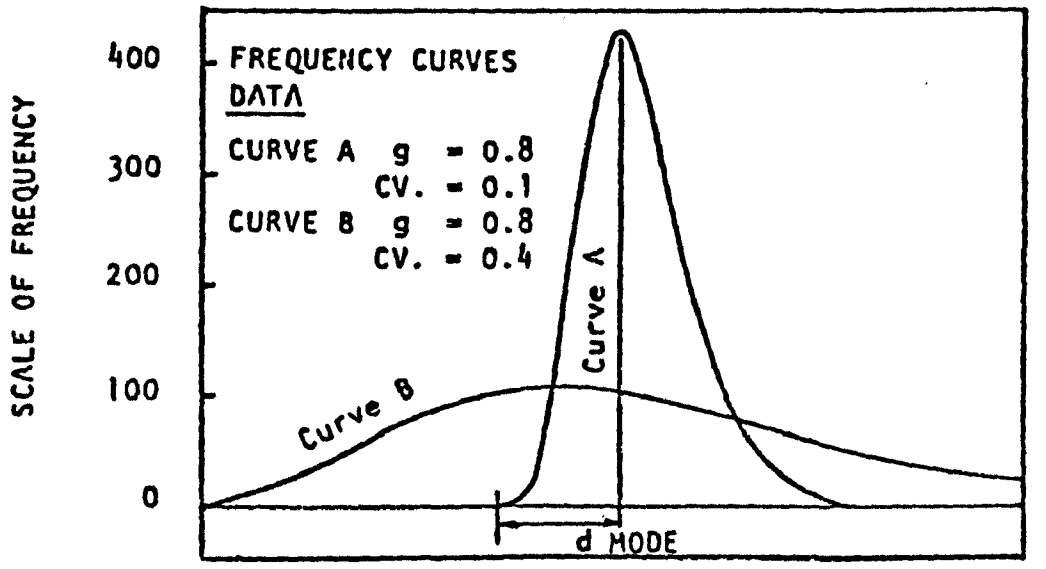


Figure 4.7 Pearson Type III probability distribution

variable X having a chi-square distribution with n degrees of freedom (denoted $X \sim \chi^2_n$) is given by

$$f_X(x) = \frac{1}{\Gamma(\frac{n}{2})\ 2^{n/2}}\ x^{n/2-1}e^{-x/2} \quad \text{for } 0 < x < \infty$$

where $$\Gamma(\alpha) = \int_0^\infty \left(\frac{x}{\beta}\right)^{\alpha-1} e^{-x/\beta}\left(\frac{1}{\beta}\right)\ dx.$$

It happens that n, the degrees of freedom, is the mean of the distribution (i.e. $n=\mu_x$) and the variance is 2n (i.e. $2n=\sigma_x^2$).

4.1.3.4 Poisson Distribution

This distribution describes the number of occurrences of an event in a period of time length 1 when events of this type are occurring randomly at an average rate of λ per unit time. This is a discrete distribution (meaning that a random variable with this type of distribution can take on only a countable number of values) which has probability mass function

$$P_X(x) = P(X=x) = e^{-\lambda}(\lambda^x/x!)$$

for positive integers x. The mean of this distribution is λ and the variance is also λ $\left(\text{i.e. } \mu_x = \sigma_x^2 = \lambda \text{ and so the pmf could be written } P_X(x)=e^{-\mu}(\mu^x/x!)\right)$.

4.1.3.5 Student's t - Distribution

A random variable X having a Student's t - distribution (denoted $X \sim t_n$) with n degrees of freedom has a pdf of the form

$$f_X(x) = \frac{\Gamma((n+1)/2)}{\sqrt{\pi n}\ \Gamma(n/2)} \left[\frac{1}{(1+x^2/n)^{(n+1)/2}}\right]$$

If $X \sim t_n$, then X can be expressed as the ratio

$$X = \frac{Z}{\sqrt{Y/n}}$$

where $Z \sim N(0,1)$
$Y \sim \chi^2_n$ (Z and Y are random variables)

This shows the relationship between the t - distribution and the standard normal and chi-square distribution.

4.1.3.6 Determination of the Type of Distribution (5)

To apply the concepts of Statistics, the type of distribution from which the observations came must be determined (or approximated). There are both graphical and numerical methods for accomplishing this.

Graphical Procedure for Small Sample (N < 30)

Step 1. Arrange the data in increasing order of magnitude (as for finding the median) and assign a ranking number, m, to each value (i.e. the smallest observation will have rank 1 and the largest will have rank n). (See column 1 of Table 4.7).

Step 2. Calculate the percent probability for each value, using the formula $P_m = \frac{50(2m-1)}{N}$ where m is the rank as defined above and P_m is the percent probability of an observation being less than or equal to the m^{th} value.

Step 3. Plot each value against its corresponding percent probability on probability paper.

An example of a data treatment is shown in Table 4.7 and Figure 4.8. If the data have a normal distribution, the plot will be a straight line. If the data have a log-normal distribution (i.e. log X has a normal distribution), then the data will yield a straight line when plotted on log probability paper.

TABLE 4.7 COMPUTATIONAL TABLE FOR GRAPHICAL NORMAL OR PEARSON TYPE III DISTRIBUTION DETERMINATION

Week (i)	Concentration (X_i)	Rank (m)	Plotting Position $p=\frac{50(2m-1)}{N}$	i	X_i	m	p
1	35.8	7	12.5	27	31.1	48	91.3
2	33.0	32	60.6	28	33.6	23	43.3
3	33.6	21	39.4	29	28.9	52	99.0
4	35.0	11	20.2	30	35.6	9	16.3
5	33.5	24	45.2	31	32.9	34	64.4
6	34.7	14	26.0	32	31.8	44	83.7
7	33.6	22	41.3	33	37.4	3	4.8
8	36.9	4	6.7	34	32.0	42	79.8
9	38.8	2	2.9	35	34.8	13	24.0
10	35.5	10	18.3	36	31.7	45	85.6
11	32.2	39	74.0	37	32.7	34	64.4
12	32.2	40	76.0	38	36.0	6	10.6
13	33.3	29	54.8	39	34.2	19	35.6
14	33.5	25	47.1	40	30.3	50	95.2
15	33.0	33	62.5	41	39.6	1	1.0
16	33.1	31	58.7	42	34.6	15	27.9
17	33.5	26	49.0	43	31.7	47	89.4
18	31.9	43	81.7	44	30.3	51	97.1
19	31.7	45	85.6	45	34.4	16	29.8
20	32.4	36	68.3	46	32.4	37	70.2
21	34.8	12	22.1	47	31.1	49	93.3
22	33.5	27	51.0	48	36.5	5	8.7
23	33.9	20	37.5	49	33.2	30	56.7
24	32.0	41	77.9	50	34.3	17	31.7
25	34.2	18	33.7	51	35.8	8	14.4
26	33.4	28	52.9	52	32.4	38	72.1

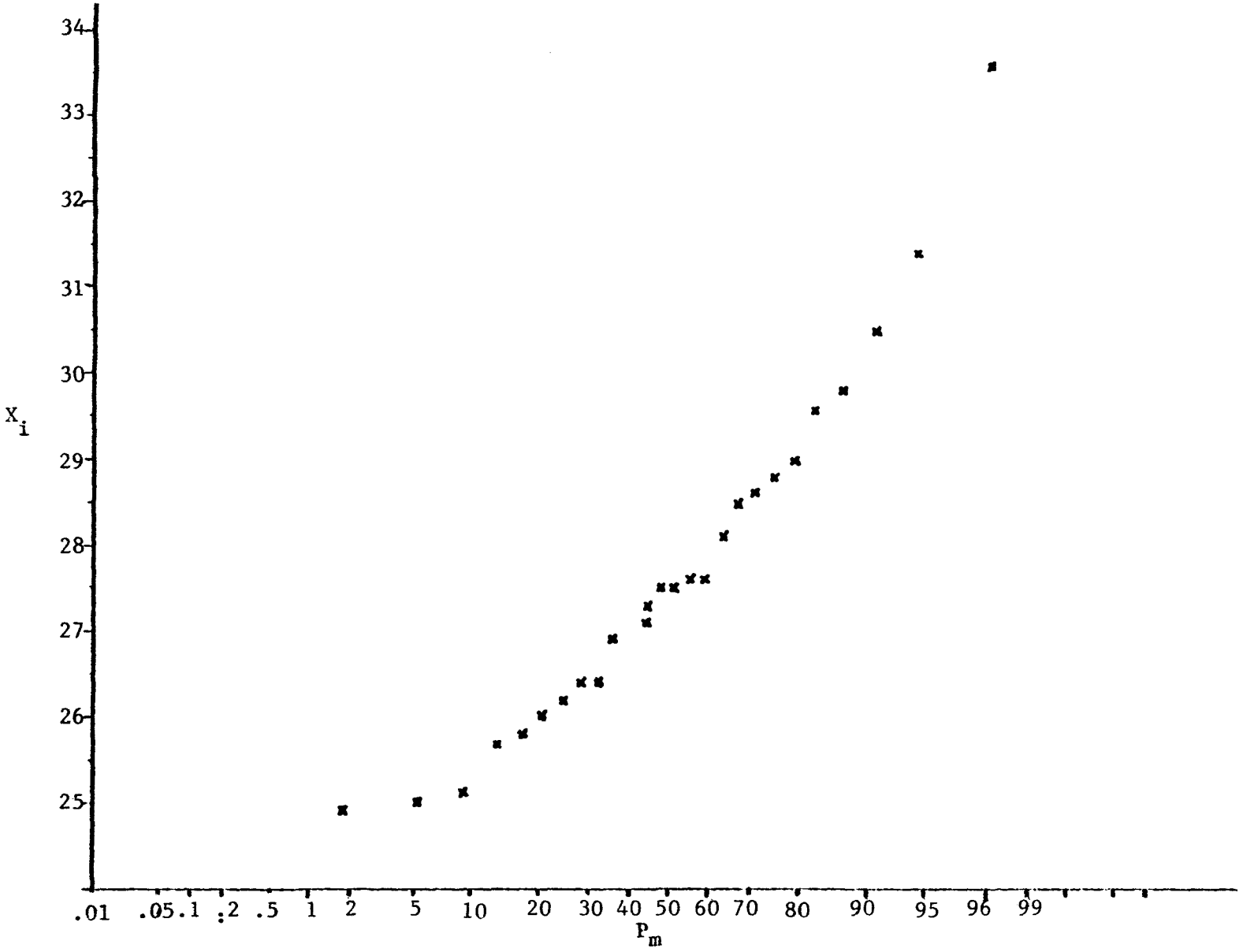


Figure 4.8 P_m vs X_i plot

Notice that in this example the data approximates a straight line fairly well except near the upper end (and one point at the lower end), and even these don't show a large deviation from the straight line. This indicates that the data have an approximately normal distribution.

Using the facts that approximately 68.3% of the values are within the interval $\bar{X} \pm S_x$ and the precent probability of the mean of the normal distribution is 50(meaning that the mean is equal to the median), we can estimate S_x graphically using Figure 4.8. To do this we find the interval, on the horizontal axis, with 50 (the mean) at its center and width 68.3 (making the endpoints 15.85 and 84.15). We then move up from the larger of these points until we reach the line that approximates the distribution. Then, moving horizontally to the left, we read from the vertical axis the observation corresponding to this percent probability. We also find the observation on the vertical axis corresponding to 50 on the horizontal axis (which, as was mentioned before, is the mean, and also the median, of the distribution and could therefore be found by finding the median of the data, which are already arranged in increasing order). The difference between these two numbers is approximately equal to S_x, the standard deviation of the data. (Note that the more the plotted points deviate from a straight line, the less accurate this estimate will be). Figure 4.8 shows that our data have an approximate normal distribution with mean 33.5 and standard deviation 35.5–33.5 = 2.0.(We found in Section 4.1.1 that $\bar{X}$ = 33.6 and S_x = 2.07).

Computational Method

Another method for estimating the distribution of a data set uses the coefficient of skewness, along with the mean and standard deviation, all of which were defined earlier. Sparr and Hann recommend the following relation

between the coefficient of skewness and the best approximating probability distribution.

Skew Coefficient, (k)	Best Fitting Probability Distribution
< 0.5	Normal
0.9 - 1.6	Pearson Type III
> 1.7	Log-Normal

Using the data from Table 4.1, we can compute the coefficient of skewness using

$$k = \frac{N \sum_{i=i}^{N} (X_i - \bar{X})^3}{(N-1)(N-2)\ S_x^3}$$

which was found in Section 4.1.1 to be .63, to find that these data are just a little too skewed to be considered to have a normal distribution, but not enough for the Pearson Type III distribution, so, for simplicity, we will assume that these data have a normal distribution with mean 33.6 and standard deviation 2.07 (i.e. $X \dot{\sim} N(33.6, 4.28)$).

4.1.3.7 Normal Tables (Table 4.8)

Statistics texts and books of mathematical tables usually contain a table which gives the area under the standard normal curve to the right of a given value z, which is P{X>z} (=P X<-z}), so that one need not evaluate the integral $\int_{-\infty}^{z} f_x(t)dt$, to find the probabilities. Appendix B briefly discusses the relation between the integral and Table 4.8.

Example 1:

Find P{X<-1.93} if X~ N(0,1)

This probability is equivalent to P{X>1.93} = 0.0268 from Table 4.8.

Example 2 :

Find the number z such that $P\{X>z\} = .14345$. Looking in the body of the table, we find that we must interpolate between 1.06 and 1.07 to find z, since .14345 is halfway between 0.1423 and 0.1446.

$$z = \frac{1.06 + 1.07}{2} = 1.065$$

4.1.4 Hypothesis Testing (1, 3)

A common use of statistics is in testing whether a sample came from a particular distribution. We know that if X has a normal distribution, then

$$Z = \frac{X-\mu_X}{\sigma_X}$$

has a standard normal distribution. A theorem in statistics states that for a large sample (N>30) from any distribution, $\bar{X}$ will have an approximately normal distribution with mean $\mu_{\bar{x}} = \mu_X$ and variance $\sigma^2_{\bar{x}} = \sigma^2_X/N$. Using this information, we can test hypotheses about μ_X.

Example :

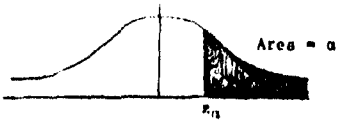
Choose a random sample of 100 observations from a population with $\mu_X = 300$ and $\sigma_X = 70$. Find the probability that $\bar{X}$, the sample mean, is 286 or less. We assume that $\bar{X}$ is normallly distributed, and so

$$Z = \frac{X - \mu_{\bar{x}}}{\sigma_{\bar{x}}} = \frac{X - \mu_X}{\sigma_X / \sqrt{N}}$$

has a standard normal distribution. In this example, $z = \frac{286-300}{70\sqrt{100}} = -2$

TABLE 4.8 AREAS UNDER STANDARDIZED NORMAL DENSITY FUNCTION (18)

Value of $\alpha = \int_{z_\alpha}^{\infty} \frac{1}{\sqrt{2\pi}} \exp(-z^2/2) = P(z > z_\alpha)$



z_α	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.5000	0.4960	0.4920	0.4880	0.4840	0.4801	0.4761	0.4721	0.4681	0.4641
0.1	0.4602	0.4562	0.4522	0.4483	0.4443	0.4404	0.4364	0.4325	0.4286	0.4247
0.2	0.4207	0.4168	0.4129	0.4090	0.4052	0.4013	0.3974	0.3936	0.3897	0.3859
0.3	0.3821	0.3783	0.3745	0.3707	0.3669	0.3632	0.3594	0.3557	0.3520	0.3483
0.4	0.3446	0.3409	0.3372	0.3336	0.3300	0.3264	0.3228	0.3192	0.3156	0.3121
0.5	0.3085	0.3050	0.3015	0.2981	0.2946	0.2912	0.2877	0.2843	0.2810	0.2776
0.6	0.2743	0.2709	0.2676	0.2643	0.2611	0.2578	0.2546	0.2514	0.2483	0.2451
0.7	0.2420	0.2389	0.2358	0.2327	0.2296	0.2266	0.2236	0.2206	0.2177	0.2148
0.8	0.2119	0.2090	0.2061	0.2033	0.2005	0.1977	0.1949	0.1922	0.1894	0.1867
0.9	0.1841	0.1814	0.1788	0.1762	0.1736	0.1711	0.1685	0.1660	0.1635	0.1611
1.0	0.1587	0.1562	0.1539	0.1515	0.1492	0.1469	0.1446	0.1423	0.1401	0.1379
1.1	0.1357	0.1335	0.1314	0.1292	0.1271	0.1251	0.1230	0.1210	0.1190	0.1170
1.2	0.1151	0.1131	0.1112	0.1093	0.1075	0.1056	0.1038	0.1020	0.1003	0.0985
1.3	0.0968	0.0951	0.0934	0.0918	0.0901	0.0885	0.0869	0.0853	0.0838	0.0823
1.4	0.0808	0.0793	0.0778	0.0764	0.0749	0.0735	0.0721	0.0708	0.0694	0.0681
1.5	0.0668	0.0665	0.0643	0.0630	0.0618	0.0606	0.0594	0.0582	0.0571	0.0559
1.6	0.0584	0.0537	0.0526	0.0516	0.0505	0.0495	0.0485	0.0475	0.0465	0.0455
1.7	0.0446	0.0436	0.0427	0.0418	0.0409	0.0401	0.0392	0.0384	0.0375	0.0367
1.8	0.0359	0.0351	0.0344	0.0336	0.0329	0.0322	0.0314	0.0307	0.0301	0.0294
1.9	0.0287	0.0281	0.0274	0.0268	0.0262	0.0256	0.0250	0.0244	0.0239	0.0233
2.0	0.0228	0.0222	0.0217	0.0212	0.0207	0.0202	0.0197	0.0192	0.0188	0.0183
2.1	0.0179	0.0174	0.0170	0.0166	0.0162	0.0158	0.0154	0.0150	0.0146	0.0143
2.2	0.0139	0.0136	0.0132	0.0129	0.0125	0.0122	0.0119	0.0116	0.0113	0.0110
2.3	0.0107	0.0104	0.0102	0.00990	0.00964	0.00939	0.00914	0.00889	0.00866	0.00842
2.4	0.00820	0.00798	0.00776	0.00755	0.00734	0.00714	0.00695	0.00676	0.00657	0.00639
2.5	0.00621	0.00604	0.00587	0.00570	0.00554	0.00539	0.00523	0.00508	0.00494	0.00480
2.6	0.00466	0.00453	0.00440	0.00427	0.00415	0.00402	0.00391	0.00379	0.00368	0.00357
2.7	0.00347	0.00336	0.00326	0.00317	0.00307	0.00298	0.00289	0.00280	0.00272	0.00264
2.8	0.00256	0.00248	0.00240	0.00233	0.00226	0.00219	0.00212	0.00205	0.00199	0.00193
2.9	0.00187	0.00181	0.00175	0.00169	0.00164	0.00159	0.00154	0.00149	0.00144	0.00139

Turning to a table of areas under the standard normal curve (Table 4.8), we find that the area to the left of -2 (which is the same as the area to the right of 2) is 0.0228, which is, then, the probability that $\bar{X}$ is less than or equal to 286 (written $P(X \leq 286) = 0.0228$). This means that if a large number of samples of size 100 are taken from this population, approximately 2.3% of them will have sample means of 286 or less.

If the population parameters (μ_x and σ_x^2) are unknown,we can use this method to make inferences about them. Suppose we know that $\sigma_x = 70$ and that the mean of a random sample ($\bar{X}$) with N=100 is 318. Can we reasonably assume that the population mean, μ_x, is 300?

We are testing to see if $\mu_x = 300$. We call this hypothesized value μ_o and the hypothesis that $\mu_x = \mu_o$ is called H_o (the null hypothesis). We write the null hypothesis:

$$H_o : \mu_x = \mu_o \quad \text{(in this case, } H_o : \mu_x = 300\text{)}$$

Our alternative is that $\mu_x \neq 300$. This is called the alternative hypothesis and is denoted $H_1 : \mu_x \neq \mu_o$.

$Z_{\alpha/2} = Z_{.025} = 1.96$ and so the critical region for the rejection of H_o is

$$\{z : z \leq -1.96 \text{ or } z \geq 1.96\}.$$

The test statistic we use is

$$z = \frac{\bar{X}-\mu_o}{\sigma_{\bar{X}}} = \frac{318-300}{70/\sqrt{100}} = 2.57.$$

In this case, $z = 2.57 > 1.96 = Z_{\alpha/2}$, and so we reject H_o and conclude that the distribution from which the sample was taken has a mean other than 300.

If both μ_x and σ_x are unknown, we can't use the z-statistic as above (since its calculation involves σ_x), and so we use the statistic

$$t = \frac{\bar{X}-\mu_o}{S_x/\sqrt{N}}$$

which has a Student's t-distribution.

Example:

If, in the above example, the standard deviation is unknown, but we find the sample standard deviation to be 70.5, then our test statistic is

$$t = \frac{318-300}{70.5/\sqrt{100}} = 2.55.$$

Using Table 4.9, which gives values of $t_{n;\alpha}$ (which is the number such that $P(t_n > t_{n;\alpha}) = \alpha$, where t_n has a Student's t-distribution with n degrees of freedom), we look under α=.025 (since we are using a two-tailed test at the .05 level of significance) and n=99. (The degrees of freedom, n, is just N-1). Since n=99 does not appear in the table, we take the number approximately 2/3 of the way between n=60 and n = 120. Our test statistic, t=2.55, is greater than that for n=60, and so we reject H_o: $\mu_x = 300$ in favor of H_1 : $\mu_x \neq 300$.

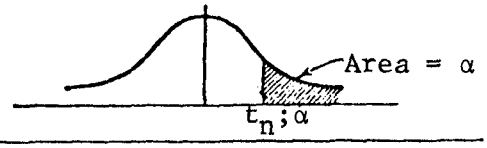
Example:

If we take a different sample (of size 121 this time) from the same population and compute a sample mean of 310 and a sample standard deviation 70.2, we find

$$t = \frac{\bar{x}-\mu_o}{S_x/\sqrt{N}} = \frac{310-300}{70.2/\sqrt{121}} = 1.56.$$

TABLE 4.9 PERCENTAGE POINTS OF STUDENT t-DISTRIBUTION (18)

Value of $t_n;a$ such that $P(t>t_n;\alpha)=\alpha$



	α				
n	0.10	0.050	0.025	0.010	0.005
1	3.078	6.314	12.706	31.821	63.657
2	1.886	2.920	4.303	6.965	9.925
3	1.638	2.353	3.182	4.541	5.841
4	1.533	2.132	2.776	3.747	4.604
5	1.476	2.015	2.571	3.365	4.032
6	1.440	1.943	2.447	3.143	3.707
7	1.415	1.895	2.365	2.998	3.499
8	1.397	1.860	2.306	2.896	3.355
9	1.383	1.833	2.262	2.821	3.250
10	1.372	1.812	2.228	2.764	3.169
11	1.363	1.796	2.201	2.718	3.106
12	1.356	1.782	2.179	2.681	3.055
13	1.350	1.771	2.160	2.650	3.012
14	1.345	1.761	2.145	2.624	2.977
15	1.341	1.753	2.131	2.602	2.947
16	1.337	1.746	2.120	2.583	2.921
17	1.333	1.740	2.110	2.567	2.898
18	1.330	1.734	2.101	2.552	2.878
19	1.328	1.729	2.093	2.539	2.861
20	1.325	1.725	2.086	2.528	2.845
21	1.323	1.721	2.080	2.518	2.831
22	1.321	1.717	2.074	2.508	2.819
23	1.319	1.714	2.069	2.500	2.807
24	1.318	1.711	2.064	2.492	2.797
25	1.316	1.708	2.060	2.485	2.787
26	1.315	1.706	2.056	2.479	2.779
27	1.314	1.703	2.052	2.473	2.771
28	1.313	1.701	2.048	2.467	2.763
29	1.311	1.699	2.045	2.462	2.756
30	1.310	1.697	2.042	2.457	2.750
40	1.303	1.684	2.021	2.423	2.704
60	1.296	1.671	2.000	2.390	2.660
120	1.289	1.658	1.980	2.358	2.617

α = 0.995, 0.990, 0.975, 0.950, and 0.900 follow from $t_n;1-\alpha = -t_n;\alpha$

Looking in Table 4.9 for $\alpha=.025$ and $n=N-1=120$, we find that $t_{120;.025} = 1.980$, and so our test statistic does not fall in the critical region. Therefore, we cannot reject H_o.

4.1.5 Confidence Intervals

4.1.5.1 Confidence Intervals for the Mean (1, 3)

In the example above, we tested a hypothesis about the population mean. In a similar way we could construct an interval within which we would consider a hypothesis for the mean tenable and outside of which such a hypothesis would be untenable. We call this interval a confidence interval and its end-points confidence limits.

In the previous example, a population mean of 300 was found to be consistent with the computed statistics. Suppose we tested $H_o:\mu_x=295$ against $H_1:\mu_x\neq295$. Then

$$t = \frac{\bar{x} - \mu_o}{s_x/\sqrt{N}} = 2.35$$

which is greater than $t_{120;.025} = 1.980$, and so we reject H_o in favor of H_1. Somewhere between 295 and 300 is a mean such that the computed t is equal to $t_{n;\alpha}$, and this number is the lower confidence limit for the population mean. Likewise, if we test $H_o:\mu_x=322$ against $H_1:\mu_x\neq322$, $t = -1.88$, which is greater than $-t_{120;.025}$, and so H_o is acceptable. But a test of $H_o:\mu_x=323$ yields $t=-2.03<-1.98$ and so we reject H_o. Therefore, the upper confidence limit is between 322 and 323. The actual confidence limits for μ_x can be computed from

$$t_{N-1,\alpha/2} = \frac{\bar{x}-\mu_x}{s_x/\sqrt{N}} \text{ and } -t_{N-1;\alpha/2} = \frac{\bar{x}-\mu_x}{s_x/\sqrt{N}}$$

which, in this example yield

$$\mu_L = -(t_{120;.025} \times \frac{S_x}{\sqrt{N}} - \bar{x}) = -(1.98 \times \frac{70.2}{\sqrt{121}} - 310) = 297.4$$

and $$\mu_U = -(-1.98 \times \frac{70.2}{\sqrt{121}} - 310) = 322.6.$$

Since $\alpha = .05$ (and so $1-\alpha = .95$), the probability that this interval contains μ_x is .95, and so it is called a 95% confidence interval for μ_x. (If $\alpha = .01$, we construct a 99% confidence interval). Without going through the above deviation, the confidence limits can be computed using the following formulas:

$$\mu_U = \bar{x} + \frac{S_x}{\sqrt{N}} \quad (t_{N-1;\alpha/2})$$

$$\mu_L = \bar{x} - \frac{S_x}{\sqrt{N}} \quad (t_{N-1;\alpha/2})$$

4.1.5.2 Confidence Interval for the Variance

4.1.5.2.1 Confidence Interval for σ_x^2 if μ_x is known

If X has a normal distribution, then

$$\frac{X-\mu_x}{\sigma_x}$$

has a standard normal distribution. If $X_1, X_2, \ldots, X_N$ all have a normal distribution with the same mean μ and the same variance σ^2, then

$$Y = \sum_{i=1}^{N} \frac{(X_i-\mu)^2}{\sigma^2}$$

has a χ^2_n distribution (i.e. a chi-square distribution with n degrees of freedom).

Using a chi-square table (Table 4.10), we can construct a 95% confidence interval for σ^2 as follows:

Find $\chi^2_{N;\alpha/2}$, which is the number that

$$P\left(Y<\chi^2_{N;\alpha/2}\right) = \alpha/2 = .025, \text{ for } \alpha = .05.$$

Also find

$$\chi^2_{N;1-\alpha/2} = \chi^2_{N;.975}.$$

Now $P\left(\chi^2_{N;\alpha/2}<Y<\chi^2_{N;1-\alpha/2}\right) = .975 - .025 = .95$, and so the numbers $\chi^2_{N;\alpha/2}$ and $\chi^2_{N;1-\alpha/2}$ are 95% confidence limits for Y.

Since

$$Y = \sum_{i=i}^{N} \frac{(X_i-\mu)^2}{\sigma^2}, \quad P\left(X^2_{N;.025} < \sum_{i=i}^{N} \frac{(X_i-\mu)^2}{\sigma^2} < X^2_{N;.975}\right) = .95,$$

which can be written as

$$P\left(\frac{1}{\chi^2_{N;.025}} \times \sum_{i=1}^{N} (X_i-\mu)^2 > \sigma^2 > \frac{1}{\chi^2_{N;.975}} \sum_{i=1}^{N} (X_i-\mu)^2\right) = .95, \text{ and so}$$

we have a 95% confidence interval for σ^2.

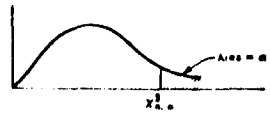
Example:

Suppose we have 10 observations from a normal distribution with mean 0 (i.e. N=10, μ_x=0). Then $(X_i-\mu_x)^2=(X_i-0)^2=X_i^2$ and so

$$\sum_{i=i}^{10} (X_i-\mu_x)^2 = \sum_{i=i}^{10} X_i^2. \quad \text{Let this sum be equal to 113.45.}$$

Table 4.10 PERCENTAGE POINTS OF CHI-SQUARE DISTRIBUTION (18)

Value of $\chi^2_{n,\alpha}$ such that Prob$[\chi_n^2 > \chi^2_{n,\alpha}] = \alpha$



	α									
n	0.995	0.990	0.975	0.950	0.900	0.10	0.05	0.025	0.010	0.005
1	0.000039	0.00016	0.00098	0.0039	0.0158	2.71	3.84	5.02	6.63	7.88
2	0.0100	0.0201	0.0506	0.103	0.211	4.61	5.99	7.38	9.21	10.60
3	0.0717	0.115	0.216	0.352	0.584	6.25	7.81	9.35	11.34	12.84
4	0.207	0.297	0.484	0.711	1.06	7.78	9.49	11.14	13.28	14.86
5	0.412	0.554	0.831	1.15	1.61	9.24	11.07	12.83	15.09	16.75
6	0.676	0.872	1.24	1.64	2.20	10.64	12.59	14.45	16.81	18.55
7	0.989	1.24	1.69	2.17	2.83	12.02	14.07	16.01	18.48	20.28
8	1.34	1.65	2.18	2.73	3.49	13.36	15.51	17.53	20.09	21.96
9	1.73	2.09	2.70	3.33	4.17	14.68	16.92	19.02	21.67	23.59
10	2.16	2.56	3.25	3.94	4.87	15.99	18.31	20.48	23.21	25.19
11	2.60	3.05	3.82	4.57	5.58	17.28	19.68	21.92	24.73	26.76
12	3.07	3.57	4.40	5.23	6.30	18.55	21.03	23.34	26.22	28.30
13	3.57	4.31	5.01	5.89	7.04	19.81	22.36	24.74	27.69	29.82
14	4.07	4.66	5.63	6.57	7.79	21.06	23.68	26.12	29.14	31.32
15	4.60	5.23	6.26	7.26	8.55	22.31	25.00	27.49	30.58	32.80
16	5.14	5.81	6.91	7.96	9.31	23.54	26.30	28.85	32.00	34.27
17	5.70	6.41	7.56	8.67	10.08	24.77	27.59	30.19	33.41	35.72
18	6.26	7.01	8.23	9.39	10.86	25.99	28.87	31.53	34.81	37.16
19	6.84	7.63	8.91	10.12	11.65	27.20	30.14	32.85	36.19	38.58
20	7.43	8.26	9.59	10.85	12.44	28.41	31.41	34.17	37.57	40.00
21	8.03	8.90	10.28	11.59	13.24	29.62	32.67	35.48	38.93	41.40
22	8.64	9.54	10.98	12.34	14.04	30.81	33.92	36.78	40.29	42.80
23	9.26	10.20	11.69	13.09	14.85	32.01	35.17	38.08	41.64	44.18
24	9.89	10.86	12.40	13.85	15.66	33.20	36.42	39.36	42.98	45.56
25	10.52	11.52	13.12	14.61	16.47	34.38	37.65	40.65	44.31	46.93
26	11.16	12.20	13.84	15.38	17.29	35.56	38.88	41.92	45.64	48.29
27	11.81	12.88	14.57	16.15	18.11	36.74	40.11	43.19	46.96	49.64
28	12.46	13.56	15.31	16.93	18.94	37.92	41.34	44.46	48.28	50.99
29	13.12	14.26	16.05	17.71	19.77	39.09	42.56	45.72	49.59	52.34
30	13.79	14.95	16.79	18.49	20.60	40.26	43.77	46.98	50.89	53.67
40	20.71	22.16	24.43	26.51	29.05	51.81	55.76	59.34	63.69	66.77
60	35.53	37.48	40.48	43.19	46.46	74.40	79.08	83.30	88.38	91.95
120	83.85	86.92	91.58	95.70	100.62	140.23	146.57	152.21	158.95	163.65

For $n > 120$, $\chi^2_{n;\alpha} \approx n\left[1 - \frac{2}{9n} + \varepsilon_\alpha\sqrt{\frac{2}{9n}}\right]^3$ where ε_α is the desired percentage point for a standardized normal distribution.

A 95% confidence interval ($\alpha/2 = .025$) for σ^2 is then

$$\left(\frac{113.45}{20.48}, \frac{113.45}{3.25}\right) = (5.5, 34.9).$$

4.1.5.2.2 Confidence Interval for σ_x^2 if μ_x is Unknown

It is also true (by the definition of S_x^2) that

$$\frac{NS_x^2}{\sigma_x^2}$$

has a chi-square distribution with N-1 degrees of freedom (X^2_{N-1}) and so if μ_x is unknown, we can find a confidence interval using S_x^2, the sample variance.

Suppose in the above example, $S_x = 3.6$. We turn to Table 4.10 again and find $X^2_{9;\ .025}$ and $X^2_{9;\ .975}$, which are 2.70 and 9.02, and so the interval is

$$\frac{NS_x^2}{X^2_{9;.975}}, \quad \frac{NS_x^2}{X^2_{9;.025}} = \left(\frac{9x12.96}{19.02}, \frac{9x12.96}{2.70}\right) = (6.1, 43.2).$$

The confidence limits for the standard deviation are found by taking the square root of those for the variance.

4.1.5.3 Relative Error of the Standard Deviation

$$\frac{\Omega}{S_x} = \sqrt{N}\left((X^2_{N-1;1-\alpha/2})^{-\frac{1}{2}} - (X^2_{N-1;\alpha/2})^{-\frac{1}{2}}\right)$$

where Ω is the width of the confidence interval of the standard deviation

$X^2_{N-1;1-\alpha/2}$ is defined above

$(1-\alpha)$ x 100% is the level of confidence of the interval.

4.2 DETERMINATION OF NUMBER OF SAMPLES (6)

The number of samples necessary to reasonably characterize a water or wastewater is determined after collecting some background data on the concentration and variance of the concentration of the parameters under consideration. These values can be estimated; however, estimation will decrease the confidence in the results. Two techniques can be used to calculate the number of samples, one based on the allowed sample variability, the other on the accuracy of the sample mean. Each will give a desired value of N, the number of samples needed, with the larger value to be chosen for application.

4.2.1 Determining Number of Samples from a Constraint on the Variability

To apply this method, the following information is needed:

1. Allowable error of the standard deviation $(\frac{\Omega}{S_x})$
2. Confidence level required $(1-\alpha)$

Therefore, for this situation, one is estimating that the value of a certain variable will occur within a specific interval. A normal distribution of the data around the mean is assumed. The data should be checked for normality as in Section 4.1.3.1.

Example:

Determine the number of samples required from a wastewater monitoring program such that the estimated standard deviation will be within 25% of its true value (i.e. ± 12.5%) at a confidence level of 98%.

Here $\alpha = 1-.98=.02$ and $\frac{\Omega}{S_x} = 0.25$. From Figure 4.9, the value of $\frac{\Omega}{S_x} = 0.25$ is found on the vertical axis and a horizontal line is followed until the curve for $\alpha = .02$ is met. Then a vertical line is dropped to the horizontal axis to find the number of observations needed (N=180 in this case).

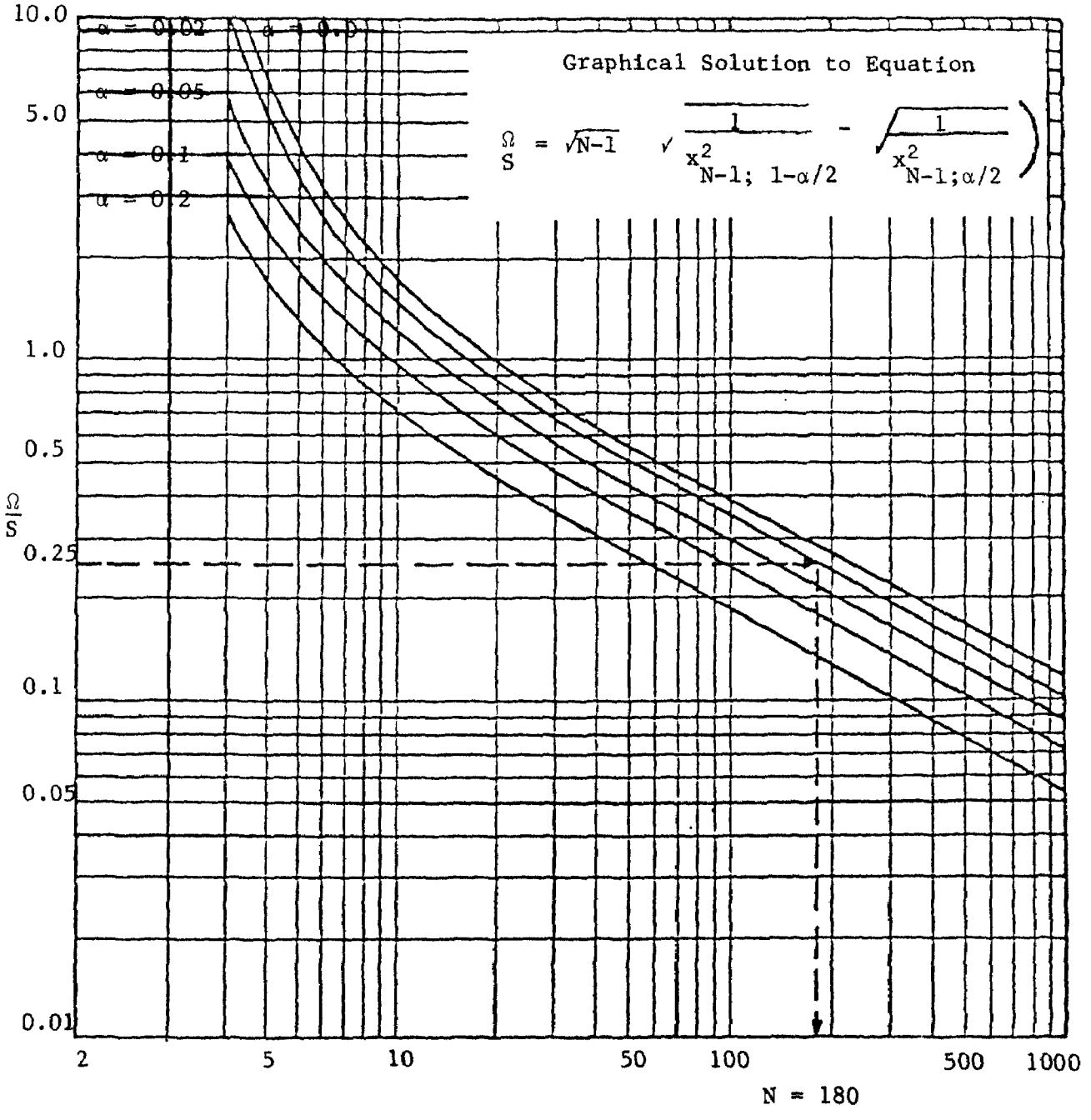


Figure 4.9 Determination of the number of samples based on the required accuracy of extreme values

4.2.2 Determining Number of Samples from a Constraint on the Mean Value

To apply this method, the following information is required:

1. Confidence level required (1-α)
2. Coefficient of variation of the source to be sampled ($CV = \frac{S_x}{\bar{X}}$)
3. The required accuracy of the sample mean.

A double iteration procedure is recommended, especially if the number of samples is found to be small (N<30). For this calculation a normal distribution is assumed.

The first iteration uses the formula

$$N = \left(\frac{CV \times Z_{\alpha/2}}{\beta/100}\right)^2$$

where

$$CV = \frac{S_x}{\bar{X}}$$

β is the allowed deviation of the sample mean from the true mean, expressed as a percent of the true mean.

$Z_{\alpha/2}$ is found in Table 4.8.

For the second iteration use

$$N = \left(\frac{CV \times t_{\alpha/2;N-1}}{\beta/100}\right)$$

where $t_{\alpha/2;N-1}$ is found in Table 4.9.

Example:

For a wastewater stream with an average daily concentration of 120 mg/l BOD and a standard deviation of 32 mg/l, determine the number of daily samples which would provide an accuracy of the daily averages within 5%.

$\beta = 5$

$\bar{X} = 120$

$S_x = 32$

$CV = \frac{S_x}{\bar{X}} = \frac{32}{120} = 0.27$

If we choose $\alpha = .05$ (95% confidence level), then $Z_{\alpha/2} = Z_{.025}$ is found in Table 4.8 to be 1.96.

Step 1 $\quad N = \left(\frac{0.27 \times 1.96}{5/100}\right)^2 = 109.3 \doteq 110$ samples

Step 2 Using N=110, find $t_{\alpha/2;N-1} = t_{.025;109}$ in Table 4.9 to be approximately 1.983 (using linear interpolation), so $N = \left(\frac{0.27 \times 1.983}{5/100}\right)^2 = 114.6 = 115$ samples.

If the accuracies of both the standard deviation and the mean are used as criteria, choose the larger of the two values of N. In the example above, $N_S = 180$ and $N_{\bar{X}} = 115$, so 180 daily samples should be taken.

4.3 DETERMINING SAMPLE FREQUENCY

Although it requires the use of a digital computer, spectral analysis is the method that should be used for determining sampling frequency because of its accuracy and the simplicity of the final interpretation.

4.3.1 Determination of the Sampling Frequency from Power Spectra (7,8,9,10)

It is imperative that a good set of historical data be available for analysis. Ideally, these data should be continuous. Practically, they should be taken at a frequency that is higher than the highest expected frequency of

harmonic variation components of the record. For example, if daily trends are to be analyzed, hourly samples may be called for. At any rate, the length and sampling interval of the record should satisfy the rules of thumb governing spectral analysis (cf. Section 4.1.2.2). Ideally, in a discrete record, there should be no missing points. Interpolation may be used if a few data points are missing, when these are widely scattered on the record. Interpolated data should account for no more than five percent of the total data.

The following examples illustrate the use of spectral analysis in the determination of sampling frequency.

Example 1: The wastewater influent for the city of Racine, Wisconsin, was sampled hourly in the summer of 1974 and TOC analyzed. The record is shown in Figure 4.10. The average and variance were calculated to be 70.56 mg/ℓ and 1262.07 mg^2/ℓ^2 respectively. Determine the optimal sampling frequency for this plant.

The power spectrum corresponding to the record of Figure 4.10 is obtained as depicted in Figure 4.11. This power spectrum exhibits a significant peak at the 1/24 hr frequency and a less significant peak at 1/8 hr. Most of the variability on the data occurs in the frequency band from 1/48 hr to 1/16 hr. Since the last significant peak in the spectrum occurs at the 1/8 hr frequency, the sampling frequency which should be at least two times the frequency of the last significant peak, corresponding to the Nyquist frequency, should be at least 1/4 hr. In order to clearly show the 1/8 hr variability a sampling interval of 3 hrs. or even 2 hrs. is recommended in accordance with the second rule of thumb. Note that this example, the first rule of thumb stated in Section 4.1.2.2 is violated as the length of the record in Figure 4.10 (7 days) is less than 10 times the longest period of interest

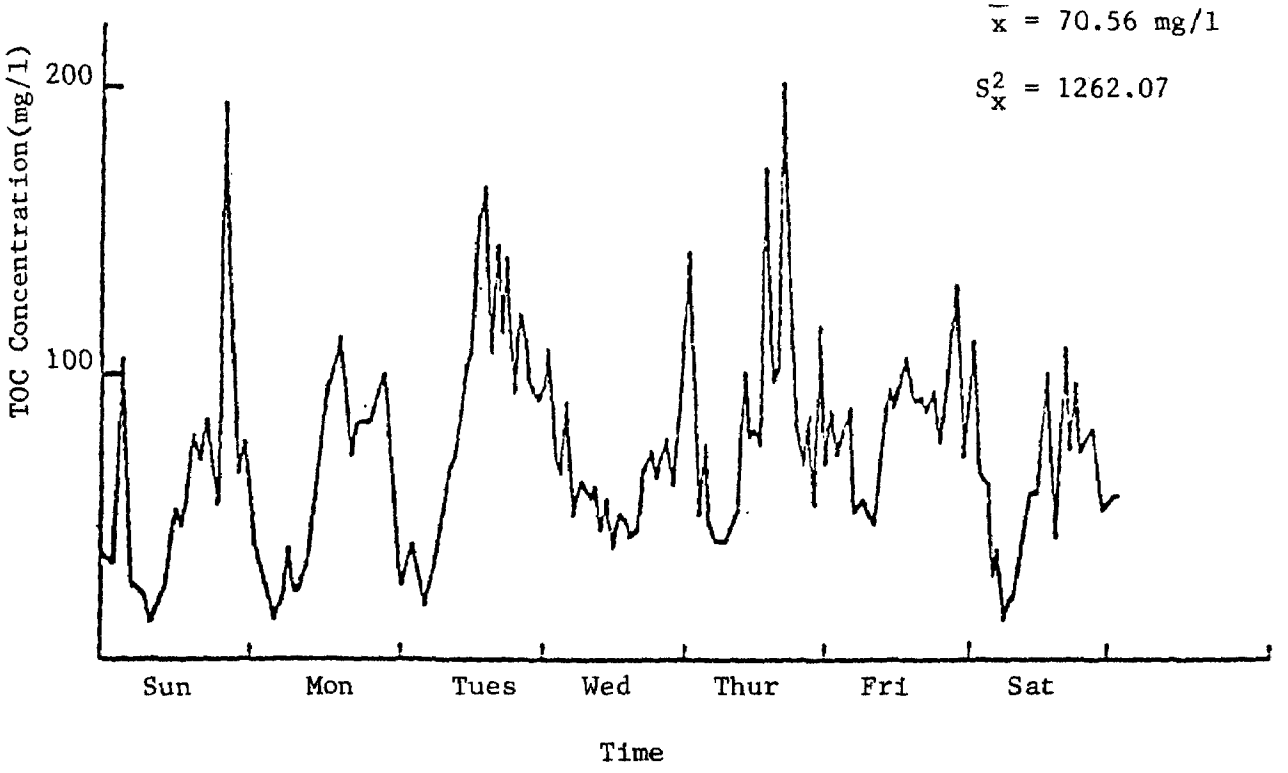


Figure 4.10 Time record of TOC of municipal wastewater at Racine, Wisconsin

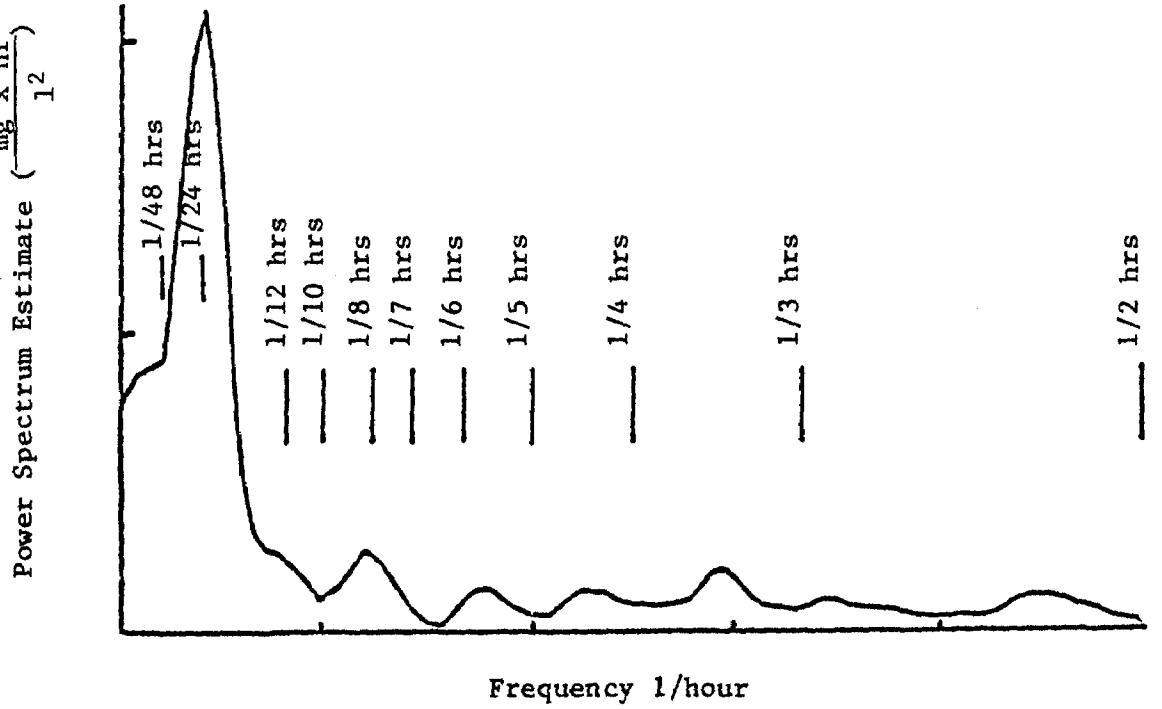


Figure 4.11 Power spectrum of TOC concentration of municipal wastewater at Racine, Wisconsin

(1 day). However the peak at the 1/24 hr frequency is so significant that it cannot be explained by aliasing distortion alone.

Example 2: The power spectra of wastewater variation corresponding to two typical types of industrial discharges are shown in Figures 4.12 and 4.13. Determine the optimal sampling frequency.

The spectrum of Figure 4.12 exhibits two strong peaks in the frequency band from 1/16 hr to 1/5 hr. This spectrum is typical for industrial plants working 24 hours a day, seven days a week, with three shifts a day. Note the absence of peaks on the low frequency region reflecting the absence of trend in the record which would then appear to be stationary. Inasmuch as the last significant peak occurs between the 1/6 hr and 1/5 hr frequency, a sampling frequency of 1/2 hr is recommended (i.e. 2 x 1/4 hr).

The spectrum of Figure 4.13 displays a strong peak at the 1/24 hr frequency and less significant peaks at the 1/12 hr and 1/6 hr frequencies. This spectrum is typical for industrial plants working with one daily shift. Here again, the absence of peaks in the low frequency region of the spectrum is an indication of the stationariness of the record. In order to clearly exhibit the 1/6 hr frequency component of the data a sampling interval of 2 hours is recommended in accordance with the second rule of thumb.

4.4 DETERMINATION OF PARAMETERS TO MONITOR

The decision as to which parameters to monitor is critical, since it is not possible to monitor all parameters. There are two statistical methods to help with this decision if prior regulations do not exist. The decision variable for the first method is the probability of exceeding a standard and the second is the correlation between parameters.

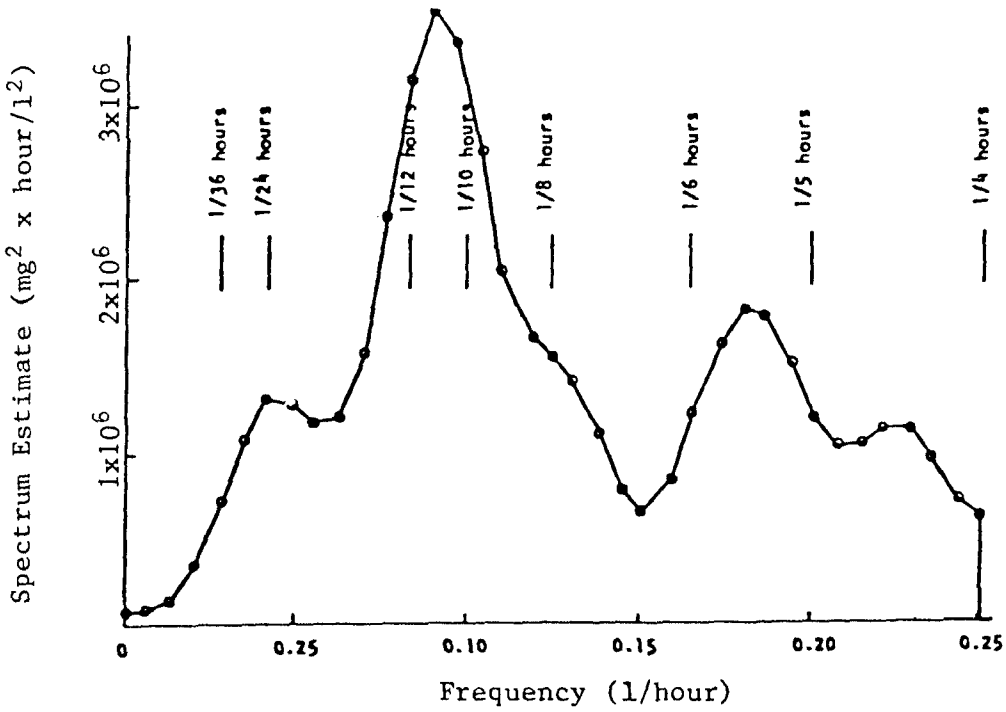


Figure 4.12 Power spectrum of industrial plant discharge, Case 1

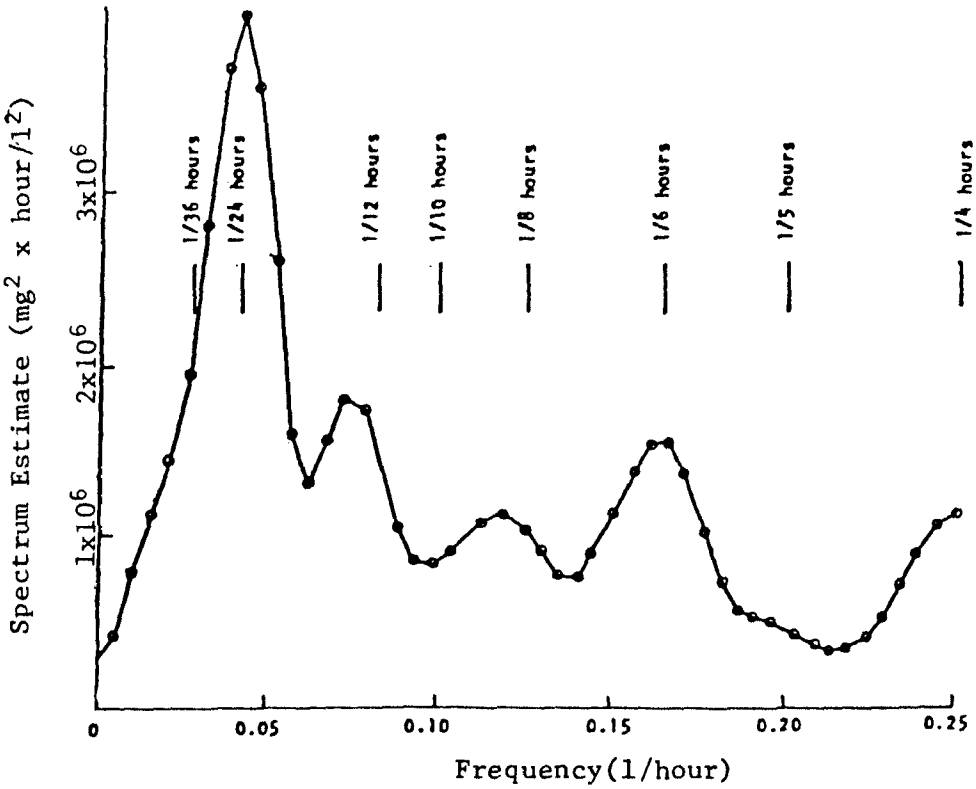


Figure 4.13 Power spectrum of industrial plant discharge, Case 2

4.4.1 Probability of Exceeding a Standard

This method requires knowledge of:

1. The mean, μ, or sample mean, $\bar{X}$,
2. The standard deviation, σ, or sample S.D., S_x,
3. The standard, X_s, not to be exceeded for that parameter.

The probability of exceeding the standard is:

$$P(X > X_s) = P(Z > Z_\alpha) = \alpha$$

where $Z_\alpha = \frac{X_s - \bar{X}}{S_x}$.

After computing Z_α, the probability, α, can be found in Table 4.8. Parameters with the largest value of α have the highest sampling priority.

Example 1:

The effluent standard for an industry was determined to be 100 mg/l of Cl^-. A wastewater quality survey has shown that the mean concentration of chlorides was 75 mg/l and the S.D. was 18 mg/l.

To determine the probability of the standard being exceeded:

1. Determine $Z_\alpha = \frac{X_s - \bar{X}}{S_x} = \frac{100 - 75}{18} = 1.39$
2. Find α from Table 4.8 such that $Z_\alpha = 1.39$. The value is .0823, or 8.23%.

Often effluent standards will be specified for several parameters. Then the parameters can be ranked in descending order of their probability of exceeding the standard. The priority of sampling will be in the same order. Table 4.11 is an example of how this is done.

Example 2:

The standard for another parameter is 4 parts per million. The average in the past was found to be 7ppm, with a S.D. of 2 ppm.

Here $X_s = 4$

$\bar{X} = 7$

$S_x = 2$

and so $$Z_\alpha = \frac{X_s - \bar{X}}{S_x} = \frac{4 - 7}{2} = -1.5$$

Because of symmetry, $P(Z < -Z_\alpha) = P(Z > Z_\alpha)$, and so, since $Z_\alpha = -1.5$ in this case, we look up +1.5 in the table, finding $\alpha = .0668$. Since we want $P(Z>-Z_\alpha)$, we use the fact that $P(Z>-Z_\alpha) = 1-P(Z<-Z_\alpha) = 1-\alpha$. So the probability of exceeding the standard is $1-\alpha = 1-.0668 = .9332$, or about 93.3%.

4.4.2 Correlation Between Measured Parameters (11)

Ideally, all important water quality parameters should be monitored, but this is usually not economically feasible, so a method is needed for deciding which parameters to omit. This is done by checking the closeness of correlation among parameters of interest. It is known that a correlation exists between many water quality parameters such as

BOD_5 and TOC

COD and TOC

Chlorides and Conductivity

Total Dissolved Solids and Conductivity

Suspended Solids and Turbidity

Acidity, Alkalinity and pH

Hardness, Calcium and Magnesium

Hardness and Alkalinity

If a strong correlation exists between two or more parameters, the monitoring of one parameter may be discontinued or monitored at a reduced frequency.

In order to apply the technique, the following must be available:

1. A data record for all parameters of interest

2. A computer program for calculating correlation coefficients.

The relationship between two parameters X and Y can be linear or non-linear (such as exponential, logarithmic, etc.). If a non-linear relationship exists, attempt to linearize the relationship, e.g. by using logarithms of the values of X and Y, or some other functional approximation. Then linear regression analysis provides a linear approximation of the form $\hat{Y} = a+b\hat{X}$. The coefficient of correlation, R_{XY}, will then be a measure of the closeness of fit. The coefficient of correlation is determined from the equation

$$R_{XY} = \frac{\sum_{i=1}^{N} (X_i-\bar{X})\ (Y_i-\bar{Y})}{\left[\sum_{i=1}^{N} (X_i-\bar{X})^2 \sum_{i=1}^{N} (Y_i-\bar{Y})^2\right]}$$

Numerous computer package subroutines are available for the above analysis.

The hypothesis that a relationship exists between X and Y can be tested at a given level of significance α (where $1-\alpha$ is the confidence that the hypothesis is true). If the obtained coefficient of correlation is such that $|R_{XY}| > R_c$, where R_c is the minimal correlation coefficient, which can be found in Table 4.12, the null hypothesis (that the correlation is zero) is rejected.

If a pair of parameters has a correlation coefficient significantly greater than the value from the table, one parameter in the pair is eligible for elimination from or reduction of monitoring. The decision on which

parameter should be eliminated will be based on the cost of data acquisition and the priority of the parameter.

Example:

A wastewater system was surveyed for an extended period of time. As a result of the survey, 25 sets of wastewater quality data were gathered. Each set contained data on pH, TOC, COD, BOD, TKN, phosphorus, conductivity, total dissolved solids, suspended solids, turbidity, lead, mercury, iron, copper, alkalinity, acidity, hardness, calcium, magnesium, coliform bacteria, fecal coliform and chlorides.

1. Determine the sampling priority of each parameter.
2. Determine which parameter measurements can be eliminated or reduced.

First we find the probability that a parameter will exceed its standard. This will determine the sampling priority of the standard.

The correlation analysis of the 22 parameters in Table 4.11 was performed by a computer, using the formula given previously. From Table 4.12, it was determined that

$$R_c = \begin{cases} 0.388 \text{ for } \alpha = .05 \\ 0.496 \text{ for } \alpha = .01. \end{cases}$$

Table 4.13 shows the results of the analysis.

Sampling for total dissolved solids (TDS) has the highest priority, but, because of the high correlation between TDS and conductivity, one of these analyses can be eliminated. Total coliforms have the second highest priority, but since the correlation between total and fecal coliforms is high, analyzing for fecal coliforms is not necessary. The high correlation among BOD, COD and TOC makes it possible to eliminate or reduce one or two of them.

TABLE 4.11 SAMPLING PRIORITIES OF PARAMETERS FOR A TYPICAL WASTEWATER

Parameter	Water Quality Standard, X_S	Mean, $\bar{X}$	Standard Deviation, S	Z	$P(X > X_S)$	Sampling Priority
pH	6.5 - 8.0	7.8	0.4	0.50	0.308	5
TOC	None	31	7.9	-	0	16 - 22
COD	70	60	11	0.91	0.181	7
BOD	30	20	8	1.25	0.125	9 - 10
TKN	5	3.5	1.5	1.00	0.158	8
Phosphates	1	0.5	0.2	2.50	0.006	15
Conductivity	None	320	80	-	0	16 - 22
Total dissolved solids	500	491	125	0.072	0.472	1
Suspended Solids	30	28	5	0.40	0.34	4
Turbidity	20	19	3	0.33	0.37	3
Lead	5	3	1.0	2.0	0.0228	14
Mercury	5	2.5	1.5	1.67	0.047	13
Iron	10	7.8	1.9	1.16	0.123	11
Copper	7	0.8	0.15	1.33	0.0918	12
Alkalinity	None	-	-	-	0	16 - 22
Acidity	None	-	-	-	0	16 - 22
Calcium	None	-	-	-	0	16 - 22
Hardness	None	-	-	-	0	16 - 22
Magnesium	None	-	-	-	0	16 - 22
Total coliforms	100	81	65	0.29	0.386	2
Fecal coliforms	10	5	64	1.25	0.125	9 - 10
Chlorides	200	156	59	0.90	0.134	6

TABLE 4.12 VALUES OF CORRELATION COEFFICIENT, p, FOR TWO LEVELS OF SIGNIFICANCE (12)

Degrees of Freedom	Percent Level of Significance, α	
n = N - 1	Five	One
1	0.997	1.000
2	0.950	0.990
3	0.878	0.959
4	0.811	0.917
5	0.754	0.874
6	0.707	0.834
7	0.666	0.798
8	0.632	0.765
9	0.602	0.735
10	0.576	0.708
11	0.553	0.684
12	0.532	0.661
13	0.514	0.641
14	0.497	0.623
15	0.482	0.606
16	0.468	0.590
17	0.456	0.575
18	0.444	0.561
19	0.433	0.549
20	0.423	0.537
21	0.413	0.526
22	0.404	0.515
23	0.396	0.505
24	0.388	0.496
25	0.381	0.487
30	0.349	0.449
35	0.325	0.418
40	0.304	0.393
45	0.288	0.372
50	0.273	0.354
60	0.250	0.325
70	0.232	0.302
80	0.217	0.283
90	0.205	0.267
100	0.195	0.254
125	0.174	0.228
150	0.159	0.208
200	0.138	0.181
300	0.113	0.148
400	0.098	0.128
500	0.088	0.115

TABLE 4.13 MATRIX OF CORRELATION COEFFICENTS

Parameter	pH	TOC	COD	BOD_5	TKN	P	Cond	TDS	SS	T	Pb	Hg	Fe	Cu	Alk	Ac	Ca	Hard	Mg	Tc	FC	Cl
pH	—																					
TOC	0	—																				
COD	0	0.8	—																			
BOD_5	0	0.68	0.63	—																		
TKN	0	0	0.15	0.18	—																	
Phosp	0	0	0.18	0.21	0.69	—																
Conduct	0	0.30	0.41	0.35	0.33	0.17	—															
TDS	0	0.25	0.35	0.48	0.41	0.20	0.91	—														
SS	0	0.25	0.40	0.38	0.25	0.75	0.10	0.18	--													
Turb	0	0.4	0.51	0.33	0.18	0.68	0.18	0.59	0.89	—												
Pb	0.18	0	0	0	0	0	0.28	0.31	0.18	0.15	—											
Hg	0	0	0	0	0	0	0.30	0.23	0.25	0.31	0.70	—										
Fe	0.1	0	0	0	0	0	0.41	0.39	0.58	0.61	0.18	0.23	--									
Cu	0	0	0	0	0	0	0.30	0.25	0.31	0.25	0.69	0.59	0.41	—								
Alk	0.6	0	0	0	0	0	0.38	0.41	0	0	0	0	0	0	—							
Acid	0.6	0	0	0	0	0	0.20	0.15	0	0	0	0	0	0	0.49	—						
Ca	0	0	0	0	0	0	0.31	0.35	0	0	0	0	0	0	0.65	0	—					
Hard	0.1	0	0	0	0	0	0.61	0.68	0	0	0	0	0	0	0.61	0.18	0.88	--				
Mg	0	0	0	0	0	0	0.40	0.31	0	0	0	0	0	0	0.18	0	0.35	0.18	--			
T. Coll	0	0.31	0.35	0.38	0	0	0	0	0.12	0.11	0	0	0	0	0	0	0	0	0	--		
F. Coll	0	0.10	0.18	0.21	0	0	0	0	0.11	0.08	0	0	0	0	0	0	0	0	0	0.79	—	
Chlor	0	0	0	0	0	0	0.58	0.88	0	0	0	0	0	0	0	0	0	0	0	0	0	—

0 = no engineering relevance; assumed no relation.

Testing for turbidity could also replace that for suspended solids. It is also possible to eliminate at least one analysis from the group hardness, coliform and alkalinity. Metals have relatively low priority and so at least one of them can be reduced. Thus, the following streamlined program is feasible:

Parameter	Priority of Sampling
pH	high
TOC or COD	high
BOD	reduced
TKN	high
Phosphates	reduced
Conductivity	high
Suspended Solids or Turbidity	high
Lead	reduced or not necessary
Mercury	reduced or not necessary
Iron	reduced
Copper	reduced or not necessary
Alkalinity	reduced
Hardness	reduced
Total Coliforms	high
Fecal Coliforms	reduced or not necessary

4.5 IN-PLANT SAMPLING AND NETWORK MONITORING

If the sampling locations have not been predetermined, there are systematic methods of determining the location of sampling points. However,

these methods are only tools to aid sampling personnel and do not replace professional judgment and experience.

4.5.1 Segmentation - Priority Technique

This technique can be applied to any large flowing network including an industrial plant collection system, a municipal sewerage system, or even a watershed network. To apply this technique the following information must be known:

1. The mass flow rate of the parameter of interest, $(Q_{wj}\ C_{wj})$.
2. The range of variation of the parameter input,

   $\rho_j = (Q_{wj}\ C_{wj})\ \max - (Q_{wj}\ C_{wj})\ \min.$
3. The approximate frequency of the fluctuations.
4. Values for the reduction in variation through each segment, α_{AB}.

Segmentation of the system is done by first isolating the locations which modify the waste stream condition, e.g. junctions of wastewater treatment units, overflows, stormwater inflow, sidestreams, or lateral sewers. An example of a municipal wastewater system segmentation is shown in Figure 4.14. The system has 16 segments, 12 inside the waste system and 4 on the receiving water body. In an ideal situation, sampling stations can be located in all segments of the system. With a limited budget, however, the number of sampling points will be limited. Therefore, there is a necessity for a measure to establish priorities of sampling for each segment. The measure can be the correlation coefficient between the segments. If a high correlation exists for the measured parameter between two segments, one can rely on measurement of the parameter in only one segment and sampling of the other segment is not necessary. Unlike the large river monitoring systems, wastewater systems have at least one fixed location of a monitoring point,

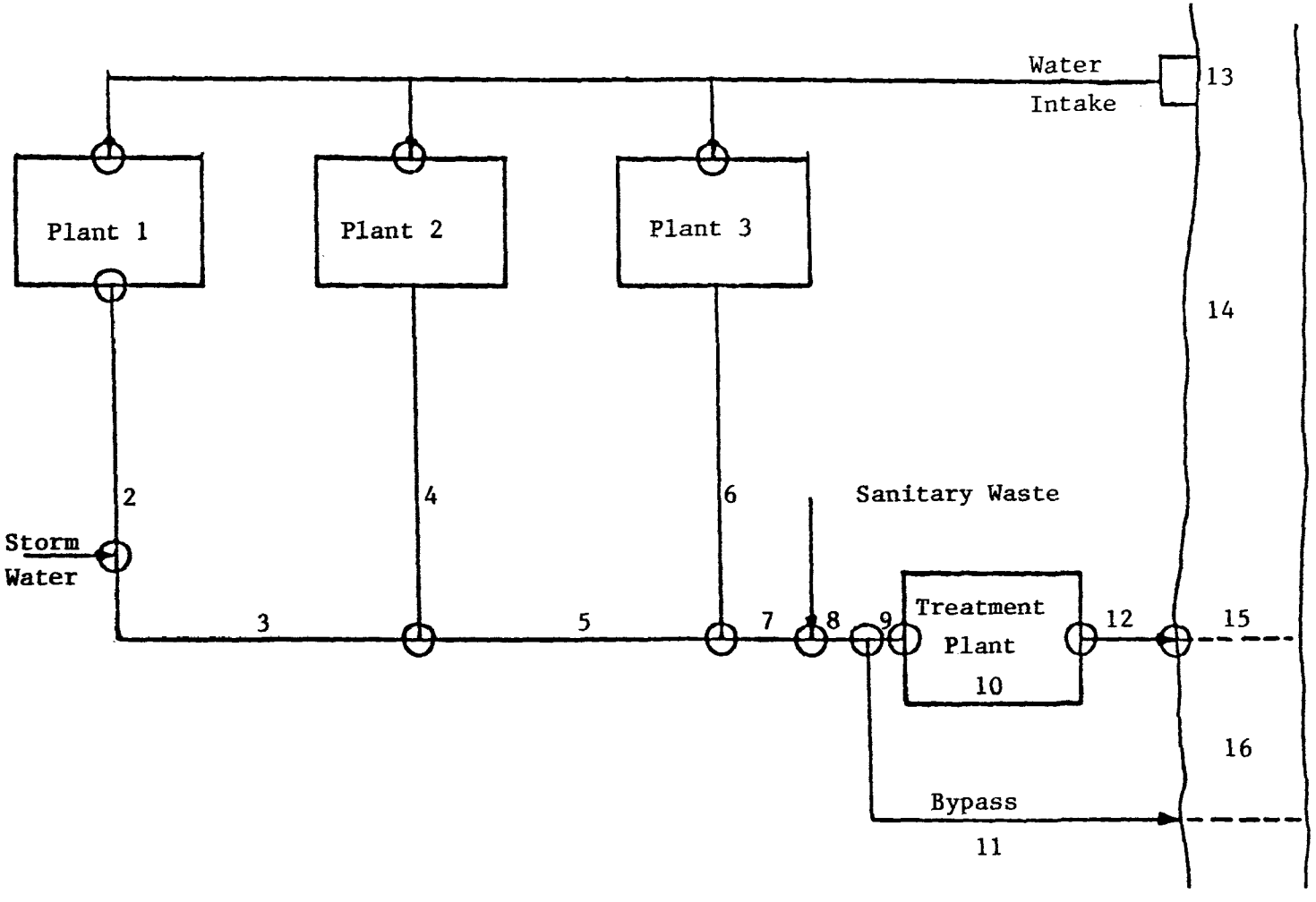


Figure 4.14 Segmentation of a wastewater system

such as the influent and/or effluent of a treatment plant. Using the correlation analysis between the monitored segment and other upstream and downstream segments, it is possible to identify segments with low correlation to the monitored segment. A second consideration should be the worth of the data measured at the segment. For example, if the magnitude of a measured parameter and its variability are insignificant when related to other segments, the segment will have a low priority for monitoring.

4.5.1.1 First Priority Sampling Points

The location of at least one sampling point is strictly determined by the basic objectives of a monitoring program, i.e. protection of the environment. This objective requires that a sampling point be located just before a wastewater discharge to a receiving water body. If the industry has several wastewater outfalls, a sampling point should be located downstream from the last outfall. In the case that the monitoring point is located in the receiving water body, an upstream station to monitor the upstream water quality and quantity is necessary. This will allow the effect of the wastewater discharge on the receiving water body to be clearly identified. If the water intake for the industry is situated on the same water body, the upstream sampling point can be conveniently located at the water intake.

4.5.1.2 Second Priority Sampling Points

Other important objectives of a sampling program can be to monitor the quality of raw wastewater and to evaluate the efficiency of a treatment process. Thus, a location for a second priority sampling point would normally be at the influent to a treatment plant.

For small and middle-sized wastewater systems, sampling at the first and second priority sampling points should be sufficient to meet most of the

objectives and requirements established by regulatory agencies.

4.5.1.3 Third Priority Sampling Points

The location of additional sampling points may be necessary for large wastewater systems with many inputs. Their purpose is to provide additional information or warning. In this case, the method of segmenting the wastewater system and determining sampling priorities for each segment can be of use in establishing additional sampling points. Segmentation of a wastewater system is accomplished by isolating the locations which substantially modify the waste stream conditions. These locations include junctions of wastewater streams, treatment units, wastewater overflow, flow dividers, storm and cooling water inflows, and storage reservoirs. The following outlines a method of segmentation.

1. It is best to represent the wastewater system by a linear graph technique. Such a graph consists of nodes or junctions and branches or lines. All wastewater inputs will enter the system through the nodes, and the nodes also separate branches with different characteristics. A branch is considered as a segment with uniform geometric, hydraulic, and transform characteristics. The following depicts the classification of some typical elements of a wastewater system.

   Nodes - manholes, changes of slope, changes in conduit diameter, flow dividers, junctions of sewers and channels, outfalls, influents and effluents to treatment steps, etc.

   Branches - conduits, channels, treatment steps, bypasses, adjacent receiving water bodies, storage reservoirs, holding ponds, etc.

For the industrial water/wastewater system of Figure 4.15, a linear graph representation is shown in Figure 4.16.

2. In segmenting the system, each node should be uniquely numbered. Wastewater input to each node should be characterized by the range of variation

$$P_j = (Q_{wj}C_{wj})\ \max - (Q_{wj}C_{wj})\ \min,$$

which is, basically, the range of waste loads to the node j. The units of P_j will be g/sec if the flow Q_w is expressed in m^3/sec and concentration C_w in mg/l. It might be convenient also to know the approximate frequency of fluctuations of the input P_j. A node table such as is shown in Table 4.14 should be prepared.

3. Each branch is identified by a double subscript AB, where A is the number of the upstream node and B is the number of the downstream node.

Coefficients of transformation β_{AB} and α_{AB} should be assigned for each branch. The coefficient of transformation β_{AB} describes roughly how the variability of the wastewater is reduced in this segment. In most cases β_{AB} can be determined approximately from the geometry of the segment and treatment parameters. The coefficient α_{AB} describes how the correlation is reduced in the segment. The following values of the coefficients are recommended:

	β_{AB}	α_{AB}
* Short sewers and channels	1.0	1.0
* Plug flow treatment steps, long sewers and channels with decay	exp(-KT)	0.9 to 1.0

* Completely mixed treatment steps with short detention time ($t<<1/f$)	$1-E_{tr}/100$	0.85 to 0.95
* Completely mixed treatment steps with long detention time ($t>>1/f$)	$\left(2(1+Kt)tf\right)^{-\frac{1}{2}}$	$(2tf)^{-\frac{1}{2}}$
* Storage and equalization reservoirs and holding ponds with no decay	$(2tf)^{-\frac{1}{2}}$	$(2tf)^{-\frac{1}{2}}$

where

K = decay coefficients in the segment (in units of day^{-1})

t = detention time in the segment (in days)

f = frequency of fluctuations of waste inputs

E_{tr} = treatment efficiency (in percent)

4. Determine and approximate ranges of wastewater quality variations for each segment. This can be done by starting at the most upstream nodes containing wastewater inputs and moving downstream, by the buffering capacity of segments and by new wastewater inputs (such as process discharges) in downstream nodes.

Figure 4.17 illustrates how this procedure is accomplished. JK is the most upstream node containing a wastewater input and would therefore be the starting point. The range of wastewater variability will be

$$r^{J}_{JK} = P_j$$

where r^{J}_{JK} is the wastewater quality variation range in segment JK downstream from J. Above, the downstream node K the variation range is determined by

$$r^{K}_{JK} = r^{J}_{JK} \times \beta_{JK}$$

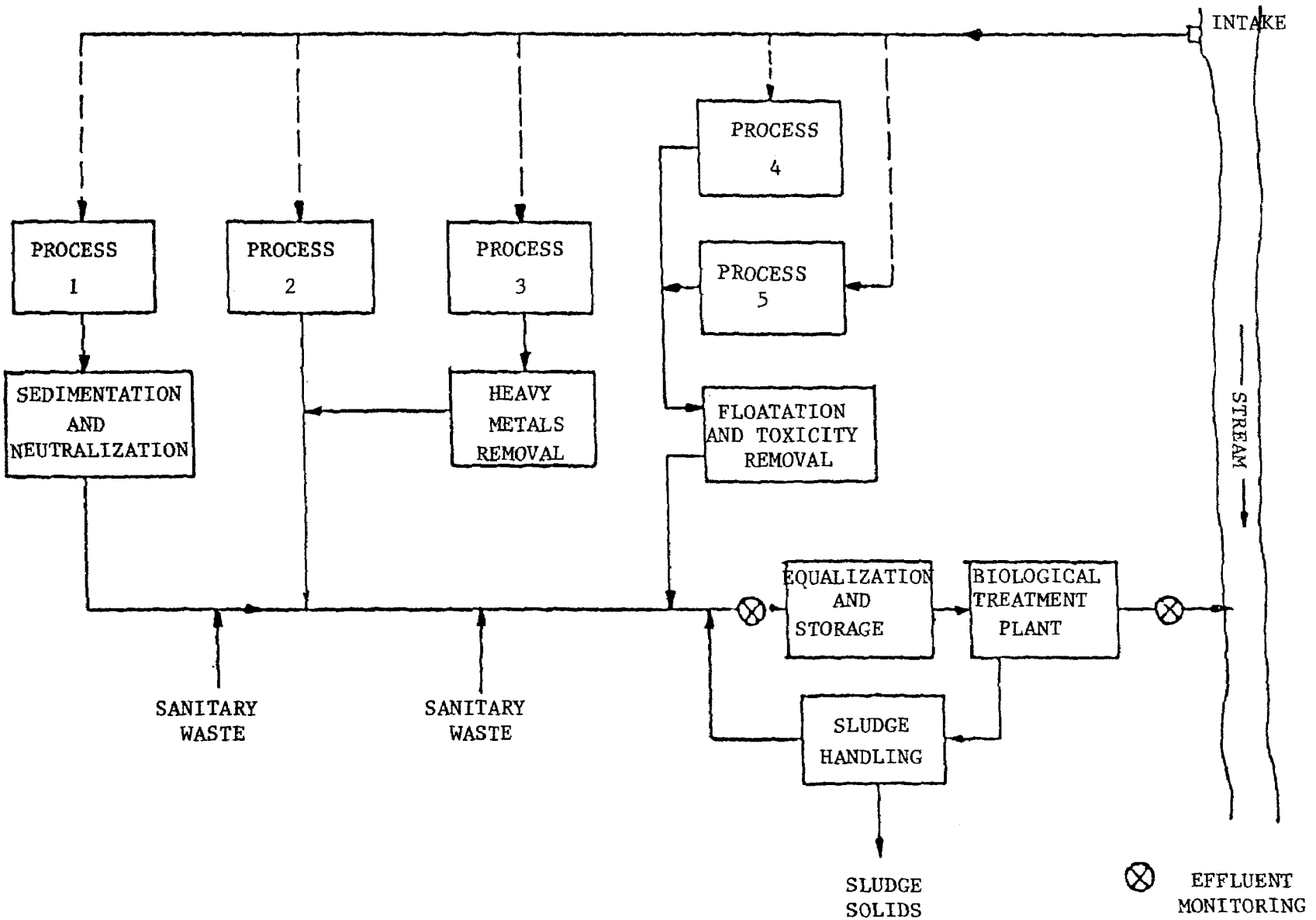


Figure 4.15 An industrial water/wastewater system

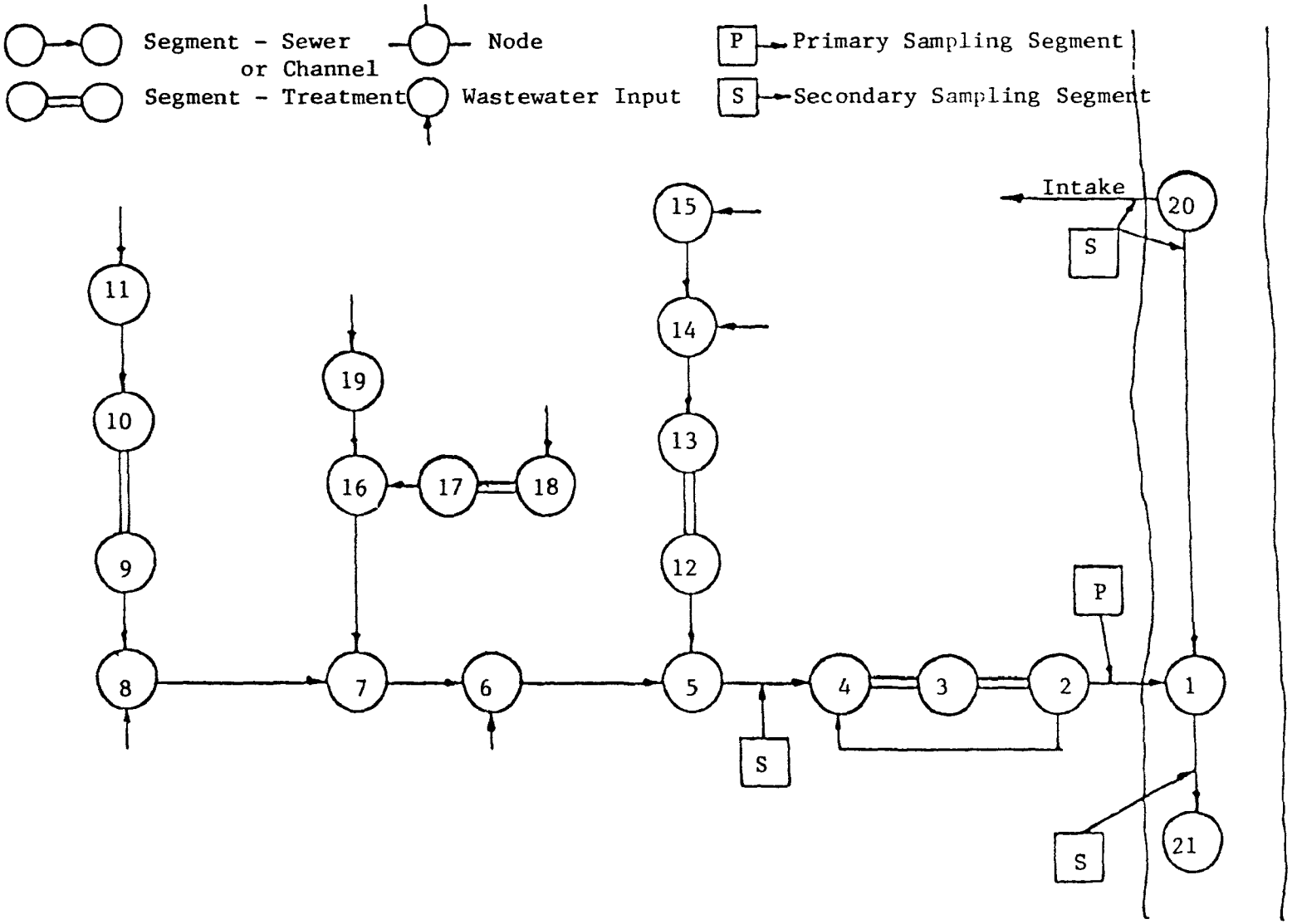


Figure 4.16 Linear graph representation of the system

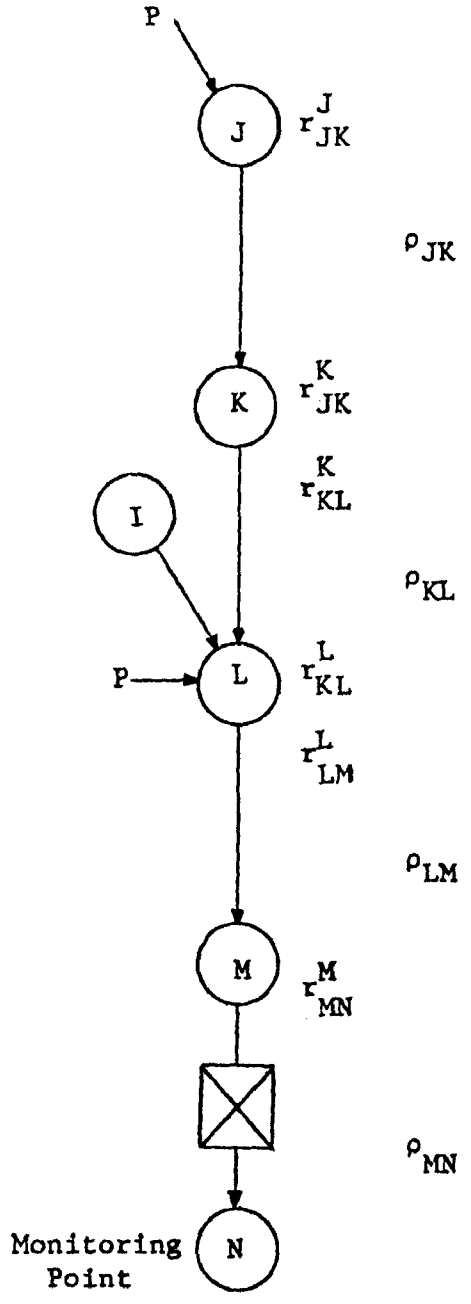
At a node the variability range can be changed by wastewater inputs to the node and by other upstream branches entering the node. For a case where more than one input enters a node, the following relationship (propogation of errors) can be used to compute the variability range:

$$r_{AB}^{A} = \left(\sum_{i} \left(r_{i_A}^{A}\right)^2 + \sum_{j} \left(P_{jA}\right)^2\right)^{\frac{1}{2}}$$

where A denotes the node under consideration, B denotes the node immediately downstream from A, iA represents the $i^{\underline{th}}$ upstream branch entering node A, and jA represents the $j^{\underline{th}}$ wastewater input entering node A. In Figure 4.17, the above formula is used for node L.

The variability ranges for all segments in a network can be computed using the relationship described above and shown in Figure 4.17. It is recommended that the variability range be checked by known data from a survey or monitoring. The above procedure should give adequate results assuming that all inputs to the system are random and uncorrelated to each other.

5. Determine the approximate correlation coefficient between each segment's water quality variations and the variations in the monitored segment. The correlation coefficient, ρ_{MN}, for the monitored segment itself equals 1.0. Moving further downstream or upstream causes the correlation coefficient to decrease as the relation between the wastewater fluctuations in the monitored segment and the segment downstream or upstream diminishes. The change



Variability Range

$$r^J_{JK} = P_J$$

$$r^K_{JK} = r^J_{JK} \times \beta_{JK}$$

$$r^K_{KL} = r^K_{JK}$$

$$r^L_{KL} = r^K_{KL} \times \beta_{KL}$$

$$r^L_{LM} = \left((r^L_{KL})^2 + (r^L_{IL})^2 + (P_L)^2\right)^{\frac{1}{2}}$$

$$r^M_{LM} = r^L_{LM} \times \beta_{LM}$$

Figure 4.17 Estimation of variability and correlation in segments

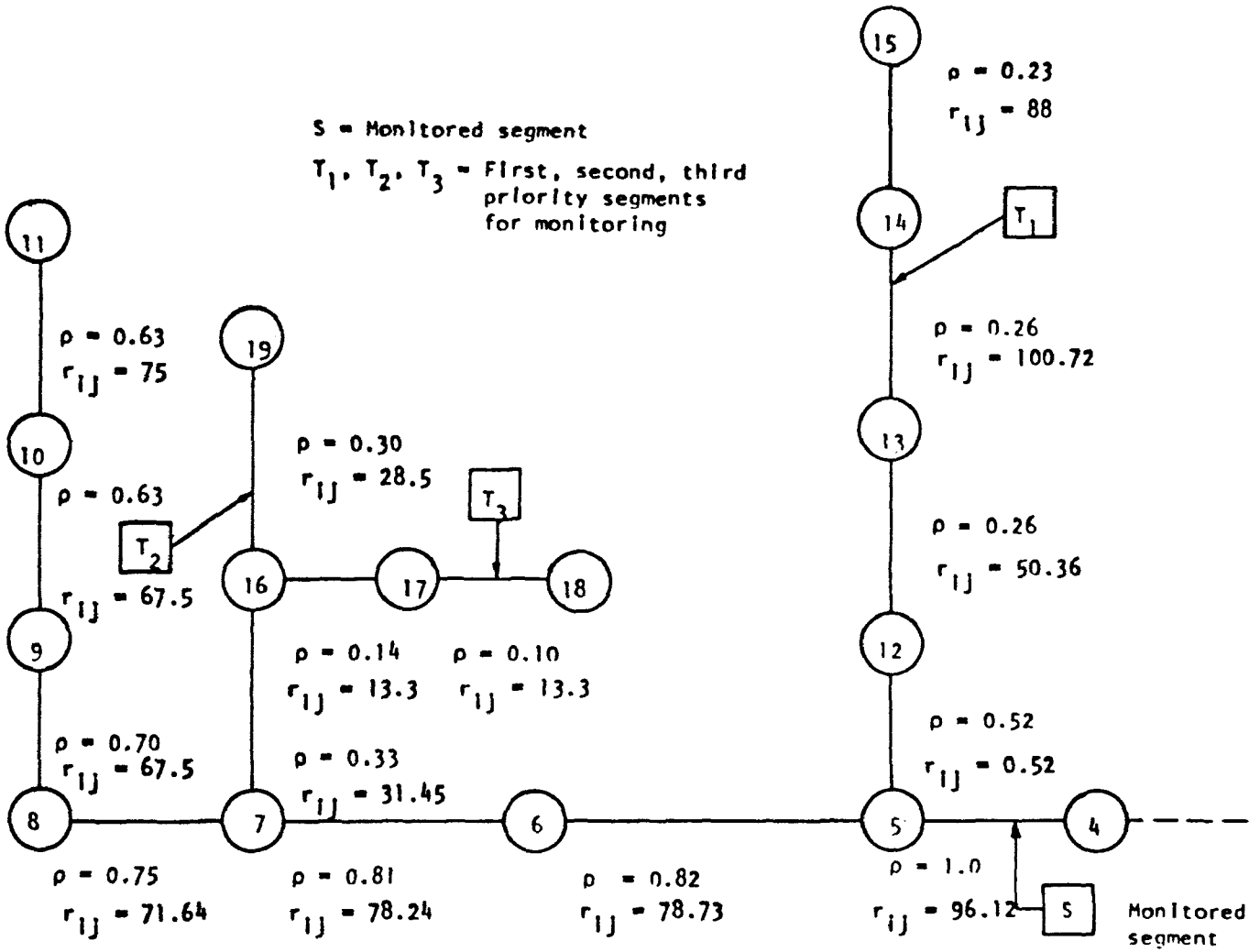


Figure 4.18 Correlograph for segments

in the correlation coefficient can be roughly estimated as follows:

In a Branch - multiply ρ by the coefficient α

In a Node - multiply ρ by the ratio r^{B}_{AB}/r^{B}_{BC}

where B is the node under consideration, AB is the branch located farther away from the monitored segment, and BC is the branch located closer to the monitored segment.

6. Additional sampling points should be located at the segment where, theoretically, the correlation with the monitored point ends. Since the correlation influence of both points extends both downstream and upstream, there will be an overlap such that each sampling point will have an influence of $r = \sqrt{R_c}$, where R_c is the critical point found in Table 4.12. If the number of samples is not known, a value of R_c between 0.25 and 0.30 will give a good estimate.
7. If there are several segments to be monitored, i.e. one or more segments have a correlation level less than R_c, the priority can be determined according to the magnitude of the variability range r_{ij} for the segment ij. The segment with the highest r_{ij} will have the highest priority.
8. Once a new sample location is established, the procedure is repeated to find the next sampling location.
9. The entire procedure should be repeated for each important parameter.

Example:

Determine the locations of sampling points for the wastewater system given in Figure 4.15. The analysis will be based on the COD information representing the organic load to the system.

Step 1 - Divide the system into segments using the linear graph representation, as in Figure 4.16.

Step 2 - Locate a first priority sampling point (P) at the effluent channel (segment 1-2). Locate second priority sampling points (S) at the influent to the treatment plant (segment 4-5) and in the receiving water body, upstream and downstream from the waste discharge.

Step 3 - Estimate the variability range of the inputs to the system (Table 4.14).

Step 4 - Estimate β and α for each segment (Table 4.15).

Step 5 - Estimate the variation range in each segment. Proceed upstream from the most downstream segment (Table 4.16).

Step 6 - Estimate the coefficient of correlation between wastewater variations in each segment and the nearest monitored segment, i.e. to segment 4-5. Proceed from the monitored segment (where R = 1.0) and work upstream (Table 4.16 right portion). Each segment is correlated to the segment immediately downstream toward the monitored point. Developing a correlograph (Figure 4.18) at this stage will aid in the decision process in Step 7.

Step 7 - Once the correlation coefficients are estimated, find those where $R<R_c$, with R_c estimated to be 0.30. Based on this criterion, the priority for monitoring the upstream segments will usually have a high correlation and, therefore, only one segment needs to be monitored. The second criterion is the magnitude of the variability, r_{ij}, for the segments with

TABLE 4.14 WASTEWATER LOADS TO NODES
CONSTITUENT: COD

Node	Maximal Loading g/sec	Minimal Loading g/sec	Pj
1	0	0	0
2	0	0	0
3	0	0	0
4			
5	0	0	0
6	10	1.2	8.8
7	0	0	0
8	30.0	6.0	24.0
9	0	0	0
10	0	0	0
11	175	100	75
12	0	0	0
13	0	0	0
14	66.0	17.0	49.0
15	109	21.0	88.0
16	0	0	0
17	0	0	0
18	42	23	19
19	121.50	93.0	28.5

Fluctuations of maximum and minimum at most nodes - 1/8 hrs^{-1}

TABLE 4.15 COEFFICIENTS OF VARIATION IN BRANCHES

Branch	Description	β	α
1-2	Effluent Channel	1.0	1.0
2-3	Activated Sludge Plant	0.1	0.4
3-4	Equalization Basin	0.2	0.2
4-5	Sewer	1.0	1.0
5-6	Sewer	1.0	1.0
6-7	Sewer	1.0	1.0
7-8	Sewer	1.0	1.0
8-9	Sewer	1.0	1.0
9-10	Neutralization Plant	0.9	0.9
10-11	Sewer	1.0	1.0
5-12	Sewer	1.0	1.0
12-13	Flotation Unit	0.5	0.5
13-14	Sewer	1.0	1.0
14-15	Sewer	1.0	1.0
7-16	Sewer	1.0	1.0
16-17	Sewer	1.0	1.0
17-18	Chemical Coagulation	0.7	0.7
16-19	Sewer	1.0	1.0

TABLE 4.16 DETERMINATION OF THE SAMPLING PRIORITIES OF SEGMENTS

Segment	Upstream variation range $r_u = (\Sigma r^2 + \Sigma p^2)^{0.5}$	Downstream variation range $r_d = r_u * 3$	Correlation coefficient in the branch at the downstream node $P_u = P_d \frac{u}{r_d}$	Correlation coefficient in the branch at the upstream node $p = p \sigma$	Priority for tertiary monitoring
16-19	28.5	28.5	0.33 * 28.51/31.45 = 0.30	0.30	T2
17-18	19.0	19 * 0.7 = 13.3	0.14	0.14 0.7 = 0.10	T3
16-17	13.3	13.3	0.33 * 13.3/31.45 = 0.14	0.14	
7-16	$(28.5^2 + 13.3^2)^{0.5} = 31.45$	31.45	0.81 * 31.45/78.24 = 0.33	0.33	
10-11	75	75	0.63	0.63	
9-10	75	75 * 0.9 = 67.5	0.70	0.7 * 0.9 = 0.63	
8-9	67.5	67.5	0.75 * 67.5/71.64 = 0.70	0.70	
7-8	$(67.5^2 + 24^2)^{0.5} = 71.64$	71.64	0.81 * 71.64/78.24 = 0.75	0.75	
6-7	$(71.64^2 + 31.45^2)^{0.5} = 78.24$	78.24	0.82 * 78.24/78.73 = 0.81	0.81	
5-6	$(78.24^2 + 8.8^2)^{0.5} = 78.73$	78.73	1.0 * 78.73/96.12 = 0.82	0.82	
14-15	88.0	88.0	0.26 * 88/100.72 = 0.23	0.23	
13-14	$(88^2 + 49^2)^{0.5} = 100.72$	100.72	0.26	0.26	T1
12-13	100.72	100.72 * 0.5 = 50.36	0.52	0.52 * 0.5 = 0.26	
5-12	50.36	50.36	1.0 * 50.36/46.12 = 0.52	0.52	
4-5	$(78.73^2 + 50.36^2)^{0.5} = 96.12$	96.12	1.0	1.0	Initial segment monitoring

low correlation levels. Both the values of R and of r_{ij} should be examined for these segments, the requirements and objectives of the program should be considered, and then professional judgment must be exercised.

In this example, segments 17-18, 16-17 and 16-19 are neighboring segments with low correlation levels. Looking at the variability values, we see that segment 16-19 has the highest value, indicating the great fluctuations in wastewater quality. Therefore, of these three, segment 16-19 might have the highest priority. Segments 14-15, 13-14 and 12-13 are also neighboring segments with low correlation levels. Segment 13-14 has the greatest variability and would therefore be chosen. Since its variability is much higher than that of segment 16-19, it would have the highest overall priority. At this stage, correlation and variability values can be recalculated to see if monitoring at these points would satisfy the program requirements. If not; the procedure should be repeated.

4.5.2 Probability of Exceeding a Standard (13)

In locating sampling points in a receiving water body, the probability of exceeding a receiving water standard should be considered. For all conservative substances and all nonconservative substances except oxygen and possibly temperature and nitrates, the critical section would be located immediately downstream from the outfall. The section with the highest probability of violating the dissolved oxygen standard will be further downstream near the "sag point." The location of the critical point can be approximately

evaluated as follows:

The probability that the dissolved oxygen standard will be exceeded is

$$P(C<C_s) = P(D>D_s) = P\left(Z>Z_s = \frac{D_s - \overline{D(x)}}{S(x)}\right)$$

which can be found in Table 4.9, where

C is the dissolved oxygen concentration

C_s is the dissolved oxygen standard

D is the oxygen deficit

D_s is the maximum allowable oxygen deficit

$$\overline{D(x)} = \frac{K_1\overline{L_o}}{K_2-K_1} \times \left[\exp\left(\frac{-K_1x}{u}\right) - \exp\left(\frac{-K_2x}{u}\right)\right] + D_o \exp\left(\frac{-K_2x}{u}\right)$$

which is the average oxygen deficit at distance x from the outfall

$S(x) = A_1 \times S_{Lo} \times U$ is the standard deviation at distance x. (13, 14, 15)

$\overline{Lo}$ is the average BOD discharge

S_{Lo} is the S.D. of the BOD discharge

K_1 is the coefficient of deoxygenation

K_2 is the coefficient of re-aeration

D_o is the initial oxygen deficit

U is the stream velocity

$$A_1 = \frac{K_1}{K_2-K_1}\left(\exp\left(\frac{-K_2X}{U}\right) - \exp\left(\frac{-K_1X}{U}\right)\right).$$

To find a maximal $P(C<C_s)$, it is sufficient to find a location x such

that $Z_s = (D_s - \overline{D(x)})/S(x)$ is a minimum. This can be accomplished by finding the location x at which $\overline{D(x)}/S(x)$ is a maximum (and so $P(D(x)>D_s)$ is a maximum. The distance x can be found by plotting $\overline{D(x)}/S(x)$ against x for given K_1, K_2, D_o, L_o and U, and then finding the x value corresponding to the highest value of $\overline{D(x)}/S(x)$.

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CHAPTER 5

SAMPLING MUNICIPAL WASTEWATERS

5.1 BACKGROUND

Municipal wastewater consisting of the spent waters from a community is treated by chemical, physical, and/or biological means prior to discharge to surface waters. Up to three stages of treatment are commonly used at municipal treatment plants (1): primary (screening, sedimentation), secondary (activated sludge, trickling filter, etc.), and tertiary (physical/chemical treatment). The wastewater characteristics vary with the size and habits of the community, the type of collection system(combined or separate), the amount of infiltration and the type of industrial discharges.

5.2 OBJECTIVES OF SAMPLING PROGRAMS

5.2.1 Regulatory

Sampling of municipal wastewaters is required by regulatory agencies for the NPDES permit program. The location of sampling points, frequency, sample type, etc. are specified in the NPDES permit. At the time of NPDES permit modifications, incorporate the recommendations of Compliance Sampling Inspection and use the statistical analysis of self monitoring data as a rationale to specify the permit requirements.

5.2.2 Process Control

In addition, sampling is performed at municipal treatment plants for process control purposes. This monitoring provides a check on the efficiency of the process allowing the operator to make adjustments to optimize the

Process efficiency.

5.2.3 Research and Development

The special needs of a research project will dictate the sampling program. Hence each project must be considered individually and no general guidelines can be given.

5.3 FREQUENCY OF SAMPLING

5.3.1 Established by Regulation

Follow the frequency requirements indicated in the permit issued by the regulatory agencies.

5.3.2 Use of Statistics

Apply spectral analysis techniques (Section 4.3.2) to establish the optimum frequency. If the data required for this technique is not available:

1. Conduct a week-long survey collecting hourly samples.(For combined municipal-industrial wastewaters choose a week of high industrial production.)
2. Determine if any unusual industrial or community discharge occurred during the sampling period (e.g. an extensive spill or extremely heavy rainstorm) which may invalidate the data and necessitate a repeat of the survey.

After data collection, the analysis of data should be performed as outlined in Section 4.3.2.

5.3.3 Surveillance Purposes

A poll of EPA Surveillance and Analysis Labs indicated a general concurrence that for normally variable domestic wastewaters a minimum of 8 evenly spaced grab samples collected over a 24 hour period, repeated for a minimum of 3 weekdays, will result in a fair estimate of water chemistry characteristics (2).

5.3.4 Other Considerations

Follow interim sampling frequencies prior to the generation of data for statistical analysis. Frequencies appear in Tables 5.1 (3) and 5.2 (4).

5.4 LOCATION OF SAMPLING POINTS

Collect the sample at the location(s) specified in the permit. At these locations collect the sample in the center of the channel at 0.4 to 0.6 depth where the flow is turbulent, well mixed, and the settling of solids is minimal. Sampling at 0.4 to 0.6 depth will avoid skimming of the water surface or dragging the channel bottom.

For BOD analysis, it is recommended that samples be collected prior to the disinfection step (5). For BOD and suspended solids, samples of plant influent and effluent must be collected in order to calculate the removal of these constituents. The sampling of wastewater for immiscible liquids, such as oil and grease, requires special attention and no specific rule can be given for selection of the most representative site for collection of an oil and grease sample because of wide range of conditions encountered in the field. In such cases, experience of the sampling team should be the guide in the selection of the most representative site. (2)

5.4.1 Influent

Influent wastewaters are preferably sampled at points of highly turbulent flow in order to insure good mixing; however, in many instances the desired location is not accessible. Preferable raw waste sampling points are (6):

a. the upflow siphon following a comminutor (in absence of grit chamber);

b. the upflow distribution box following pumping from main plant wet well;

c. aerated grit chamber;

TABLE 5.1 PROCESS TESTING GUIDE[a] (3)

Process	Test	Frequency
	PRETREATMENT	
Grit Removal	Volatile Solids	Daily
	Total Solids	Daily
	Moisture Content	Daily
	PRIMARY TREATMENT	
Primary Sedimentation	Settleable Solids	Daily
	pH	Daily
	Total Sulfides	Daily
	Biochemical Oxygen Demand	Weekly
	Suspended Solids	Weekly
	Chemical Oxygen Demand	Weekly
	Dissolved Oxygen	Weekly
	Grease	Weekly
	SECONDARY TREATMENT	
Activated Sludge	Suspended Solids	Daily
	Dissolved Oxygen	Daily
	Volatile Suspended Solids	Weekly
	Turbidity	Daily
Trickling Filter	Suspended Solids	Daily
	Dissolved Oxygen	Daily
Oxidation Ponds	Dissolved Oxygen	Daily
	Total Sulfides	Daily
	Total Organic Carbon	Weekly
	Total Phosphorus	Weekly
	Settleable Solids	Daily
	pH	Daily
	Total Sulfides	Daily
Final Sedimentation	Biochemical Oxygen Demand	Weekly
	Suspended Solids	Weekly
	Chemical Oxygen Demand	Weekly
	Dissolved Oxygen	Weekly
	Turbidity	Daily
	MBAS	Weekly

[a] This is a minimum sampling guide, and is subject to change with plant site, complexity of operation, and problems encountered.

(continued)

TABLE 5.1 (continued)

Process	Test	Frequency
	DISINFECTION	
Chlorination	Chlorine Residual	Daily
	MPN Coliform	Weekly
	SOLIDS HANDLING	
Thickening	Suspended Solids	Daily
	Volatile Solids	Daily
Digestion	Total Solids	Weekly
	Volatile Solids	Weekly
	pH	Daily
	Gas Analysis	Weekly
	Alkalinity	Weekly
	Volatile Acid	Weekly
Centrifuging	Suspended Solids	When in Operation
	Volatile Solids	When in Operation
Vacuum Filters	Sludge Filterability	When in Operation
	Suspended Solids	When in Operation
	Volatile Solids	When in Operation
Incineration	Ash Analysis	When in Operation
	ADVANCED TREATMENT	
Chemical Coagulation & Flocculation	Jar Test	Weekly
	Phosphorus Analysis	Weekly
	Apparent Density	Weekly
Activated Carbon	COD	Weekly
	TOC	Weekly
Recarbonation	pH	Weekly
Ammonia Stripping	Ammonia Nitrogen	Weekly
	pH	Weekly
Filters	Suspended Solids	Daily
	Turbidity	Daily
Microscreen	Suspended Solids	Daily
	Chemical Oxygen Demand	Weekly

[a] This is a minimum sampling guide, and is subject to change with plant site, complexity of operation, and problems encountered.

TABLE 5.2 RECOMMENDED MINIMUM SAMPLING PROGRAMS FOR MUNICIPAL WASTEWATER TREATMENT PROCESSES (4)

	Overall		Grit Removal		Primary-Clarification		Activated Sludge		Trickling Filter		Aerated Pond		Secondary Ponds		Secondary Clarifier		Chlorine Contact		Chemical Treatment		Nitrogen Removal		Two Stage Nucarbon		Filtration		Activated Carbon		Centrifugation		Sludge Concentration		Solids Reduction		Aerobic Digestion		Solids Reduction		Anaerobic Digestion	
	S[1]	F[2]	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F
Temp	G 1/D										G 1/D		G 1/W				G 1/D				G 3/D												G 1/D		Mo			
pH	G 1/D						G 5/W				G 3/W		G 1/W		G 1/D		G 1/D		G 1/D		G 3/D		Mo				Mo						G 1/D		G 1/D			
BOD	C 2/W				C 2/W		C 2/W		C 2/W						C 2/W				or mo						G Back-wash				G 1/W		G 2/W		G Dump		G 1/D			
DO	G 3/W						G 5/W				G 1/D		G 1/W																				G 3/W					
SS	C 3/W				C 3/W		C 5/W								C 3/W				C 1/D						G Back-wash				G 1/D		G 1/D		G Dump		G 1/W			
NH_3-N	C 1/W						C 1/D								C 1/D						C 1/W																	
TKN	C 1/W						C 1/D								C 1/W						C 1/W																	
NO_3-N	C 1/W						C 1/D								C 1/D						C 1/W																	
P-T	C 1/W						C 3/W								C 1/D				C 3/W																			
Turb	R														Mo				R						R													
TS	C 2/W		G 2/W		G 1-3/W										G 3/W				G 1-3/W				C 1/W						G 1/D		G 1/D		G 2/W		C 1/W			
TVS	C 2/W		G 2/W				C 3/W																										C 2/W		C 2/W			
Set. S					G 3/W										G 1/D																							
Sl. Vol.																													G 1/H				G 3/W					
COD					C 1/W		C 2/W		C 2/W										G 3/D								C 3/W											
V. SS					C 3/W																																	
Air Input							R																										R					

(continued)

TABLE 5.2 (continued)

	Overall		Grit Removal		Primary Clarification		Activated Sludge		Trickling Filter		Aerated Pond		Secondary Ponds		Secondary Clarifier		Chlorine Contact		Chemical Treatment		Nitrogen Removal		Two Stage Recarbon		Filtration		Activated Carbon		Centrifugation		Sludge Concentration		Solids Reduction	Aerobic Digestion	Solids Reduction	Anaerobic Dilution
	S[1]	F[2]	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F	S	F
Micro Analysis							G 2/W																											
Ortho-P							C 3/W								C 1/D				C 3/W															
Chlor. Resid.																	G 1/D																	
																	R																	
Colifora																	G 1/W																	
Fecal Coliform																	G 1/W																	
Alk.	C 2/W														C 1/W				C 2/W				C 1/D								G 2/W		G 1/D	
Jar Test																	C 1/W																	
Hardness																	C 1/W				C 1/W													
Sludge Vol.					G 3/D										G 3/D																			
Dis. S	C 2/M																				G 3/W		C 1/W											
MBAS																											C 1/D							
Metals	C 2/M																																	
Plant Flow	R																																	

1. S = type of sample
2. F = frequency

G = Grab
C = 24 hour composite
D = Day
W = Week

M = Month
R = Record continuously
Mo = Monitor continuously

d. flume throat; and

e. pump wet well.

In all cases, samples should be collected upstream from recirculated plant supernatant and sludges.

5.4.2 Effluent

Collect effluent samples at the most representative site downstream from all entering waste streams. When manually compositing effluent samples according to flow where no flow measuring device exists, use the influent flow measurement without any correction for time lag. The error in influent and effluent flow measurement is insignificant except in those cases where extremely large volumes of water are impounded (such as in reservoirs) as a result of influent surges coupled with highly restrictive effluent discharge (7).

5.4.3 Pond Sampling

Composite samples should be employed even for ponds with long detention times because of the tendency of lagoons to short circuit. If dye studies or past experience indicate a homogeneous discharge, a grab sample may be taken as representative of the waste stream.

5.4.4 In-Plant Location

Apply the statistical technique outlined in Section 4.5 to determine in-plant sampling locations. In addition to these locations, sample all other unit processes periodically or when the variability of a parameter adversely affects the efficiency of a unit process.

5.5 NUMBER OF SAMPLES

Use one or more of the following methods to determine the number of samples:

1. Follow permit requirements by regulatory agencies.
2. Apply statistical methods in Section 4.2 to the data from the preliminary survey.
3. Use the frequency data to establish number of samples (e.g. 1 sample every 6 hours will establish 4 samples per day).

5.6 PARAMETERS TO MEASURE

The NPDES permit for each municipal treatment plant spells out in detail the effluent limitations and monitoring requirements for that particular plant. For evaluating the plant performance, regardless of the size, these parameters: Biochemical Oxygen Demand (5 day), solids, pH and flow should be monitored routinely (8).

Secondary analyses include:

1. Fecal Coliform and Chlorine Residual
2. Temperature
3. Dissolved Oxygen
4. Total Solids
5. Total Volatile Solids
6. Nitrogen Series
7. Phosphorus
8. Dissolved Solids
9. Alkalinity
10. Metals
11. COD
12. Oil and Grease
13. Organic Priority Pollutants as required

Table 5.2 indicates the parameters to analyze the efficiency or the effectiveness of the various unit processes. Changes are allowed to compensate for specific plant conditions.

5.7 TYPE OF SAMPLE

Use composite samples for all overall monitoring (6) and grab samples for checking individual unit processes. Use one of the following types of composite samples to properly estimate mass loading:

1. Periodic, time constant, sample volume proportional to stream flow.
2. Periodic, sample volume constant, time proportional to stream flow since the last sample.

Other composite types may be used if comparable results can be demonstrated.

5.8 METHODS OF SAMPLING

Choose manual or automatic sampling depending on how the advantages and disadvantages of the methods apply to the specific program. (Refer to Chapter 2). Adequate care should be exercised in sample collection. Only trained personnel should be entrusted the task of sample collection. Much of the uncertainty regarding the collection of suspended solids can be minimized if samples are collected at isokinetic conditions or at higher intake velocities.

5.8.1 Automatic Sampler

Automatic samplers for municipal wastewaters must be capable of collecting representative suspended solids samples throughout the collection and treatment system. While sampler selection will depend on site conditions, the following guidelines are suggested:

1. For sampling raw wastewater and primary effluent, use a sampler having an intake velocity greater than 0.76 m/sec. (2.5 ft./sec.). For sampling a final effluent with no visible solids, a sampler having a lower intake velocity may be acceptable (2).
2. To determine the effectiveness of an automatic sampler to collect suspended solids, statistically compare the suspended solids value of the composite sample from the automatic sampler with the mean value of the manual grab samples. The minimum compositing period

should be six hours with a maximum individual sample frequency of one hour (7). The ratio of the automatic sampler suspended solids value to the manual grab suspended solids value varies throughout the plant. For influent and primary effluent the acceptable ratio is 1.6 - 2.0 and for the final effluent it is 0.9 - 1.3.(9)

5.9 VOLUME OF SAMPLE AND CONTAINER TYPE

The volume of sample obtained should be sufficient to perform all the required analyses plus an additional amount to provide for any split samples or repeat examinations. Although the volume of sample required depends on the analyses to be performed, the amount required for a fairly complete analysis is normally 7.57 liters (2 gallons) for each laboratory receiving a sample. The laboratory receiving the sample should be consulted for any specific volume requirements. Individual aliquot portions of a composite sample should be at least 100 milliliters (0.21 pints) in order to minimize sampler solids bias. Depending on the sampling frequency and sample volume, the total composited sample should be at least 7.57 liters (2 gallons) (6). Use a separate sterilized container for coliform analysis. See chapter 12 for organic collection methods. Collect chlorine residual or oil and grease samples in a glass container. Plastic is acceptable for the other recommended analyses. Specific information for water quality or organic parameter types is given in chapter 17.

5.10 PRESERVATION AND HANDLING THE SAMPLES

Follow the guidelines establishing test procedures for the Analysis of Pollutants (40 CFR 136) as amended in Federal Register Vol. 41, No. 232, December 1, 1976, and for organics, vol. 44, No. 233, December 3, 1979.

Techniques indicated in Chapter 17 to collect and preserve the sample can be used as a general guide.

5.11 FLOW MEASUREMENTS

The flow measurement technique selected should be in relation to the sampling location, type of flow, etc. Follow the guidelines enumerated in Chapter 3 on Flow Measurements. Primary and secondary flow measurement devices should be calibrated prior to taking flow measurements.

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CHAPTER 6

SAMPLING INDUSTRIAL WASTEWATERS

6.1 BACKGROUND

Industrial wastewaters vary significantly in pollution characteristics. This chapter presents general guidelines and considerations so that effective sampling programs can be established for varied situations.

6.2. OBJECTIVES OF SAMPLING PROGRAMS

6.2.1 Regulatory

Sampling of industrial wastewaters is required by regulatory agencies for the NPDES permit program. The location or sampling points, frequency, sample type, etc. are specified in the NPDES permit. At the time of NPDES permit modifications, incorporate the recommendations of Compliance Sampling Inspection and use the statistical analysis of self monitoring data as a rationale to specify the permit requirements.

6.2.2 Process Control

In addition, sampling is performed within the plant to monitor individual waste streams, as an indirect check on the process efficiencies, to compute material balances, etc.

6.2.3 Research and Development

The special needs of a research and development project will dictate the sampling program; such projects are summarized below (1);

1. To explore potential recovery from a given department or unit

process, considering process modifications and studying the economics thereof.

2. To define factors influencing character of wastes from a given department or unit process.
3. To investigate and demonstrate variations in the character and concentration of combined waste.
4. To establish a sound basis for the treatment of residual wastes.

Each such project must be considered individually and no general guidelines can be given.

6.3 FREQUENCY OF SAMPLING

6.3.1 Established by Regulation

Use permit requirements when compliance monitoring is the objective. If the sampling frequency is not specified by regulation, sampling interval should be less than one hour (3), and if data is available use the statistical methods as a tool to determine the frequency of sampling.

6.3.2 Use of Statistics

Apply the statistics outlined in Section 4.3., to obtain frequency of sampling whenever possible. Background data must be collected to determine mean and variance. One of the following procedures can be used to obtain this information (listed in order of preference) if it has not been previously collected:

1. Conduct a week long preliminary survey consisting of the hourly samples to characterize the system.
2. Conduct one 24 hour survey taking hourly samples (as outlined in chapter 2). Analyze individual samples if batch dumps are suspected. Any weekly pattern must be considered and samples taken on the day

of the greatest variation of the parameters of interest.

3. Obtain data from a plant with the same type of industrial operation. However, where processes differ, take samples to quantify the variation.

After data collection, use production figures to determine extreme values, assuming a linear operating relationship (which is not always the case).

6.3.3 Other Considerations

Consider variable plant operations when determining frequency:

1. Seasonal operation
2. Less than 24 hour per day operation
3. Special times during the day, week or month set aside for cleanup
4. Any combination of the above

When monitoring these types of operations, it is necesssary to sample during normal working shifts in the season of productive operation. Figure 6.1 gives procedures for the various situations.

6.4 LOCATION OF SAMPLING POINTS

6.4.1 Effluent Monitoring

Regulatory permits establish effluent monitoring points within a plant. The permit may specify only the total plant discharge or a specific discharge from a certain operation or operations. Consult permits for these locations, or use those recommendations for obtaining representative samples given in chapter 2.

6.4.2 In-Plant Locations

To achieve process control or to design and implement in-plant pollution control programs, in-plant sample locations are necessary. Use the following procedures to determine the sampling locations:

1. Become familiar with the plant processes and sources of wastes from unit operations.
2. Ascertain the sewer layout in the plant. If a sewer plan exists thoroughly review the sewer plan and examine each sewer to determine its course and destination. Where a sewer plan is not available, the only practical way to determine the sewer layout is by dye-tracing.
3. Determine the exact source and the point at which each waste stream enters the sewer.
4. Sample each waste stream and the plant outfall. By doing so, each waste stream is characterized and the outfall characterizes the total plant effluent.
5. Sample each batch discharge.
6. If a point of upset exists within the plant, establishment of a sampling station or monitoring equipment at that point will allow early detection.
7. If data on different waste streams is available from past records, use statistical techniques outlined in Section 4.5.1 as an aid to establish the critical sampling locations within the plant.

6.5 NUMBER OF SAMPLES

Determine the number of samples from the following:

1. Follow NPDES permit requirements
2. Where NPDES permit is not applicable:
   - Apply statistical methods (Section 4.2) to data from a preliminary survey.
   - To effectively determine the concentration and types of pollu-

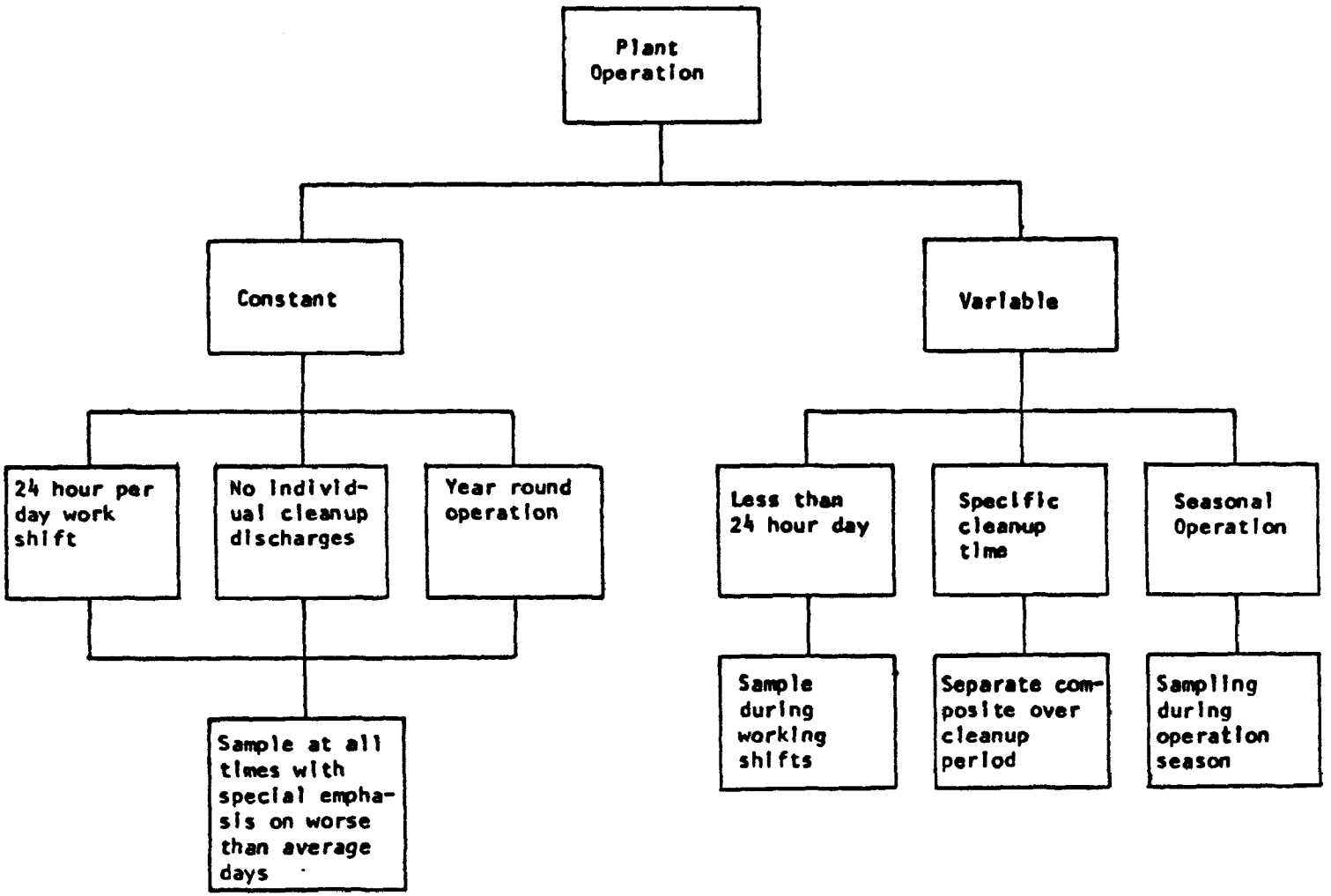

Figure 6.1 Factors of plant operation to be considered in the design of the sampling program.(2)

TABLE 6.1 NPDES EFFULENT LIMITATION PARAMETERS BY INDUSTRY

	Dairy Products	Grain Mills	Canned & Preserved Fruit & Veg.	Canned & Preserved Seafood	Sugar Products	Textiles	Cement	Feedlots	Electroplating	Organic Chemicals	Inorganic Chemicals	Plastics & Synthetics	Soap & Detergents	Fertilizer Mfg.	Petroleum Refining	Iron & Steel Mfg.	Non-Ferrous Metals	Phosphate Mfg.	Stationary Electric Power Generating Equip	Ferroalloy Mfg.	Leather Tanning and Finishing	Glass Manufacturing	Asbestos Mfg.	Rubber Products	Timber Products	Pulp, Paper, etc.	Builders Paper & and Board	Meat Products	Printure Ink and Paint	Paving & Roofing Materials
Temperature Discharges					X		X												X											
BOD - 5 Day	X	X	X	X	X	X		X		X		X	X		X				X		X	X		X	X	X	X	X	X	X
Suspended Solids	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X
Oils, Fats & Grease				X		X							X		X	X			X		X	X		X				X		X
Ammonia														X	X	X	X		X									X		
Nitrite-Nitrogen																			X											
Nitrate-Nitrogen														X		X			X											
Nitrogen (Kjeldahl)														X					X											
Phosphorus														X				X			X	X								
Sulfite																			X											
Sulfide						X									X	X			X		X									
Sulfate																														
Chloride																														
Chlorine																														
Fecal Coliform Bact.					X	X		X																						
Fluoride											X			X		X	X	X			X							X		
Arsenic																														
Barium																														
Boron																														
Cadmium																														
Chromium						X			X		X	X			X				X	X	X									
Cobalt																														
Copper									X								X													

TABLE 6.1 (Continued)

	Dairy Products	Grain Mills	Canned & Preserved Fruit & Veg.	Canned & Preserved Seafood	Sugar Products	Textiles	Cement	Feedlots	Electroplating	Organic Chemicals	Inorganic Chemicals	Plastics & Synthetics	Soap & Detergents	Fertillizer Mfg.	Petroleum Refining	Iron & Steel Mfg.	Non-Ferrous Metals	Phosphate Mfg.	Stationary Electric Power Generating Equip	Farroalloy Mfg.	Leather Tanning and Finishing	Glass Manufacturing	Asbestos Mfg.	Rubber Products	Timber Products	Pulp, Paper, etc.	Builders Paper & Board	Meat Products	Printure Inck and Paint	Paving & Roofing Materials
Lead											X					X			X											
pH	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Manganese																X			X	X										
Mercury											X								X										
Nickel									X										X										
Zinc									X			X				X			X										
Phenols						X				X		X				X			X										
PCB$_5$																														
Aldrin																														
Dieldrin																														
Heptachlor																														
Color						X																				X				
COD						X				X	X	X	X		X		X					X	X	X	X					
Cyanide									X	X						X			X	X										
Iron										X																				
Surfactants													X																	
Aluminum																		X												
Arsenic																		X												
Settleable Solids																										X				

tants discharged, collect no less than three operating day composite samples (3)

6.6 PARAMETERS TO MEASURE

6.6.1 NPDES Requirements

Parameters required for measurement in NPDES permits are listed by industry in Table 6.1 (2). These are the parameters commonly required and are to be used as a minimum guideline where exact permit specifications do not exist.

6.6.2 Other Parameters

Application of the techniques from Section 4.4 is a rational method of establishing parameters to measure. However, if process control is desired, measure the critical constituent. For example, if a distillation tower is to be controlled, monitoring the organic carbon content of the discharge stream may provide early information of leaks in the system.

6.7 TYPE OF SAMPLE

In any program, the type of sample, either composite or grab must be established. Permit restrictions will determine the type for effluent monitoring, but for in-plant surveys both types should be considered and the most appropriate chosen. For in-plant surveys where data does not exist carry out a preliminary survey to determine the variability of individual streams to arrive at a decision on the type of sample to be collected. Collect proportional composite samples to determine the average waste water quality of each waste stream or total plant effluent, depending upon the sampling objective.

Collect grab samples in the following situations:

1. If a batch discharge is to be characterized.

2. If the flow is homogeneous and continuous with relatively constant waste characteristics so a grab sample is representative of the stream.
3. When the extremes of flow and quality characteristics are needed (e.g., for design purposes).
4. When one is sampling for a parameter which requires that the entire sample be used for analysis with no interior transfers of containers (e.g., oil and grease).
5. When sampling for parameters which change character rapidly such as dissolved gases or those which cannot be held for a long length of time before analyses (e.g., bacteria counts, chlorine, dissolved oxygen and sulfide).

6.8 METHOD OF SAMPLING

Choose manual or automatic sampling depending upon how the advantages and disavantages of the methods apply to the specific sampling program. (Refer to chapter 2). Adequate care should be exercised in sample collection, and only trained personnel should be entrusted the task of sample collection.

6.8.1 Automatic Samplers

If an automatic sampler is to be used, the actual type of sampler is determined by the constituents in the wastewater. A list of samplers and their features are given in Table 2.3. The features and techniques for use of automatic samplers are discussed in Section 2.3.2. To choose a sampler, list the features needed for sampling the type of industrial wastewater, as outlined in Section 2.3.2.3. If the variablity of the wastewater is not known or expected to be high, a multiplex feature which takes more than one sample into a single bottle is desirable. This would allow samples to be

collected at short time increments such as once every 10-15 minutes. Another possible feature would be to fill more than one sample bottle at a time interval. This multiple bottle technique would allow use of one bottle for the composite and the other for possible discrete analysis. Once the needed features have been established, the sampler which best matches these features can be selected. Available samplers may need adaptation. It is imperative that the stream be well mixed at the sampling point to avoid problems when using automatic samplers in streams with a high solids content.

6.9 VOLUME OF SAMPLE AND CONTAINER TYPE

The volume of sample to be taken is determined by the number of analyses to be performed on the sample. If this has not been determined, a grab sample volume, a minimum of 7.57ℓ (2 gal.) and an individual composite volume of 0.4ℓ (0.11 gal.) should be taken. The container type is also contingent upon the analysis to be run.

6.10 PRESERVATION AND HANDLING OF SAMPLES

This procedure is contingent upon the types of parameters to be analyzed. Follow "Guideline Establishing Test Procedures For the Analysis of Pollutants" (40 CFR 136) as amended in Federal Register, Vol. 41, No 232, December 1, 1976. Specific techniques are indicated by the parameter in US EPA's "Methods of Chemical Analyses of Water and Wastewater, 1979", (4) and Table 3.1.

6.11 FLOW MEASUREMENT

Flow measurement techniques adopted should be in relation to the sampling location, type of flow, etc. Follow the guidelines enumerated in Chapter 3 on Flow Measurements. Primary and secondary devices should be calibrated prior to taking flow measurements.

6.12 REFERENCES

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CHAPTER 7

SAMPLING AGRICULTURAL DISCHARGES

7.1 BACKGROUND

Agricultural discharges can be separated into two broad wastewater categories: 1. concentrated animal waste or manure from a confined feedlot; 2. runoff from an agricultural watershed. These two types of wastewater differ mainly in the concentration of pollutants. Runoff from fields, associated almost entirely with rainfall and snowmelt events, is characteristically much less polluted, while feedlot runoff is a highly concentrated point source. The values for constituents of field runoff depend on the amount and intensity of rainfall or snowmelt, land use, topography, soil type, use of manure or fertilizer, etc.

7.2 OBJECTIVES

There are two main objectives in sampling agricultural discharges:

1. Research - to study both field and feedlot runoff.
2. Regulatory - to monitor field or feedlot runoff or effluent from feedlot runoff treatment.

7.3 FREQUENCY OF SAMPLING

7.3.1 Feedlot Discharge

7.3.1.1 Regulatory

Follow the sampling frequency given in the discharge permit. Daily sampling is the maximum requirement in most permits.

7.3.1.2 Other

Apply the spectral analysis techniques as outlined in Section 4. . Collect preliminary data if not available by conducting one of the following (in order of preference)

a. A one week survey collecting hourly grab samples where the discharge is continuous.

b. A 24-hour survey collecting hourly grab samples.

Calculate the mean and variances as indicated in Section 4. and apply a computer program for spectral analysis (Section 4.).

7.3.2 Field Runoff

Apply the statistical methods outlined in Section 4. if possible. Collect preliminary data by sampling every 5 minutes for the duration of several runoff events (1). Collect and analyze samples individually or composite them proportional to flow, depending on the objectives of the study. Since most of the variability in the runoff occurs during the initial part of the runoff hydrograph on the rising side of flow crests, sampling is the most critical at this time.

7.4 LOCATION OF SAMPLING POINTS

7.4.1 Feedlot Discharge

Channel feedlot runoff to a central point by sloping or trenching if no treatment is provided. If treatment is provided, sample effluent from the treatment system.

7.4.2 Field Runoff

Select a site downstream of the runoff area at a point where runoff collects into a channelized flow. Use the topography of the area to locate this

point. Choose a location with sufficient depth to cover the sampler intake without excavation.

7.5 NUMBER OF SAMPLES

The number of samples for both feedlot discharge and field runoff are calculated in the following manner:

1. Follow regulatory requirements.
2. Apply the statistics in Section 4. after the mean and variance are determined through a preliminary survey (see Section 7.3).

7.6 PARAMETERS TO ANALYZE

7.6.1 Established by Regulation

Analyze all parameters required by discharge permits.

7.6.2 No Requirements

Analyze the following parameters (2,3,4):

1. Nutrients (total phosphate and nitrogen series)
2. Demand
3. Physical/Mineral (total and suspended solids)
4. Microbiological (fecal coliform and fecal streptococci)

Other analyses such as metals or pesticides may be necessary depending on the nature of the study.

7.7 TYPE OF SAMPLE

Do not collect a single grab sample due to the high variability of runoff. Collect a series of samples for analysis, or form a composite sample according to flow using one of three methods:

1. Constant sample volume, time between sampling periods proportional to stream flow.

2. Sample volume proportional to total stream flow since last sampling period; constant time between sampling periods.

3. Sample volume proportional to instantaneous stream flow rate; constant time between sampling periods.

Use method 1 whenever possible, since this technique will allow a large number of samples to be taken at high flows. Choose a flow volume increment that will not exceed the bottle supply. An automatic sampler and integrated flow measurement device is necessary for this type of sampling. Both methods 2 and 3 are acceptable also, but not preferred.

7.8 METHOD OF SAMPLING

Collect samples either automatically or manually; analyze the discrete samples separately or composite them proportional to flow. For sampling field runoff, use an automatic system activated by runoff through the flume. Typical sampling/flow measurement stations are shown in Figures 7.1 and 7.2. If feedlot runoff contains large particulate matter (e.g., corn cobs), manual sampling will be necessary.

7.9 VOLUME OF SAMPLE AND CONTAINER TYPE

Use multiple sample containers to provide the best preservation for specific parameters. For example, if the parameters given in Section 7.6.2 (nutrients, demand, physical/mineral, microbiological) are to be analyzed, three containers and three preservation techniques would be required for each sample.

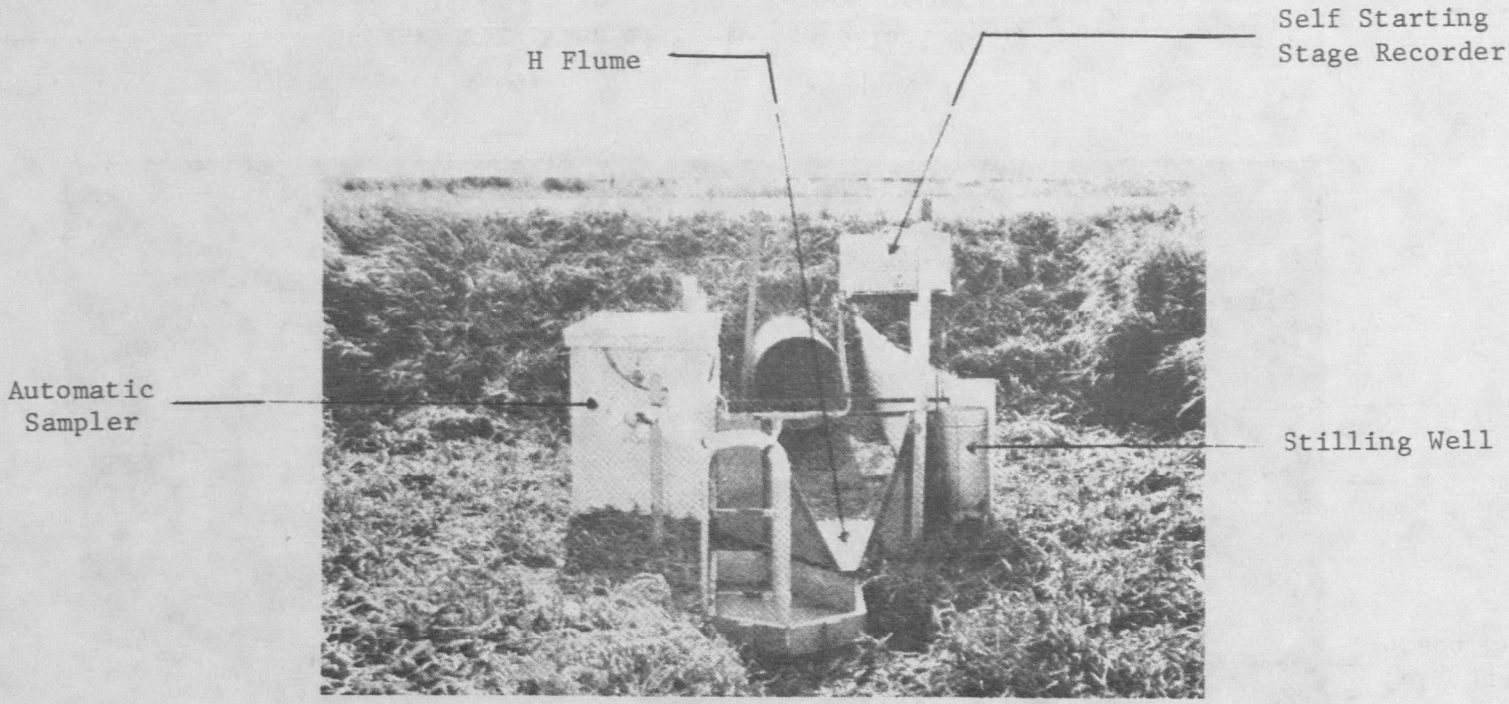

Figure 7.1 View of field installation (from 5)

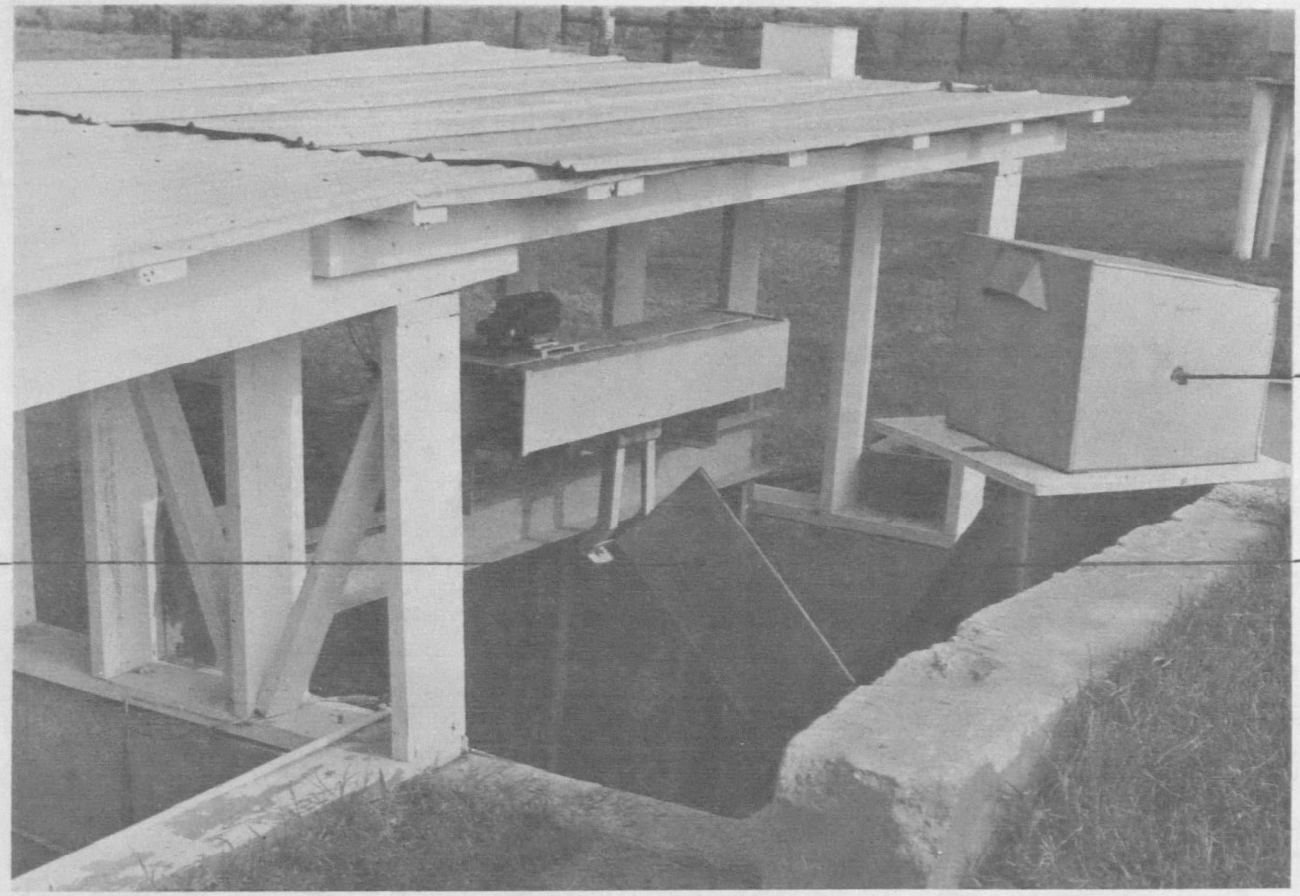

Figure 7.2 View of field installation (7)

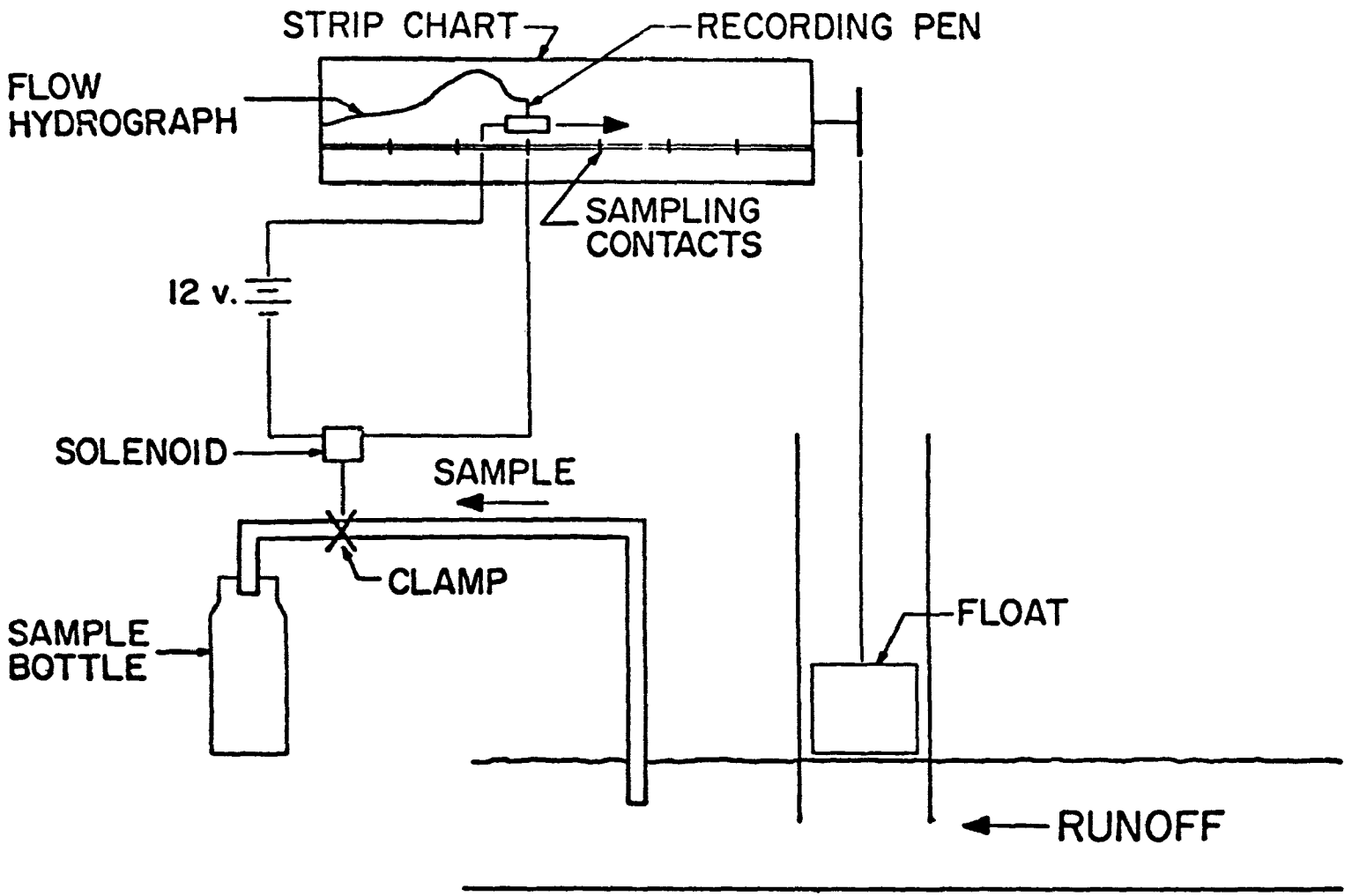

Figure 7.3. Schematic of water level recorder and sampler arrangement (from 5)

Container	Parameter Group	Technique
1	Nutrients	Add H_2SO_4 to pH 2 or 40-400 mg/l $HgCl_2$ and refrigerate at 4°C
2	Demand (Physical/Mineral)	Ice as soon as possible after collection
3	Microbiological	Collect in sterile container and ice as soon as possible

7.10 FLOW MEASUREMENT

Select the flow measurement device based on the specific application and the need for accuracy. A type H flume is advantageous because of its wide range of accuracy (3,6). The measurement instrumentation should include a continuously recording flow chart, with a pressure-sensitive record preferred to ink. A schematic of a typical installation is shown in Figure 7.3. More detailed information on flow measurement is given in Chapter 3.

7.11 REFERENCES

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CHAPTER 8

SAMPLING SURFACE WATERS, AQUATIC ORGANISMS, AND BOTTOM SEDIMENTS

8.1 BACKGROUND

The sampling of rivers and streams, estuaries, lakes and oceans, biological organisms, and their associated bottom sediments are considered in this chapter. Methods of sampling are directly affected by the objectives of the study and parameters which are to be analyzed. Therefore, the decisions regarding parameters must be made at the beginning of the study in order to develop a rational sampling program.

8.2 OBJECTIVES OF THE STUDY

The main objectives of sampling surface waters, aquatic organisms, and sediments are:

1. Evaluation of the standing crop, community structure, diversity, productivity and stability of indigenous aquatic organisms.
2. Evaluation of the quality and trophic state of a water system.
3. Determination of the effect of a specific discharge on a certain water body.

8.3 PARAMETERS TO ANALYZE

Selection of parameters is dependent on the objectives and extent of the program or study and must be performed prior to the development of the sampling plan. Surface waters and sediments are commonly analyzed for the chemical and biological parameters listed in Table 8.1.

TABLE 8.1 COMMON ANALYSES FOR SURFACE WATER, AQUATIC ORGANISMS AND SEDIMENT SAMPLING

Chemical	Biological
Dissolved Oxygen	Fish
Phosphate	Benthic Macroinvertebrates
Nitrogen Series	Periphyton
Alkalinity	Phytoplankton
Silica	Zooplankton
pH	Macrophytes
Specific Conductance	Macroalgae
Solids (TDS, TS, TSS)	
Organic Matter and Demand	
Color	
Turbidity	
Pesticides	
Heavy Metals	

8.4 LOCATION OF SAMPLING POINTS

Select the study site based on the program objectives, the parameters of interest, and the sampling units. For example, the following guidelines are suggested in the EPA Model State Water Monitoring Program (1) for selecting long-term biological trend monitoring stations:

1. At key locations in water bodies which are of critical value for sensitive uses such as domestic water supply, recreation, propagation, and maintenance of fish and wildlife.

2. In major impoundments near the mouths of major tributaries.

3. Near the mouths of major rivers where they enter an estuary.

4. At locations in major water bodies potentially subject to inputs of contaminants from areas of concentrated urban, industrial, or agricultural use.

5. At key locations in water bodies largely unaffected by man's activities.

In order to avoid bias, use one of the following random sampling plans to determine sampling points within the study site. Random sample selection is discussed in more detail in the EPA Biological Field and Laboratory Methods Manual (2).

8.4.1 Simple Random Sampling

Use a simple random sampling plan when there is no reason to subdivide the population from which the sample is drawn. Then the sample is drawn such that every unit of the population has an equal chance of being selected. First, number the universe or entire set of sampling units from which the sample will be selected. This number is N. Then from a table of random numbers select as many random numbers, n, as there will be sampling units selected for the sample. Select a starting point in the table and read the numbers consecutively in any direction (across, diagonal, down, up). The number of observations, n (sample size), must be determined prior to sampling. For example, if n is a two-digit number, select two-digit numbers ignoring any number greater than n or any number that has already been selected. These numbers will be the numbers of the sampling units to be selected.

8.4.2 Stratified Random Sampling

Use a stratified random sampling plan if any knowledge of the expected size or variation of the observations is available. To maximize precision, construct the strata such that the observations are most alike within strata and most different among strata, i.e., minimum variance within strata and maximum variance among strata. Perhaps the most profitable means of obtaining information for stratification is through a prestudy reconnaissance (a pilot study). For information on conducting a pilot study, consult the EPA Biological Methods Manual (2). Stratification is often based upon depth, bottom type, isotherms, or other variables suspected of being correlated with the parameter of interest. Select as many strata as can be handled in the study. In practice, however, gains in efficiency due to stratification usually become negligible after only a few divisions unless the characteristic used as the

basis of stratification is very highly correlated with the parameter of interest (2).

8.4.3 Systematic Random Sampling

Use a systematic random sampling plan to assure an adequate cross section while maintaining relative ease of sampling. A common method of systematic sampling involves the use of a transect or grid. However, choose a random starting point along the transect or grid to introduce the randomness needed to guarantee freedom from bias and allow statistical inference.

8.4.4 Nonrandom Sampling

Use a nonrandom sampling plan if justified by the study site, or parameters of interest, or the type of study being undertaken. For example, the following sample locations might satisfy the program objectives:

Parameter	Sampling Location
Fish	Shoreline sampling
Benthic macroinvertebrates	Right, left bank, midstream or transect
Periphyton	Shoreline sampling
Phytoplankton	Transect or grid
Zooplankton	Transect or grid
Macrophytes	Shoreline sampling or transect
Chemical	Transect or grid

8.4.4.1 Impact of Point Discharges

A transect sampling scheme may be used to determine the impact of a point discharge.

1. Place lines transecting the receiving water at various angles from the discharge point.
2. Choose sampling intervals randomly or uniformly or by the methods described in Section 8.4.4.2.
3. Choose two remote control points to use as background.
4. See Figure 8.1 for example.

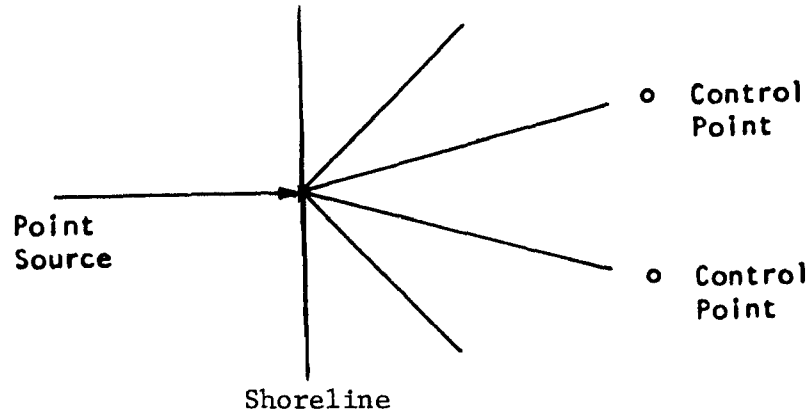


Figure 8.1 Example of transect sampling scheme in reservoirs, lakes and coastal waters

A grid sampling scheme may also be used but is not applicable to all biological parameters. Grid placement must be contained in a similar environment (e.g. all ripples or all pools) for a valid comparison.

1. Set up grids across and through the area to be sampled (i.e., in both width and depth directions versus length) as required by the program.

2. The grid size is dependent upon the degree of lateral and vertical mixing. If the amount of mixing is unknown, then take a larger number of samples across and through the stream than would be otherwise desirable.

3. Choose the number of samples randomly, uniformly or using the procedure in Section 8.4.4.2.

4. Choose a control point upstream of the grid system.

5. See Figure 8.2 for an illustration of the grid method.

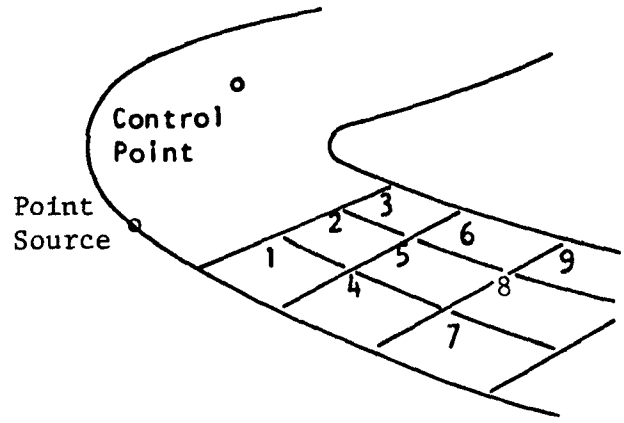


Figure 8.2 Example of grid sampling scheme in rivers

8.4.4.2 Spatial Gradient Technique

This technique may be used for the rational selection of sampling station locations (3,4). It presupposes the existence of historical data or some reasonable estimate of the expected variability of the parameters to be monitored over the region of interest, say, along the length of the river. This technique has greater applicability for chemical than biological parameters.

1. Collect historical or comparable data to estimate the mean and variance of the parameter of interest, Y.

2. Plot the maximum and minimum values of the parameter concentration versus distance along the river (Figure 8.3).

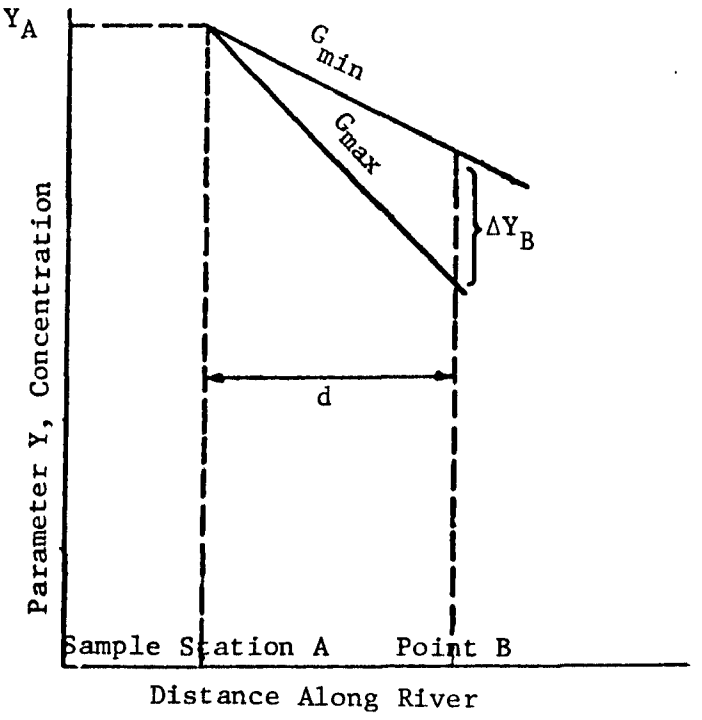


Figure 8.3 Use of spatial gradient technique for maximum spacing of sampling stations

3. Calculate a slope for both lines(G_{max} and G_{min}).

4. Determine the difference between the slopes, i.e., $G_{max} - G_{min}$

5. Determine the maximum allowable error in the estimates of the parameter value at Point B.

6. $$d_{max} = \frac{\Delta Y_{max}}{G_{max} - G_{min}}$$

7. Use this d to determine distance between points on a transect or grid in a grid pattern.

8.5 NUMBER OF SAMPLES

The following information is summarized from the EPA Biological Methods Manual (2).

8.5.1 Simple Random Sampling

Use one of the following two methods depending on the decision variable.

1. Estimation of a Binomial Proportion - An estimate of the proportion of occurrence of the two categories must be available. If the categories are presence and absence, let the probability of observing a presence of P ($0 < P < 1$) and the probability of observing an absence by Q ($0 < Q < 1$, $P + Q = 1$). The second type of information which is needed is an acceptable magnitude of error, d, in estimating P (and hence Q). With this information, together with the size, n, of the population, the formula for n as an initial approximation (n_o), is:

$$n_o = \frac{t^2PQ}{d^2}$$

   a. For $n_o > 30$, use $t = 2$. This n_o ensures with a 0.95 probability that P is within d of its true value.

   b. For $n_o > 30$, use a second calculation where t is obtained from a table of "Student's t" with $n_o - 1$ degrees of freedom. If the calculation results in an n_o, where

$$\frac{n_o}{N} < 0.05$$

   no further calculation is warranted. Use n_o as the sample size. If $\frac{n_o}{N} > 0.05$, make the following computation:

$$n = \frac{n_o}{1 + \frac{n_o - 1}{N}}$$

2. Estimation of a Population Mean for Measurement Data - In this case an estimate of the variance, S^2, must be obtained from some source, and a statement of the margin of error, d, must be expressed in the

same units as are the sample observations.

a. For $n_o > 30$, use $n_o = \frac{t^2 s^2}{d^2}$

b. For $n_o < 30$, recalculate using t from the tables, and if $\frac{n_o}{N} >$

$$n = \frac{n_o}{1 + \frac{n_o}{N}}$$

After a sample of size, n, is obtained from the population, the basic sample statistics may be calculated. If the sample size, n, is greater than 5 percent of the population ($\frac{n}{N} > 0.05$), a correction factor is used so that the calculation for the sample variance is:

$$s^2 = \frac{N-n}{N} \frac{\Sigma X_1^2 - \frac{(\Sigma X_1)^2}{n}}{n-1}$$

8.5.2 Stratified Random Sampling

Conduct a pilot study or obtain from other sources reliable estimates of the variance within strata. If historical data has been collected, use optimal allocation to determine the total number of samples.

$$n = \frac{\frac{t^2(\Sigma N_k s_k)^2}{N^2 d^2}}{1 + \frac{t^2 \Sigma N_k s_k^2}{N^2 d^2}}$$

Where t = Student's t value (use 2 for estimate)

N_k = number of sampling units in stratum k

s_k^2 = variance of stratum k

$s_k = \sqrt{s_k^2}$ = standard deviation of stratum k

N = total number of sampling units in all strata

d = *acceptable parameter error*

If no data is available, use proportional allocation to determine the total number of samples:

$$n = \frac{\frac{t^2 \Sigma N_k s_k^2}{Nd^2}}{1 + \frac{\Sigma N_k s_k^2}{N^2 d^2}}$$

Use the following equations to determine the number of samples to be collected in each stratum, n_k:

Optimal allocation: $n_k = \frac{nN_k s_k}{\Sigma N_k s_k}$

Proportional allocation: $n_k = \frac{nN_k}{N}$

8.5.3 Systematic Random Sampling

Determine the number of samples to be taken on the grid or transect using the methods given in Section 8.4.4.2 or 8.5.1.

8.6 FREQUENCY OF SAMPLING

While the frequency of sampling will often be determined by the program, use the Model State Water Monitoring Program (1) guidelines for guidance in trend monitoring (Table 8.2).

8.7 METHOD OF SAMPLING

While compositing of individual grab samples is permitted for most chemical parameters, as a rule do not composite biological samples. For biological parameters collect single grab samples in replicate.

8.8 TYPES OF SAMPLERS FOR AQUATIC ORGANISMS

Choose the type of sampler that meets the needs of the sampling program by considering the advantages and disadvantages of the sampler type. In general, equipment of simple construction is preferred due to ease of operation and maintenance plus lower expense. Advantages and disadvantages of various water bottles are shown in Table 8.3 and illustrated in Figure 8.4. This equipment is useful for chemical, phytoplankton and zooplankton sampling. Corers and bottom grabs (Tables 8.4 and 8.5 and Figures 8.5 and 8.6) are useful for sediment sampling. Nets and substrate samplers are covered in Tables 8.6 and 8.7 and Figures 8.7 and 8.8.

There are inherent advantages of using a diver for sediment sampling. The diver can ascertain what is a representative sample in addition to taking pictures and determining qualitatively the current velocity.

TABLE 8.2 MODEL STATE WATER MONITORING PROGRAM GUIDELINES FOR BIOLOGICAL MONITORING (1)

Community	Parameter	Priority[a]	Collection & analysis method[b]	Sampling frequency[c]
Plankton	Counts and identification	1	Grab samples	Once each; in spring, summer and fall
	Chlorophyll a;			
	Biomass as ash-free weight			
Periphyton	Counts and identification;	1	Artificial substrate	Minimally once annually during periods of peak periphyton population density and/or diversity
	Chlorophyll a;	2		
	Biomass as ash-free weight	2		
Macrophyton	Areal coverage;	2	As circumstances prescribe	Minimally once annually during periods of peak macrophyton population density and/or diversity
	Identification;	2		
	Biomass as ash-free weight	2		
Macroinvertebrate	Counts and identification	1	Artificial and natural substrates	Once annually during periods of peak macroinvertebrate population density and/or diversity
	Biomass as ash-free weight	2		
	Flesh tainting;	2		
	Toxic substances in tissue[d]			
Fish	Toxic substances in tissue[d]	1	Electrofishing or netting	Once annually during spawning runs or other times of peak fish population density and/or diversity
	Counts and identification;	2		
	Biomass as wet weight;	2		
	Condition factor;			
	Flesh tainting	2		
	Age and growth	2		

a Priority: 1) Minimum program; 2) Add as soon as capability can be developed.
b See EPA Biological Methods Manual. c. Keyed to dynamics of community.
d See Analysis of Pesticide Residues in Human and Environmental Samples, "USEPA, Perrine Primate Research Lab, Perrine, FL 32157 (1970)," &"Pesticide Analytical Manual," USDHEW, FHA, Wash,D.C.

TABLE 8.3 COMPARISON OF WATER SAMPLERS

Device	Application	Container Type	Advantages	Disadvantages
Nansen Bottle	Phytoplankton	Teflon lined	Able to use in series	Small volume
Kemmerer Bottle	Chemical Bacteriological Zooplankton	PVC Brass Acrylic plastic	No cross contamination	Fixed capacity from 0.4-16 L
Van Dorn Bottle	Chemical Bacteriological Zooplankton Phytoplankton	PVC	No cross contamination	Fixed capacity from 2-30 L
Simple Bottle	Chemical Bacteriological	Glass	Easy to make	Cross contamination
Pumps	Chemical Zooplankton Phytoplankton	Vanes	Large volume, samples a vertical water column, continuous sample	

TABLE 8.4 COMPARISON OF BOTTOM GRABS

Device	Advantages	Disadvantages
Ponar	Safe, easy to use, prevents escape of material with end plates, reduces shock wave, combines advantages of others, preferred grab in most cases	Can become buried in soft sediments
Ekman	Use in soft sediments and calm waters, collects standard size sample (quantitative), reduces shock wave	Not useful in rough water; not useful if vegetation on bottom
Tall Ekman	Does not lose sediment over top; use in soft sediments and calm water, standard sample size, reduces shock wave	Not useful in rough waters, others as for Ekman
Peterson	Quantitative samples in fine sediments, good for hard bottoms and sturdy and simple construction	May lose sampled material,premature tripping, not easy to close; does not sample constant areas; limited sampling capacity
Smith-Mcintyre	Useful in bad weather, reduces premature tripping, use in depths up to 1500 m (3500 ft), flange on jaws reduces material loss, screen reduces shock waves, good in all sediment types	Large, complicated and heavy, hazardous for samples to 7 cm depth only, shock wave created
Diver	Can determine most representative sampling point and current velocity	Requires costly equipment and special training

TABLE 8.5 COMPARISON OF CORING DEVICES

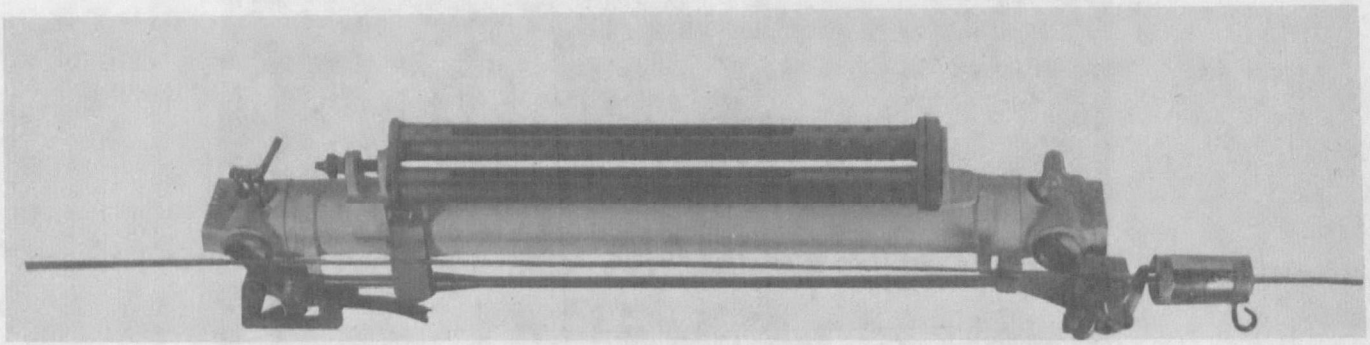
Device	Advantages	Disadvantages
Kajak or K.B. Corer	Does not impede free flow of water, no pressure wave, easily applied to large area	
Moore (Pfleger)	Valve allows sample to be held	Careful handling necessary to avoid sediment rejection, not in soft sediments
O'Conner	Can sample water with hard bottoms	Not in deep water
Elgmork's	Sample easily removed, good in soft muds, easy to collect, easy to remove sample	Not in hard sediments
Jenkins	Good in soft sediments and for collecting an undisturbed sediment-water interface sample. Visual examination of benthic algal growth and rough estimates of mixing near the interface after storms can be made	Complicated
Enequist	Good in soft/medium sediments, closing mechanism	Does not penetrate hard bottom
Kirpicenko	Soft and hard bottoms, various sizes, closes automatically	Not for stony bottoms

TABLE 8.6 COMPARISON OF NET SAMPLING DEVICES

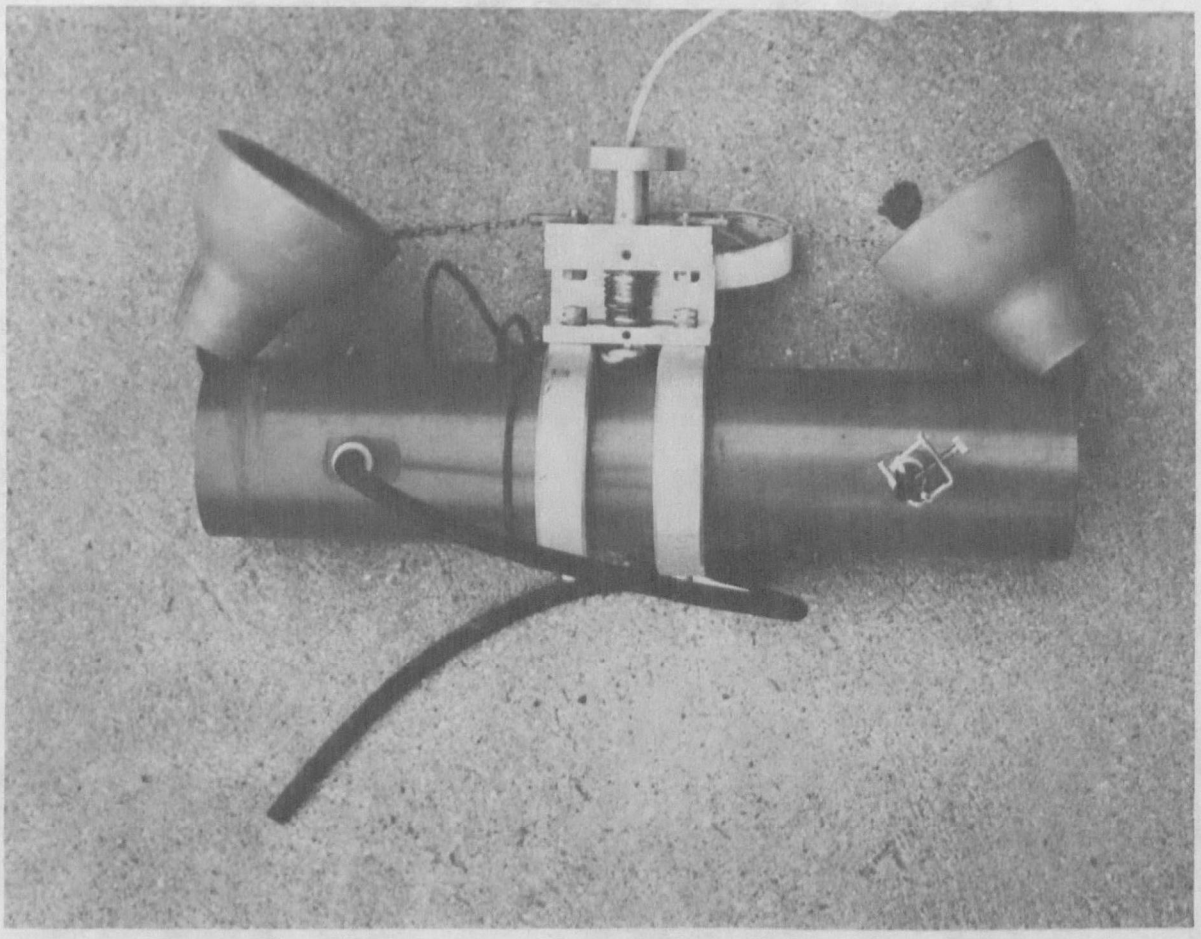
Devices	Application	Advantages	Disadvantages
Wisconsin Net	Zooplankton	Efficient shape concentrates sample	qualitative
Clarke-Bumpus	Zooplankton	Quantitative	No point sampling, Difficult to measure accurately depth of sample

TABLE 8.7 COMPARISON OF SUBSTRATE SAMPLERS

Type of Substrate	Advantages	Disadvantages
1. Artificial	Reduces compounding effects of substrate differences	---
Modified Hester-Dendy	Reduces compounding effects of substrate differences, multiplate sampler	Long exposure time, difficult to anchor, easily vandalized
Fullner	Wider variety of organisms	Same as modified Hester-Dendy
EPA Basket Type	Comparable data, limited extra material for quick lab processing	No measure of pollution on strata, only community formed in sampling period, long exposure time, difficult to anchor, easily vandalized
EPA Periphyton Sampler	Floats on surface, easily anchored, glass slides exposed just below surface	May be damaged by craft; easily vandalized
2. Natural	---	May be difficult to Quantitate
Any bottom or sunken material	Indicate effects of pollution, gives indication of long term pollution	Possible lack of growth



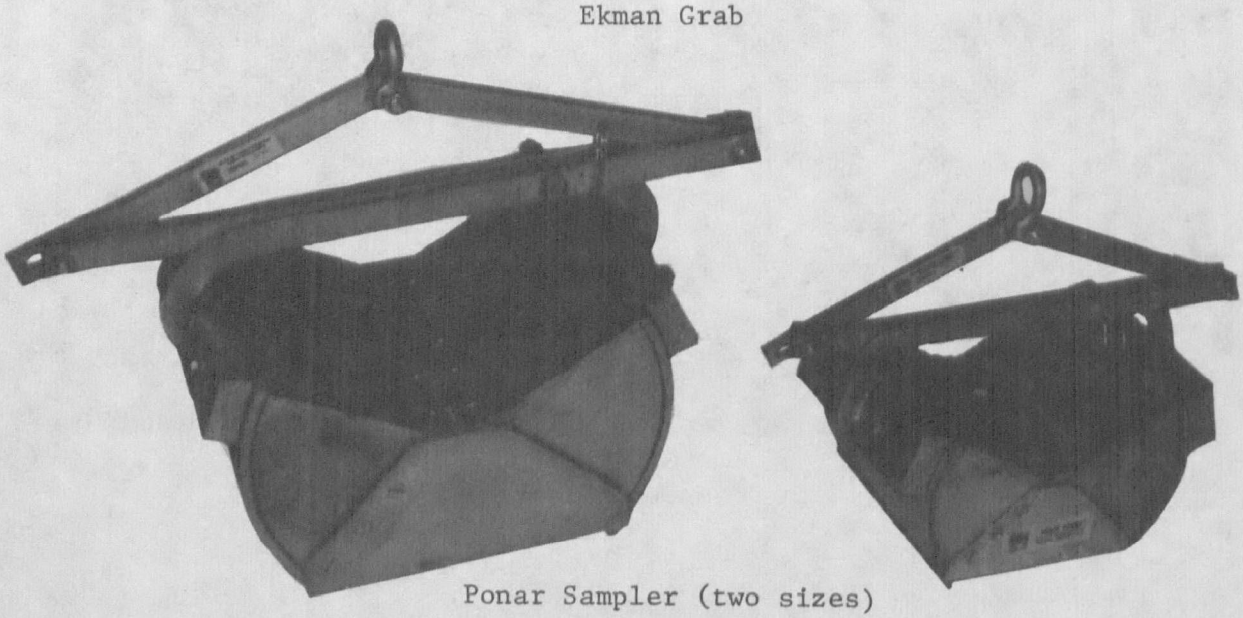
Nansen Water Bottle



Van Dorn Sampler

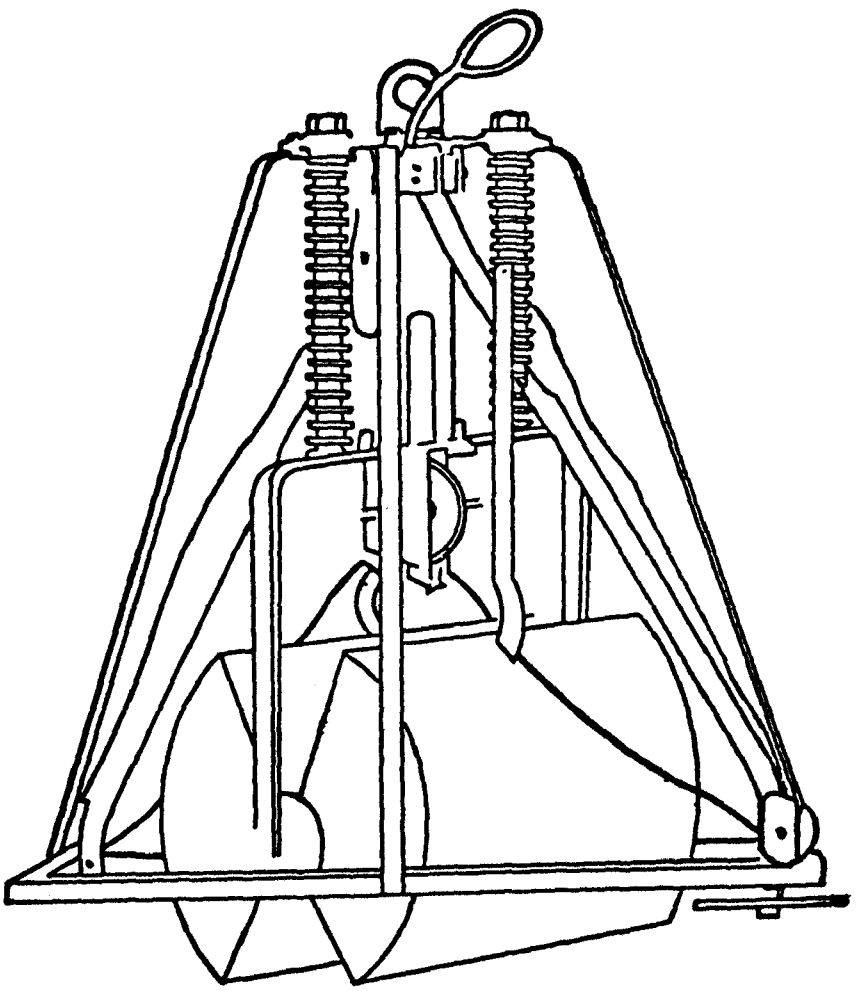
Figure 8.4 Water Bottles
(Courtesy of Wildlife Supply Co.)

Ekman Grab



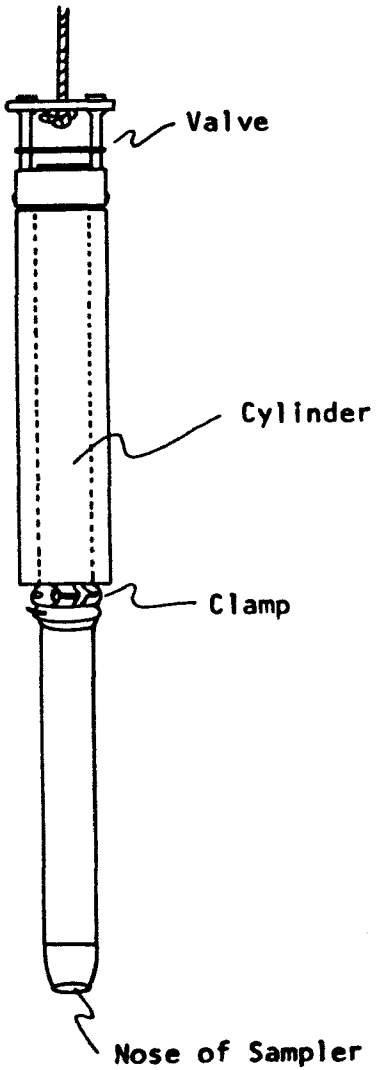
Ponar Sampler (two sizes)

Figure 8.5 Bottom Grab Samplers
(Courtesy of Wildlife Supply Co.)

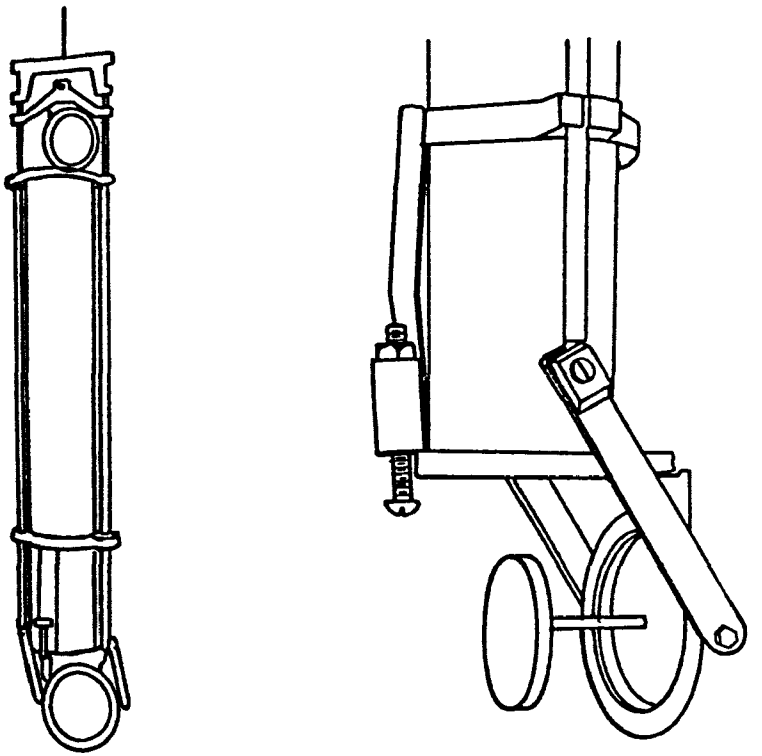


Smith-McIntyre (Aberdeen) Grab

Figure 8.5 (continued) Bottom Grabs

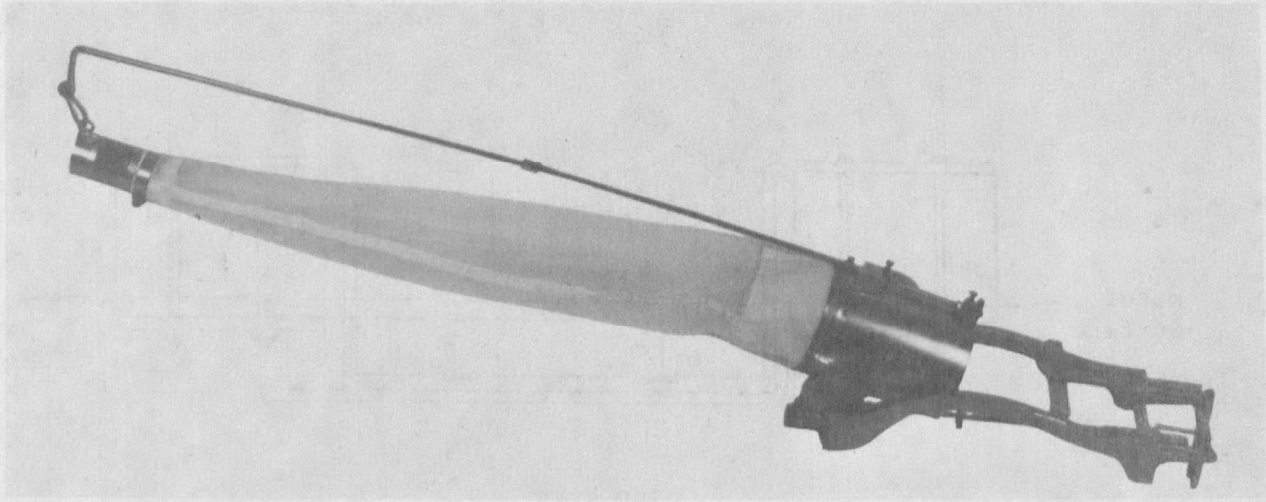


Side View-Vertical Core Sampler

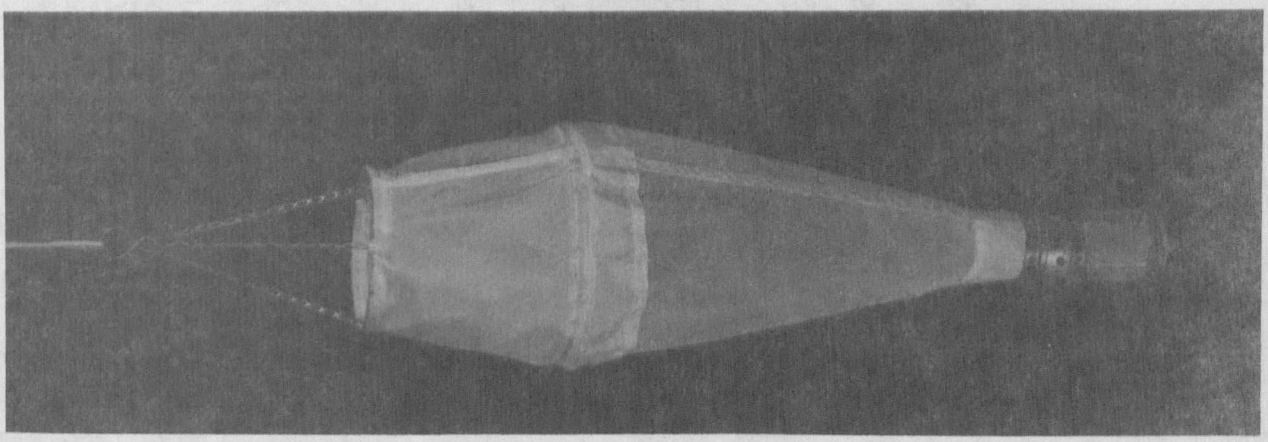


Elgmork's Core Sampler

Figure 8.6. Core samplers

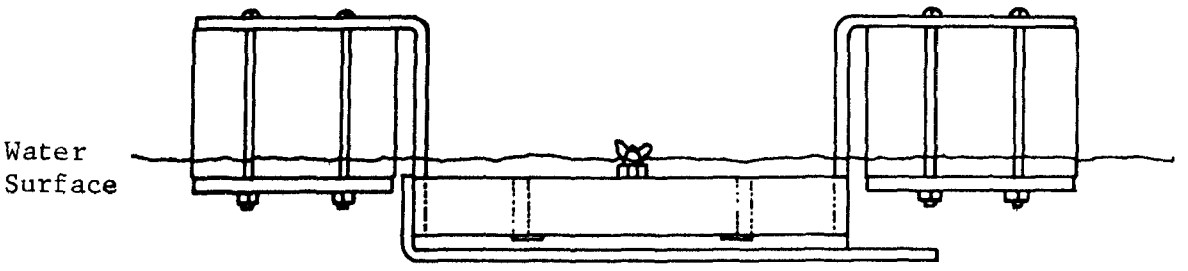


Clark-Bumpus Sampler

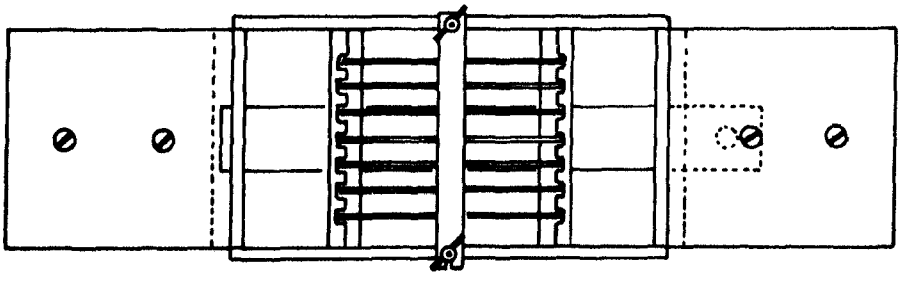


Wisconsin Net

Figure 8.7 Nets and Related Samplers



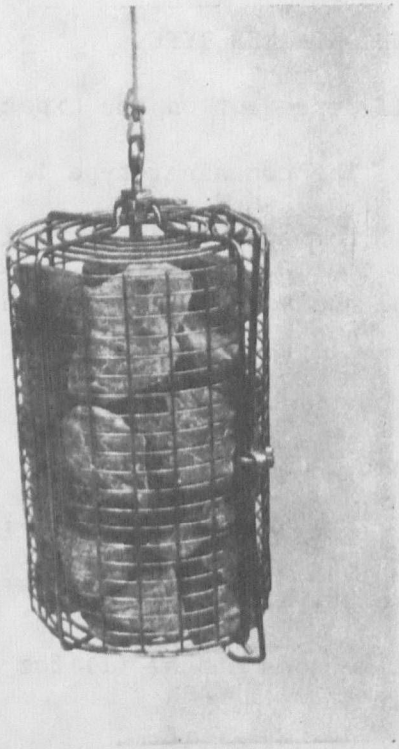
Side View



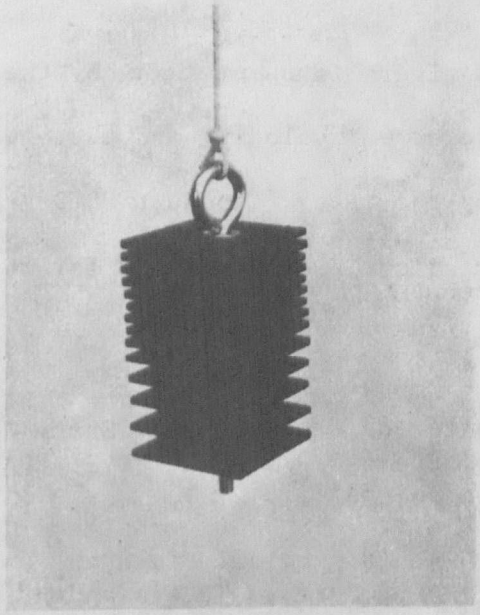
Top View

EPA Periphyton sampler. Plexiglass frame supported by two styrofoam floats. Rack holds eight glass microscope slides.

Figure 8.8 Periphyton samplers



Limestone filled basket sampler



Modified Hester-Dendy type multiple-plate artificial substrate

Figure 8.8 (Continued)

8.9 VOLUME OF SAMPLE AND CONTAINER TYPE

The size of sample is dependent on the expected amount of the chemical parameter to be analyzed. The container type is also dependent on parameter type. Refer to Section 17 for specific information relative to the chemical parameters which are to be analyzed. Refer to the Biological Methods Manual (2) for container type and sample volumes, where applicable.

8.10 PRESERVATION AND HANDLING OF SAMPLES

Refer to Section 17.1 for specific information regarding preservation and handling of samples relative to the chemical parameters to be analyzed, and to the EPA Biological Methods Manual (2) for aquatic organism preservatives.

8.11 FLOW MEASUREMENT

Flow measurement in rivers is accomplished by the combined use of a current meter to measure the stream velocity and a stage recorder to measure the surface elevation of the river. Consult USGS gaging stations for additional or historic information. See Section 3 for more details.

8.12 REFERENCES

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CHAPTER 9

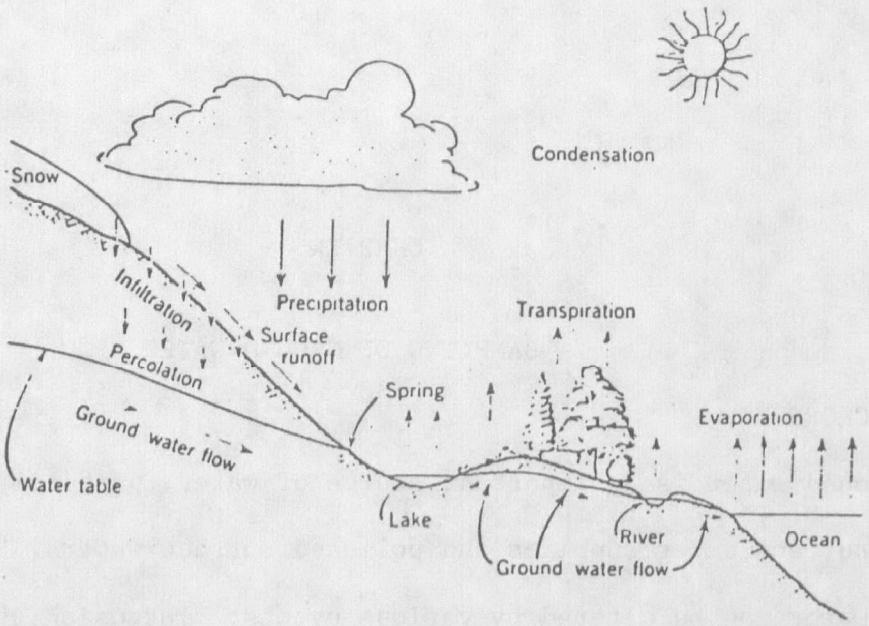
SAMPLING OF GROUND WATER

9.1 BACKGROUND

Ground water is an important source of water, particularly in regions of scarce surface water supplies and polluted surface waters. The quality of ground water can be altered by various events: intrusion of sea water, seepage from waste injection wells, leachate movement from landfill, waste-water lagoon seepage, etc. Increased use of ground waters for drinking, industrial and other purposes necessitates monitoring the quality of ground-water.

The hydrologic cycle (1) shown in Figure 9.1 illustrates the various components involved in ground waters, their interrelation and necessity of considering all components in a monitoring program. It is evident that the quality and quantity of waters entering and leaving the subsurface have an immense influence on the quality and quantity of ground water.

A comprehensive ground water monitoring program goes beyond sampling subsurface waters and includes sampling appropriate waters at the land surface (springs, ponds, lakes, rivers, lagoons, etc.), surface soils and sub-surface soils. Therefore, knowledge is required of hydrogeology, well hydraulics, geochemistry, and physical chemistry.



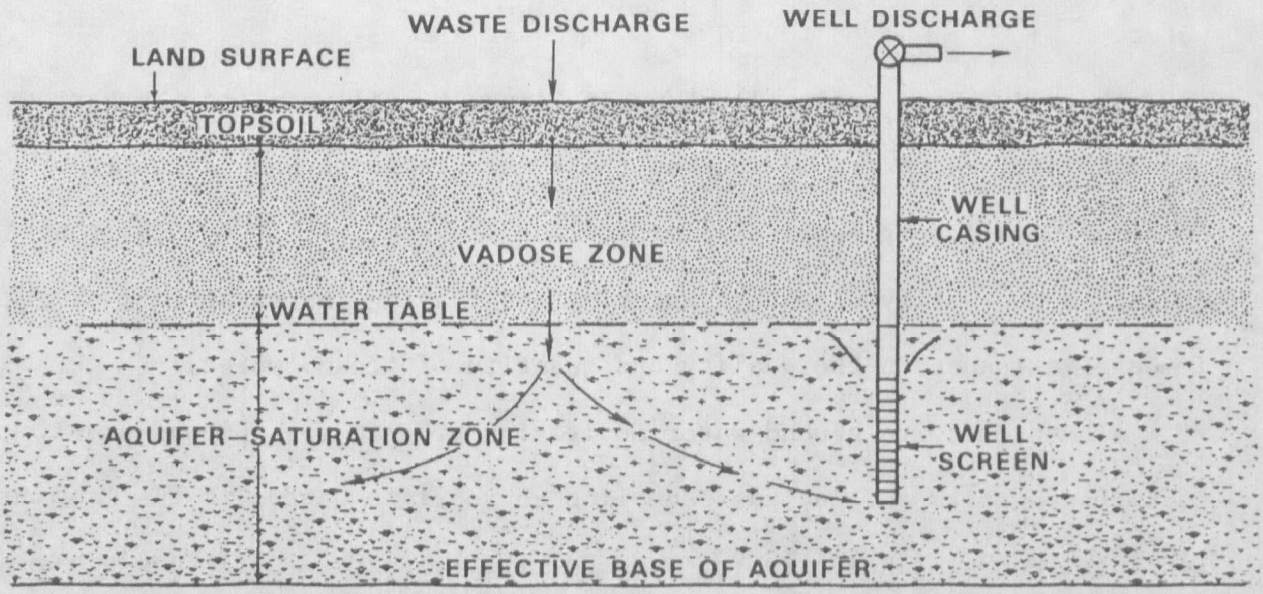


Figure 9.1 The hydrologic cycle

The subsurface environment is exceedingly complex with contrasting conditions existing at short vertical and horizontal distances from one another (2). Therefore, subsurface soil sampling is needed to assess any interactions between subsurface soil and water. These interactions can be classified into three general processes which may affect the quality of ground water:

1. Physical processes
   - . filtration
   - . dispersion
   - . dilution
   - . adsorption-desorption
2. Geochemical processes
   - . complex ion pair formation
   - . acid-base reaction
   - . inorganic redox reactions
   - . ion exchange
   - . precipitation-solution
3. Biochemical processes
   - . solute uptake in biosynthesis
   - . solubilization
   - . mineralization of organics
   - . catalysis of inorganic redox reaction

These interactions can act on substances to slow migration, increase concentrations, decrease concentrations, or alter the original substance. Without sampling and analysis of subsurface solids, the data generated by a ground water sampling program can be misinterpreted. For example, the reduction of a constituent in water percolating through a soil may be by filtration, ion exchange, biological uptake or any combination of these processes. An increase in the concentration of the constituent in the filtrate can be attributed to a change in the percolating water, a failure of the soil retention mechanism, or another water source. Without the proper solids analysis many questions arise.

What was the removal mechanism? Has the capacity of the mechanism been

exceeded or exhausted? Is the mechanism renewable? Can the increase be attributed to a leaching or solution process?

This chapter addresses the sampling of ground water in the subsurface environment with the realization that it constitutes one part of a complete ground water monitoring program.

9.2 FREQUENCY OF SAMPLING

The frequency of sampling is selected by considering the factors listed in this section.

9.2.1 Program Objectives

A program's objective can be classified as planning, regulatory, process control or research and development. In general the frequency of sampling required increases as one moves from planning to research and development.

9.2.2 Statistics

Application of statistical techniques to establish the optimum sampling frequency is dependent upon the availability of sufficient and reliable data. General guidelines are set forth in Section 4.3.1 on sampling frequency and data required for spectral analysis applications.

9.2.3 Budgetary Limitations

A sampling program is required to operate within monetary limits. These limits are reflected in three forms: (1) Manpower, (2) Sampling facilities, and (3) analytical facilities. However, because water quality changes are the result of the slow movement of water in the aquifer,frequency can be related to the direction of movement and the travel time to minimize cost.

9.2.4 Ground Water Basin Characteristics

Basin characteristics may require irregular sampling frequency. Such characteristics include:

- hydrogeology
- climatology
- seasonal variations in vegetation
- flooding
- tides

9.2.5 Other Considerations

Additional influences that affect sampling frequency include:

- seasonal utilization of surface recharge, injection or extraction sites
- sampling location in relation to elevation (e.g. topsoil, vadose zone or zone of saturation)
- non-point sources of contamination
- removal or addition of overlaying sediments by natural actions or man's activities
- geochemical properties

9.2.6 General Guidelines for Sampling Frequency

Under natural conditions, the quality of ground water will change with time. Rates of change are related to rate of flow which in turn is governed by the hydrogeologic situation. Some ground water basins unaffected by man show annual fluctuations in quality produced by seasonal variations in recharge, level changes, and discharge. Some general guidelines for sampling frequency are:

- Sanitary landfill sites, 50-100 days (4)
- Trends in water quality, annually (5)
- Salt water intrusion, frequently (6)
- Rapid changes - continuous, daily or weekly
- Sampling period to define periodic changes, every two years
- Near or down stream from a known pollution source, semi-monthly,

monthly, or bimonthly

Ground water flowing toward wells or being pumped from wells, semi-annually

9.3 LOCATION OF SAMPLING POINTS

9.3.1 General

Sampling location guidelines applicable to all ground water sampling situations cannot be devised. Each sampling program has unique characteristics based upon its geological setting as shown in Figure 9.2. Therefore, a three dimensional approach, i.e. the latitude, longitude and mean sea elevation of the sampling point must be specified.

Most sampling programs assess the potential of ground water pollution. Major sources and causes of ground water pollution, methods of waste disposal and categories of pollutant discharge are shown in Table 9.1.

9.3.2 Preliminary Investigation

A systematic investigation of an area by highly trained personnel is essential in determining the optimum location of sampling points. The type and number of professional services essential to the program of investigation will vary with the magnitude and complexity of the sampling program. As a minimum, at least one geologist is required, while those of a complex nature may require more than one geologist and other professionals such as environmental engineers, geotechnical engineers, and chemists.

A preliminary investigation should consist of:

- Determining pertinent features of geological framework.
- Characteristics of contaminants
- Man-made contingencies causing the movement of water, whether from pumping from wells, disposal of waste, or accidents that

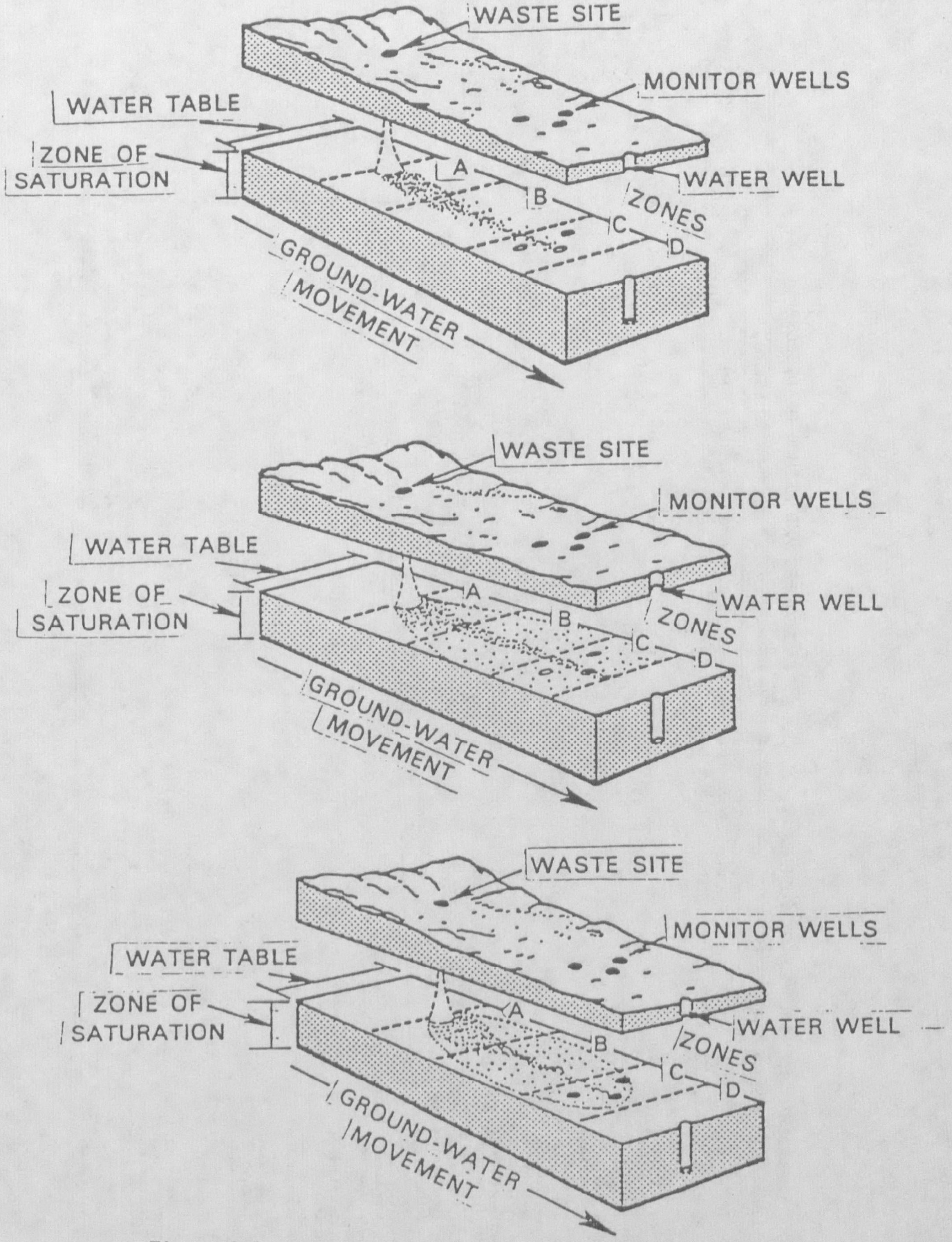


Figure 9.2 Types of Dispersion of Contaminated Wastewater

TABLE 9.1 SOURCES OF POLLUTION, DISCHARGE CATEGORIES AND METHOD OF DISPOSAL (3)

Source	Category			Common Method of Disposal						
	Point	Line	Diffuse	Percolation Pond	Surface Spreading and irrigation	Seepage Pits and Trenches	Dry Stream Beds	Landfills	Disposal Wells	Injection Wells
Municipal										
Sewer leakage	X	X		na	na	na	na	na	na	na
Sewage effluent	X	X	X	X	X		X		X	
Sewage sludge	X		X		X	X		X		
Urban runoff	X	X	X	X	X		X		X	
Solid wastes	X				X			X		
Lawn fertilizers			X		X					
Agricultural										
Evapotranspiration and leaching (return flow)			X		X					
Fertilizers			X		X					
Soil admendments			X		X					
Pesticides and herbicides			X		X					
Animal wastes (feedlots and daires)	X		X	X	X	X		X		
Stockpiles	X			na	na	na	na	na	na	na
Industrial										
Cooling water	X		X	X					X	
Process waters	X			X					X	
Storm runoff	X		X	X	X		X		X	
Boiler blowdown	X			X					X	
Stockpiles	X			na	na	na	na	na	na	na
Water treatment plant effluent	X			X				X	X	
Hydrocarbons	X			X					X	X
Tank and pipeline leakage	X	X		na	na	na	na	na	na	na
Oilfield wastes										
Brines	X	X	X	X	X	X	X			X
Hydrocarbons	X			X					X	X
Mining wastes	X	X	X	X			X	X	X	X
Miscellaneous										
Polluted precipitation and surface water		X	X	na	na	na	na	na	na	na
Septic tanks and cespools			X		X	X		X		
Highway deicing		X		na	na	na	na	na	na	na
Seawater intrusion			X	na	na	na	na	na	na	na

cause pollution.

Sources of geologic information are the United States Geological Survey (USGS), United States Soil Conservation Service, state geological agencies, local health departments, universities, commercial geotechnical firms, and professional societies.

The location and characteristics of past, present and future developments can be determined from various maps and studies produced by government agencies and private concerns. Land use plans, areawide assessments, transportation studies, open space plans, and zoning plats are a few examples. Such items as sewers, lagoons, storage facilities, mining activities, agriculture activities, and flood protection facilities should be examined.

When necessary geophysical methods should be utilized to confirm and expand existing information. These methods can be classified under two general categories: (1) surface and (2) subsurface investigations.

9.3.2.1 Surface Investigation

Surface investigation of subsurface conditions by geophysical methods in this category is at best an estimate of the extent of contamination underground. These methods however are useful as a complement to existing information and are economically attractive when compared to subsurface investigative methods.

Geophysical methods are based on the measurement or detection of physical properties and consist of seven basic types of geophysical measurements:

- Electrical - resistivity measurement which relates soil characteristics to extent of mineral contamination
- Seismic - change in the propagation of sound from small explosion to determine degree of porosity of soil
- Radioactive - gamma and beta measurements to determine the degree of natural radiation or from other radioactive sources.

- Thermal - temperature measurement to indicate dilution from a pollutant source
- Gravity - change in density of material
- Magnetic - detection of magnetic pollutants
- Electro-magnetic - remote sensing of electromagnetic energy from earths surface.

These measurements are interpreted in terms of porosity, water content, density, mineral content, water quality and geologic formation. Correct interpretation usually requires auxiliary subsurface investigation. The electrical resistivity and seismic refractory methods are most commonly employed.

After assessing available information and the data collected, and taking into account the sampling program objectives, the need for subsurface investigation should be determined.

9.3.2.2 Subsurface Investigation

Regardless of the methods utilized in subsurface investigations, a hole or shaft in the earth is required. The exploration is conducted at the surface by placement of equipment in the hole or shaft. Both existing and new-made wells and test holes are commonly chosen as access points for the subsurface equipment. Wells can be constructed by the following principles: (1) dug, (2) augered (3) driven, (4) jetted, and (5) drilled.

A prudent approach is utilization of existing wells when possible and correlation of the data and measurements gathered through them with preexisting information to determine the necessity and location of new holes or wells.

Geophysical measurements obtainable from a test hole or well include:

- potential logging
- resistivity logging
- temperature logging
- radioactive logging
- caliper logging

The preexisting information, surface investigation data and subsurface investigation data should be correlated to determine the necessity, extent and location of ground water sampling points required to meet the program objectives.

9.3.3 Vertical and Horizontal Sampling Points

Consider the following factors for location of sampling points:

. Ground water movement - movement of water from a high to low gradient stagnant areas, movement induced by sampling and production wells, and inflow-outflow from surface water. Tracers in ground water have limited value; chlorides and tritium move with water, dyes and cations sorb on earth materials.

. Horizontal placement - Govern the number and placement of wells by the geohyrologic conditions and the disposal operation of the pollution source. The routine practice of placing wells in a circle around the site may not be acceptable. Use a minimum of 2 or 3 wells when the direction of movement is known. For refuse disposal sites (8), use:

  (a) up-land sites - place wells within the site and below the refuse cells

  (b) valley floor sites - place wells outside the site and on the down flowside.

Vertical placement - locate withdrawal point at a representative depth; to average concentration gradients or at a depth commensurate with the objective, e.g. early detection of salt water intrusion. Well depth should be at a depth to collect samples regardless of seasonal fluctuation in the water table. Contaminated water from waste site tends to be more concentrated in upper part of zone of saturation; salty water lower part.

9.3.4 Representative Samples

- Sample Collection - Pump from well until temperature, pH, and specific conductance are constant; standby, observation, new or little used wells may require one day of pumping. At a minimum pump until pH is constant.
- Cased Wells - Backfill and plug with cement the annular space between the zone of saturation and the surface to avoid contamination from drilling muds and additives.
- Pump Type - Do not use airlift pumps when analyzing for such parameters as pH, carbonate, bicarbonate, temperature, and purgeables.
- Preservation - Preserve samples for organic analyses according to EPA procedures (4°C)-do not acidify since this procedure enhances volatilization of undissociated fatty acids, precipitates humic-like organics and facilitates hydrolysis and oxidation of complex organics.
- Trace Metal Samples - Use plastic construction for well casing material. Most wells already contain metallic casing, screens, and pump column, therefore minimize contact time with walls.
- Contamination - Avoid contamination of the sample from soil bacteria, particulate matter, and atmospheric oxygen.
- Small Springs - Collect samples from small springs in unconsolidated deposits by driving a well point or slotted pipe to a depth of 1 meter or less into ground adjacent to spring.
- Large Springs - Sample from large springs in consolidated rock rather than other types of springs. Sample spring in upswelling water by forcing a bottle held by hand or attached

to a rod for oxygen contaminated sample. Use a thief sampler for manual metal sampling or collect samples using an all plastic submersible electrical pump and garden hose. Dissolved Parameters - Filter water through a 0.45 μ filter; some metals, i.e. iron and manganese, form colloidal particles that pass through this filter. Use a 0.1 μ filter to correct this problem.

9.4 PARAMETERS TO MEASURE

9.4.1 General

The analyses performed on samples should be a function of the sampling program objective. Some analyses must be performed in situ or on site and others in the laboratory.

Table 9.2 shows the classification of pollutants and pollution indicators in ground water. Table 9.3 summarizes major inorganic pollutants and pollution indicators in the ground water. Table 9.4 shows the relation between pollution sources and pollution types.

9.4.2 Parameters for Planning Objectives

The data required for planning should be of a general nature. The parameters utilized for collecting data should generally not indicate specific pollution problems but overall water quality and quantities of an area. Some commonly employed measurements are:

pH	nitrate
oxidation reduction potential	chloride
total coliforms	water level
total dissolved solids	TOC

TABLE 9.2 CLASSIFICATION OF POLLUTANTS AND POLLUTION INDICATORS IN GROUNDWATER

Physical	Organic Chemical	Inorganic Chemical	Bacterio-logical	Radio-logical
Temperature	Carbon	Major constituents	Coliform group	Gross alpha activity
Density	Chlorophylls	Other constituents	Pathogenic micro-organisms	Gross beta activity
Odor	Extractable organic matter	Trace elements	Enteric viruses	Strontium
Turbidity	Methylene blue active substances	Gases		Radium
	Nitrogen			Tritium
	Chemical oxygen demand			
	Phenolic material			
	Pesticides (insecticides and herbidides)			

TABLE 9.3 INORGANIC CHEMICAL POLLUTANTS AND POLLUTION INDICATORS

Pollutant or Pollution Indicator				
Major	Others	Drinking Water Trace	Other Trace	Gases
calcium	silica	iron	vanadium	methane
magnesium	boron	manganese	molybdenum	hydrogen sulfide
sodium	fluoride	arsenic	bromide	carbon dioxide
potassium	nirogen forms	barium	iodide	dissolved oxygen
carbonate	phosphorus forms	cadmium	nickel	residual chlorine
bicarbonate	hardness	hexavalent chromium	aluminum	organic purgeables
sulfate		copper	cobalt	
chloride		cyanide	lithium	
nitrate		lead	sulfide	
total dissolved solids		selenium	beryllum	
pH		silver		
electrical conductivity		zinc		
oxidation potential		mercury		

TABLE 9.4 *RELATION BETWEEN POLLUTION SOURCES AND POLLUTION TYPES*

Source	Physical	Inorganic Chemical	Trace Elements	Organic Chemical	Bacterio-logical	Radio-logical
Municipal						
Sewer leakage	minor	primary	secondary	primary	primary	minor
Sewage effluent	minor	primary	secondary	primary	primary	minor
Sewage sludge	minor	primary	primary	primary	primary	minor
Urban runoff	minor	secondary	variable	primary	minor	minor
Solid wastes	minor	primary	primary	primary	secondary	minor
Lawn fertilizers	minor	primary	minor	minor	minor	minor
Agricultural						
Evapotranspiration and leaching	minor	primary	minor	minor	minor	minor
Fertilizers	minor	primary	secondary	secondary	minor	minor
Soil amendments	minor	primary	minor	minor	minor	minor
Pesticides	minor	minor	minor	primary	minor	minor
Animal wastes (feedlots & dairies)	minor	primary	minor	secondary	primary	minor
Stockpiles	minor	primary	minor	variable	variable	minor
Industrial						
Cooling water	primary	minor	primary	minor	minor	minor
Process waters	variable	primary	primary	variable	minor	variable
Storm runoff	minor	secondary	variable	primary	minor	minor
Boiler blowdown	primary	secondary	primary	minor	minor	minor
Stockpiles	minor	primary	variable	variable	minor	variable
Water treatment plant effluent	minor	primary	secondary	minor	minor	minor
Hydrocarbons	secondary	secondary	secondary	primary	minor	minor
Tank & pipeline leakage	variable	variable	variable	variable	minor	variable

(continued)

TABLE 9.4 (continued)

Source	Physical	Inorganic Chemical	Trace Elements	Organic Chemical	Bacterio-logical	Radio-logical
Oilfield wastes						
Brines	primary	primary	primary	minor	minor	minor
Hydrocarbons	secondary	secondary	secondary	primary	minor	minor
Mining wastes	minor	primary	primary	cariable	minor	variable
Miscellaneous						
Polluted precipitation and surface water	variable	variable	variable	variable	variable	variable
Septic tanks and cespools	minor	primary	minor	secondary	primary	minor
Highway deicing	minor	primary	minor	secondary	minor	minor
Seawater intrusion	primary	primary	primary	minor	minor	minor

9.4.3 Parameters for Regulatory Objectives

Parameters employed for regulatory purposes are used in the areas of permit compliance, surveillance, pollution detection and water quality assessment. The parameters selected or specified for measurement should be a direct function of the process or discharge under consideration. In addition to parameters that may be listed in a permit, minimum standards are set under legislation such as the Federal Water Pollution Control Act, the Safe Drinking Water Act and the Resource Conservation and Recovery Act.

9.4.4 Parameters for Process Control Objectives

Process control parameters may be viewed by the relations the process has to ground water. The ground water may function as a water source or disposal method or both. For example: a water to be used for non-potable purposes should not require the same analyses as when potable purposes are intended; parameters appropriate for assessing the effects of aquifer recharge with municipal waste water would not be appropriate for assessing the effects of a sanitary landfill on aquifer quality.

9.4.5 Parameters for Research and Development Objectives

Parameter selections for research and development needs are usually more specific and involve fewer numbers than the previous categories. This is the result of the nature of the research and development work, i.e. an area of limited extent.

9.5 TYPE OF SAMPLE

9.5.1 General

Collect ground water samples by manual or composite methods as discussed in Chapter 2 or by accumulation columns in Chapter 12. Manual grab samples are most commonly collected since movement of water is slow and water quality does not normally exhibit sudden drastic changes.

9.5.2 Grab Samplers

Collect grab samples by one of the following methods: (1) transport the water to the surface in a container, (2) transport the water through a closed conduit and discharge on the surface, and (3) construct tile or ditch lines for relatively high water tables.

9.5.2.1 Container Transport

Collect ground water samples with a depth integrated or point sampler.

A depth integrating sampler shown in Figure 9.3 (9) is simply a container equipped with a holding and submerging mechanism which collects water throughout the vertical profile. Other depth integrating samplers known as bailers (10,11) Figures 9.4a and 9.4b, are lowered through the water and are filled through the bottom inlet which contains a check valve for retaining water when retrieved.

Use point samplers to collect a sample at a specific depth. Two types are the flow-through and water-tight samplers. Flow-through samplers are shown in Figures 9.5.a(12), 9.5.b(13), 9.6.a, and 9.6.b(14). Water tight samplers are shown in Figure 9.7 (9).

9.5.2.2 Closed Conduit Transport

Use a pump, compressed gas or a vacuum to transport the water sample to the surface. **Do not use vacuum systems for organic purgeables.**

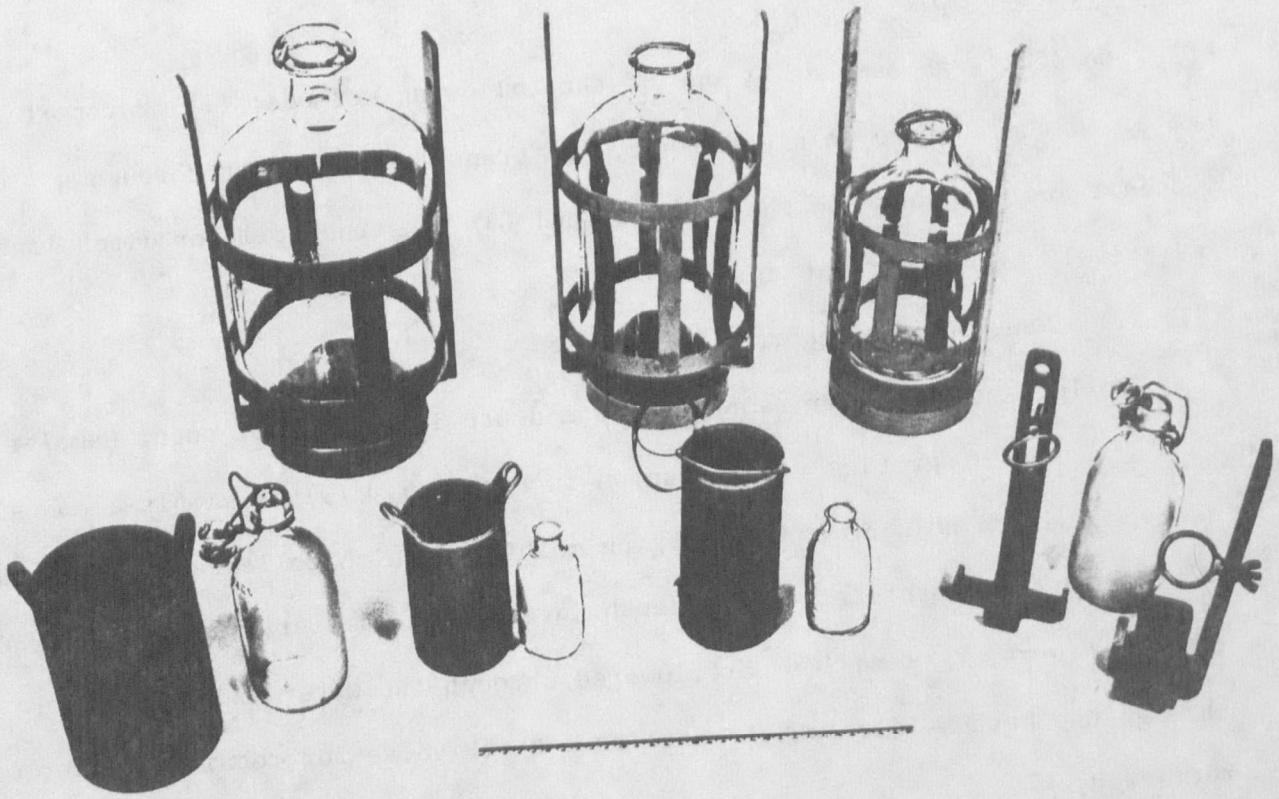
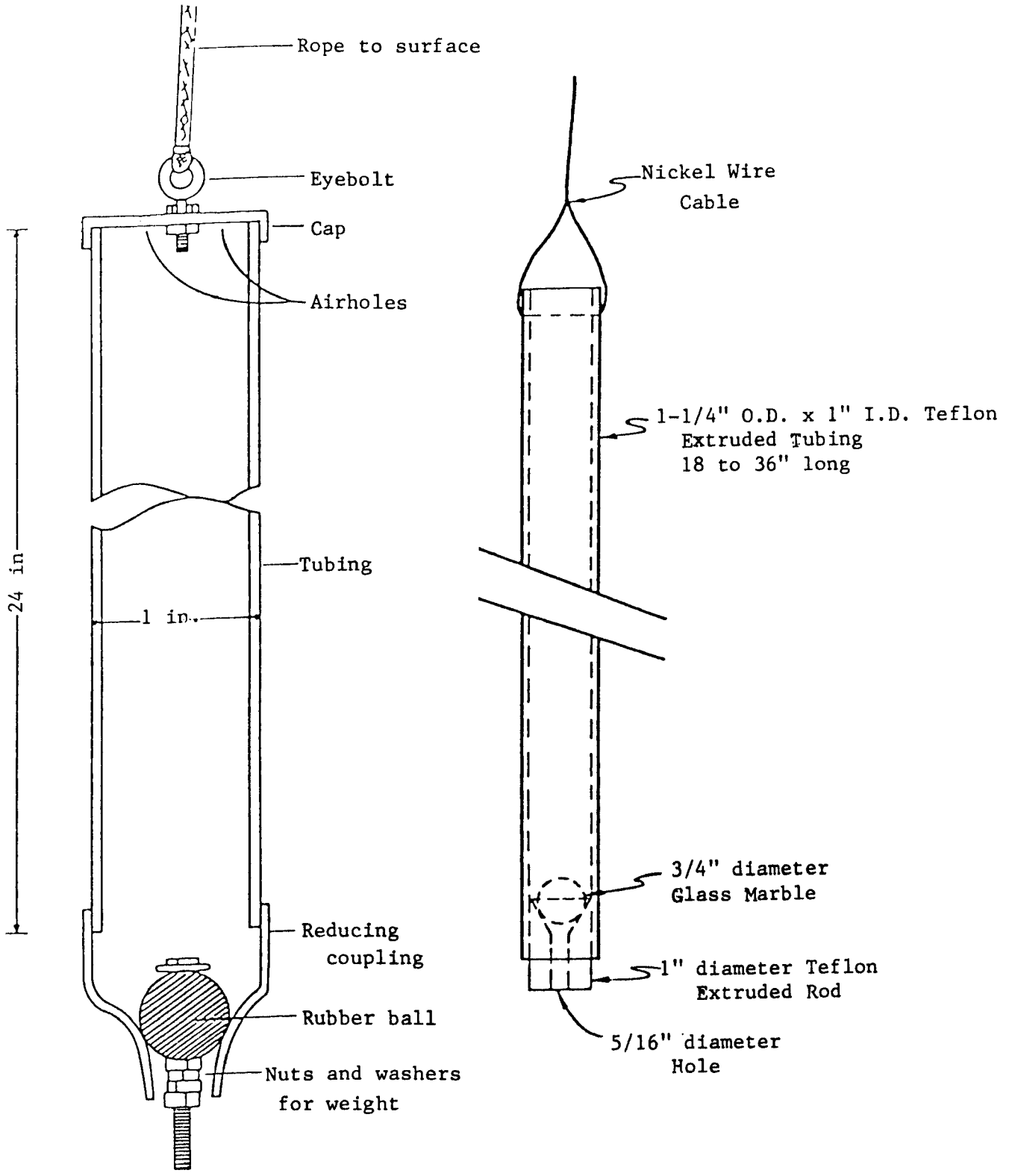


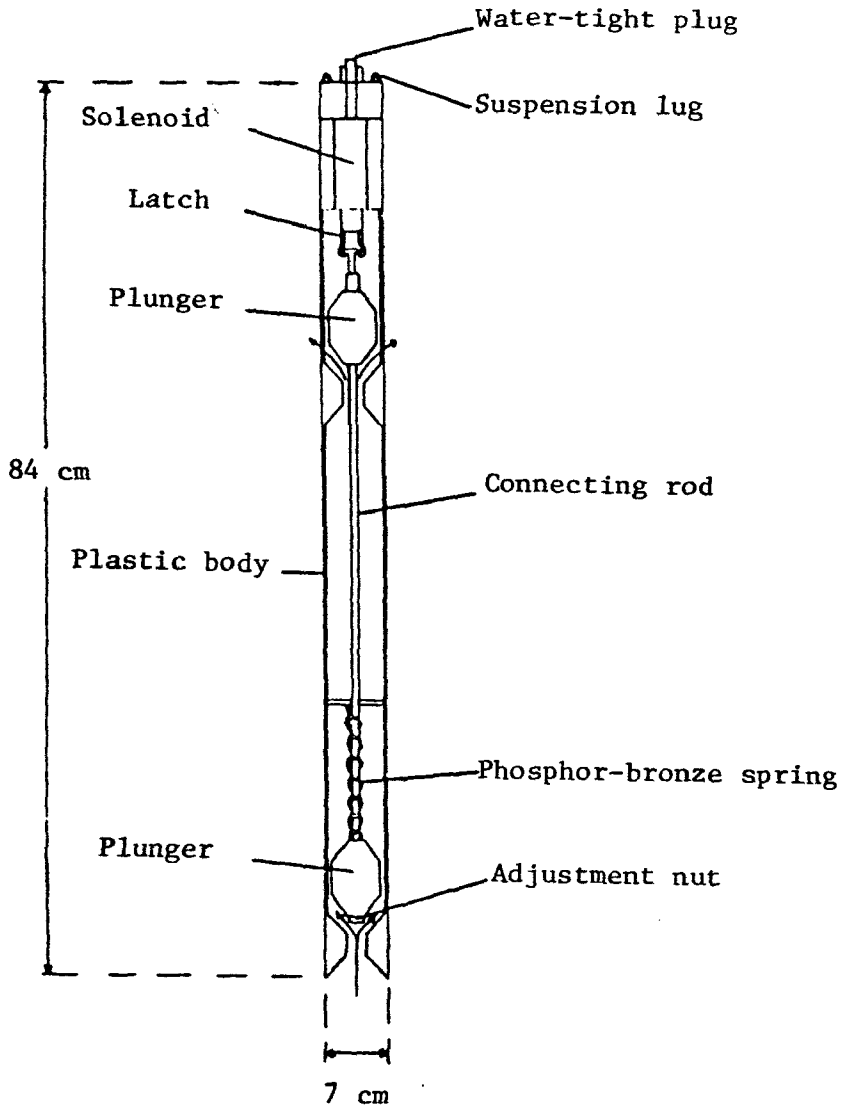
Figure 9.3 Depth-integrating samplers



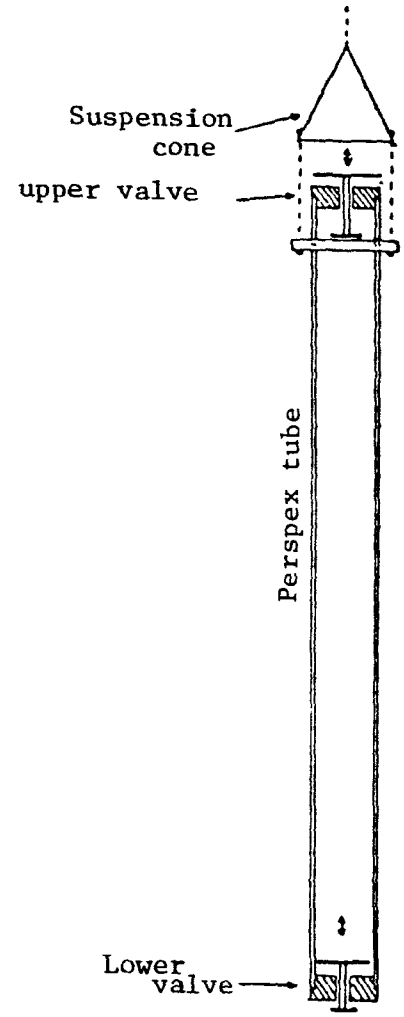
a. Depth-integrating bailer

b. EPA bailer

Figure 9.4

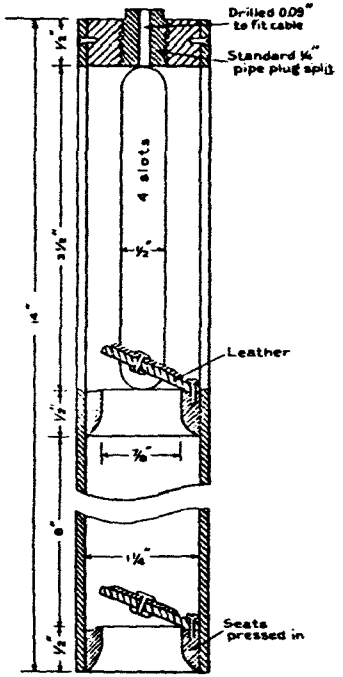


a. Tate Sampler

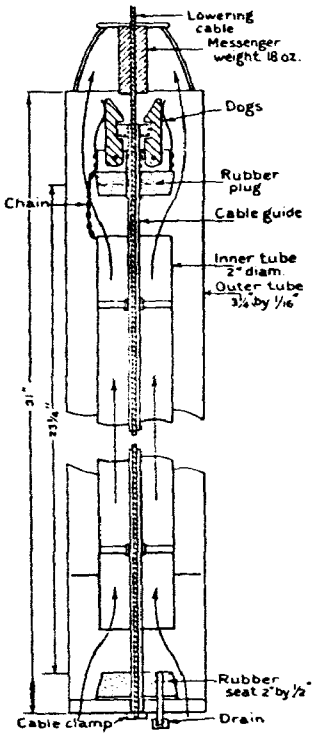


b. Frost Sampler

Figure 9.5 Point Flow-through Samplers



a. Flap type



b. Thief type

Figure 9.6 Point Flow-through USGS Samplers

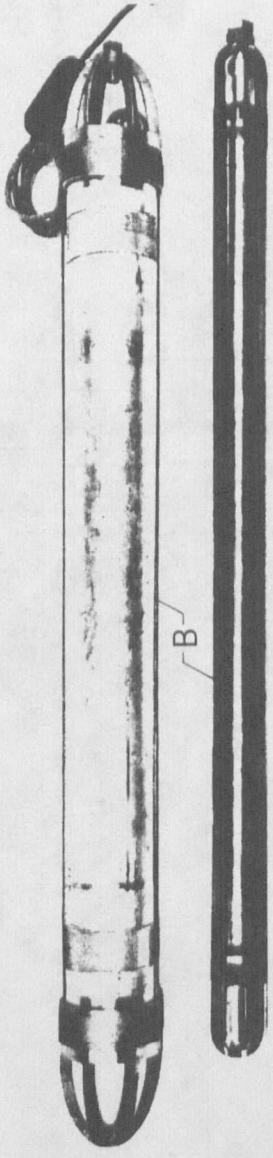


Figure 9.7 Ball-valve Samplers

Wells permanently equipped and continuously flowing may be sampled from a tap in the conduit; submersible electrical pumps and pitcher pumps (up to 23 feet head) may be used where applicable to pump water to the surface.

Use pressure or vacuum (not purgeables) lysimeters to collect samples from the vadose zone, i.e., the zone above the water table. (15, 16, 17, 18) This device consists of a porous ceramic cup equipped with a small diameter PVC pipe (not for organics) for sample accumulation as shown in Figures 9.8.a, 9.8.b, and 9.8.c. Operation consists of applying a slight vacuum to the cup during filling, releasing the vacuum, and applying pressure to the cup to transport the water to the surface. Excessive pressure will cause air bubbling with loss of dissolved gases in the sample.

Use a piezometer installed in a boring, Figure 9.9 (19), to also collect water from the vadose zone utilizing either an air lift, Figure 9.10.a (20) or pressure system, Figure 9.10.b, to transport water to the surface.

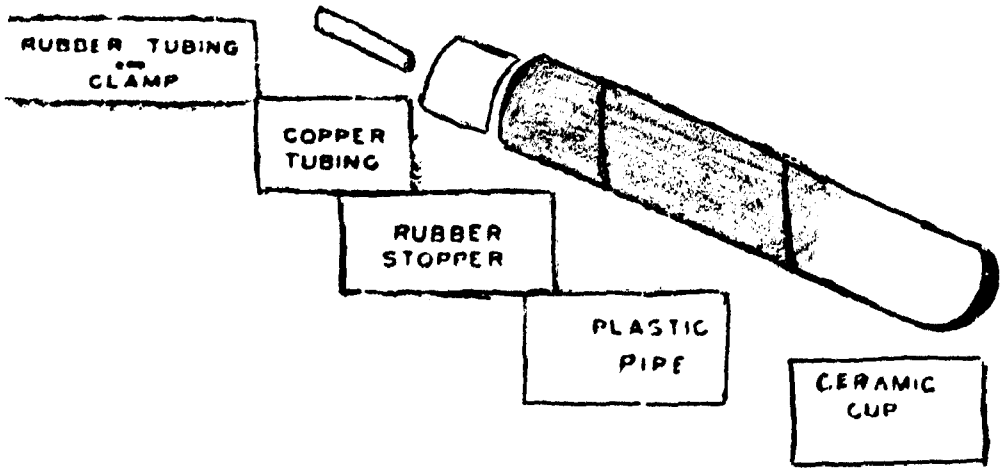


Figure 9.8.a Wallahan Lysimeter

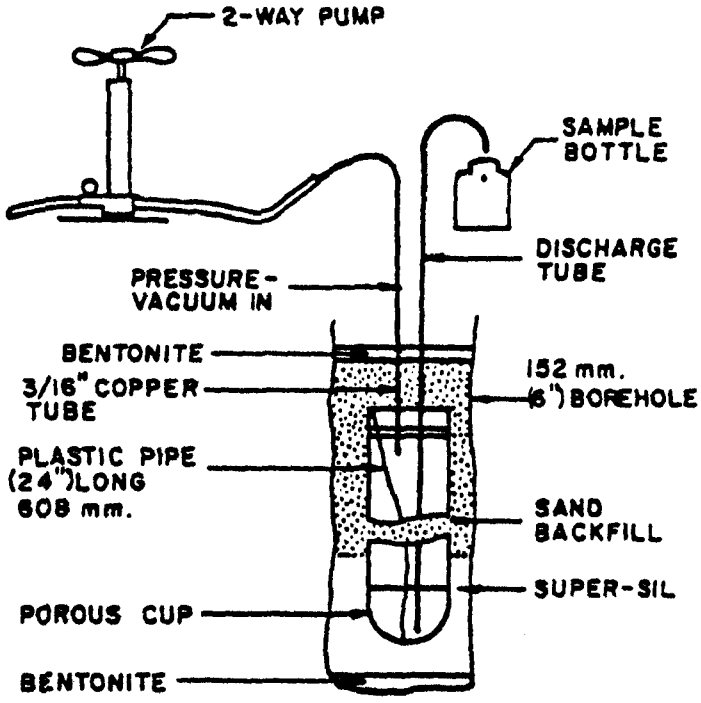


Figure 9.8.b Parizek and Lane Lysimeter

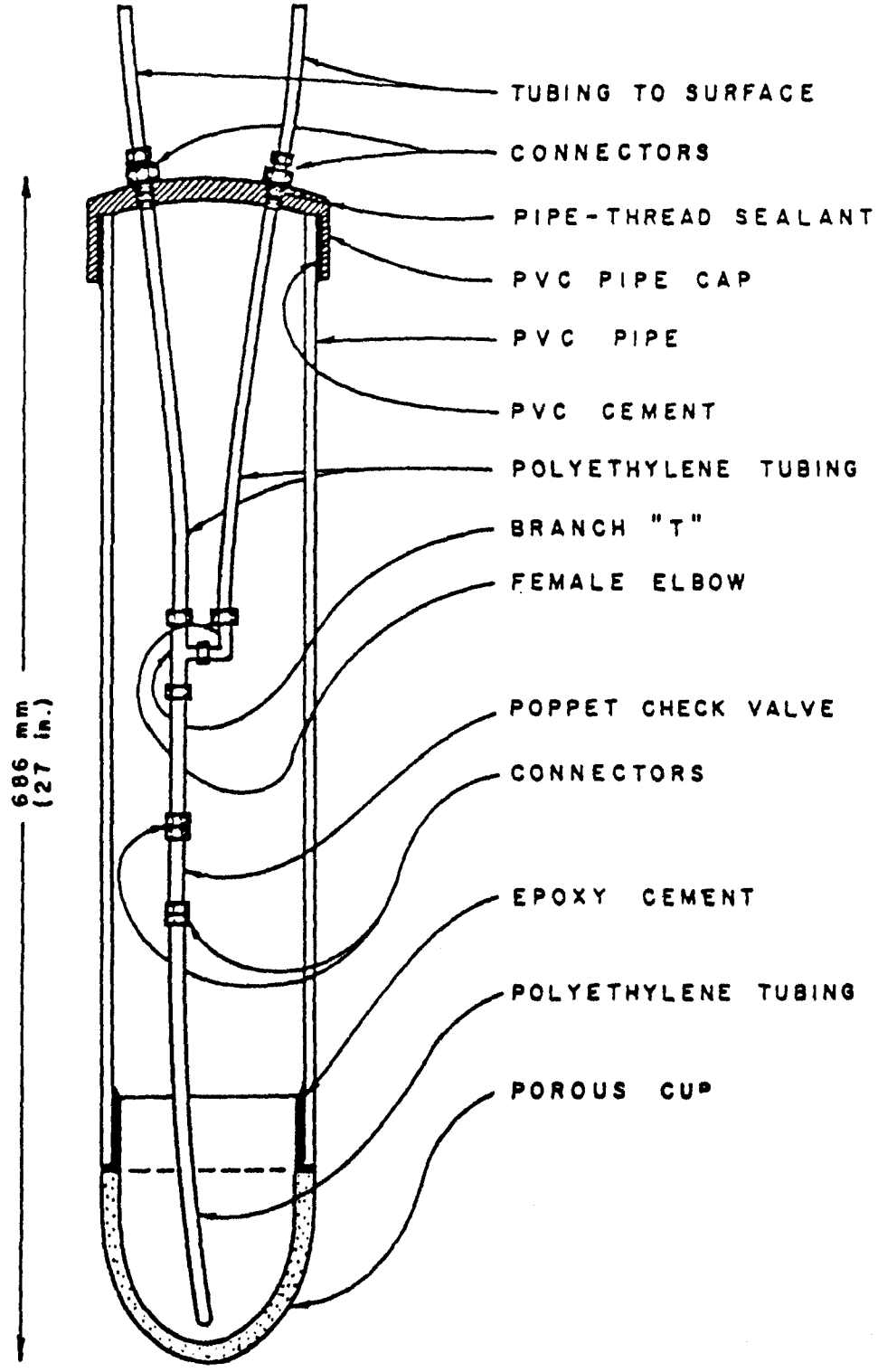


Figure 9.8.c Wood Lysimeter

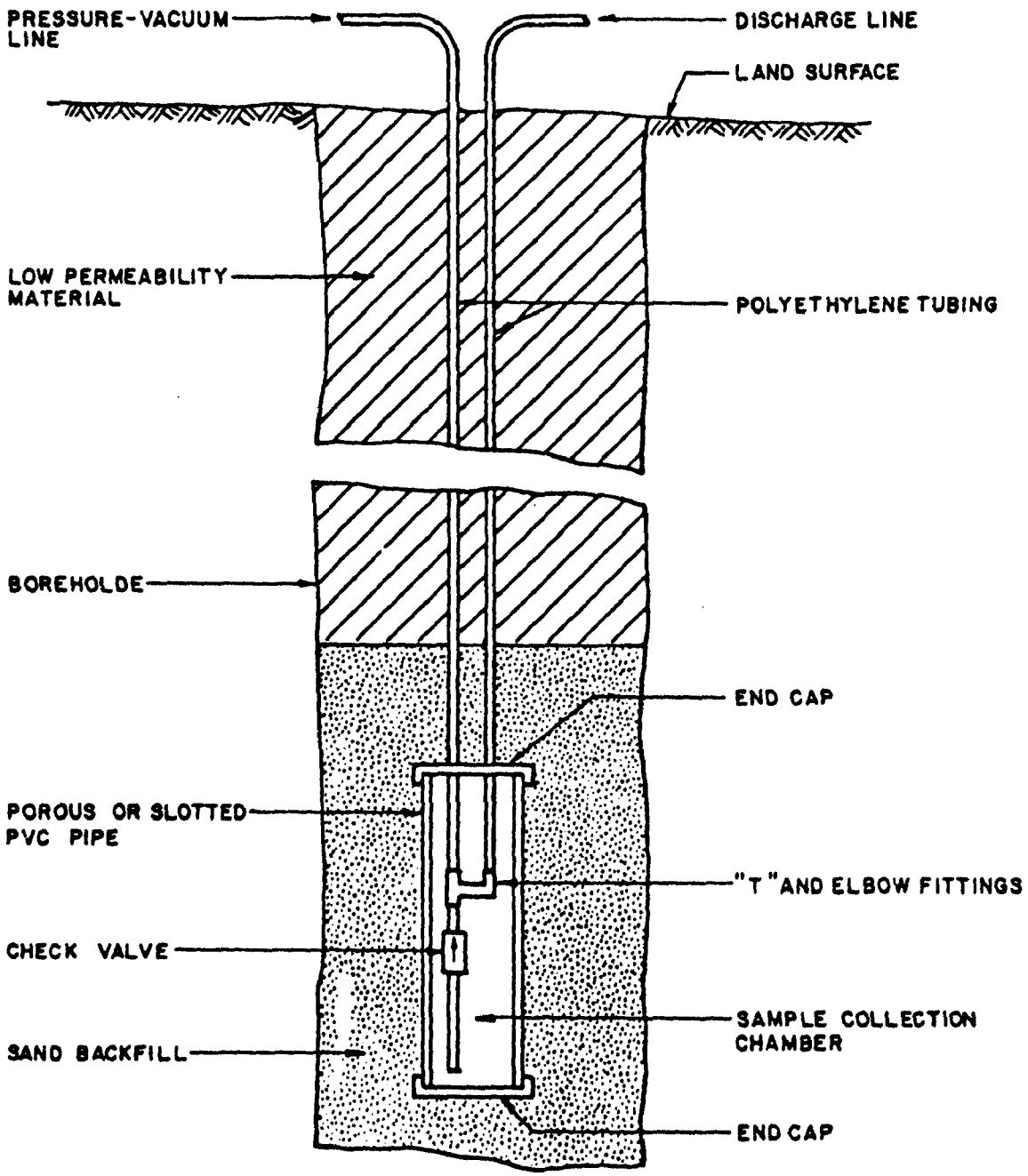
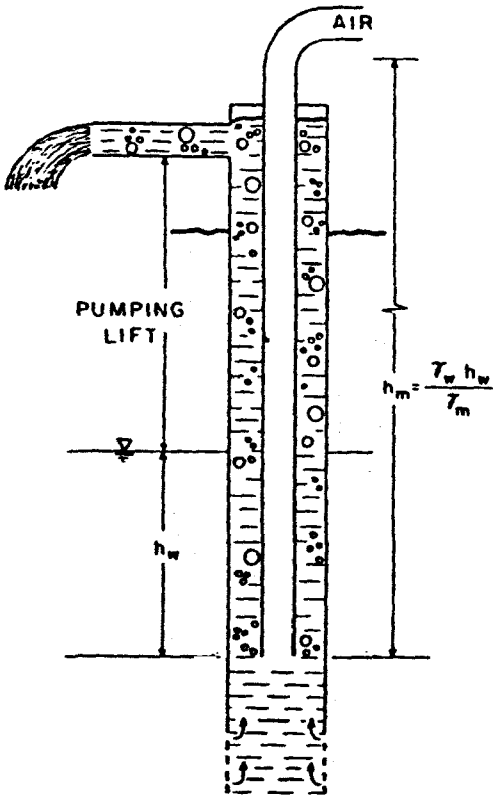


Figure 9.9 Details of a Low-cost Piezometer Modified for Collection of Water Samples



h_m = Maximum height to which the air-water mixture will rise

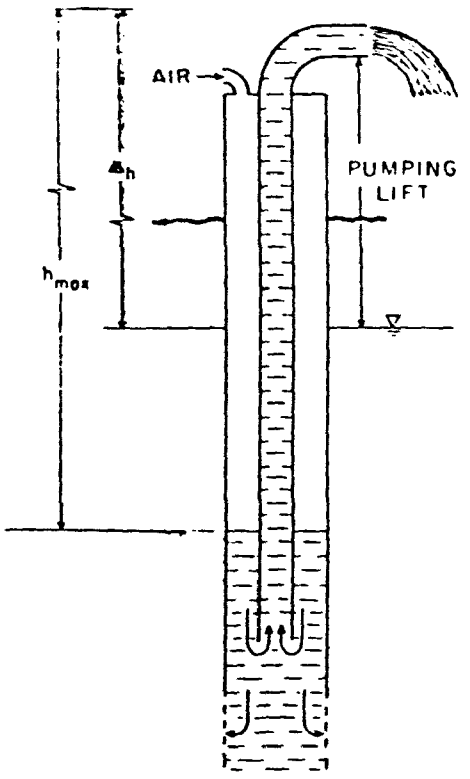
h_w = Submerged length of the air line

γ_m = Density of the air-water mixture

γ_w = Density of water

∇ = Potentiometric surface

Figure 9.10.a Air-lift System



h_{max} = Maximum height to which water in the nylon hose will rise relative to the water level between the hose and piezometer casing

Δh = Difference between h_{max} and the hydraulic head in the formation

∇ = Potentiometric surface

Figure 9.10.b Pressure System

9.6 REFERENCES

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CHAPTER 10

SAMPLING SLUDGES

10.1 BACKGROUND

The quantity and composition of sludge varies with the characteristics of the wastewater from which it is concentrated and with the concentration process used. Some common types of sludge are:

1. Coarse screenings from bar racks
2. Grit
3. Scum from primary settling tanks
4. Primary settling tank sludge
5. Return and waste activated sludge
6. Flotation or gravity thickened sludge
7. Aerobic or anaerobic digester sludge
8. Drying bed sludge
9. Vacuum filter cake
10. Sludge press cake
11. Centrifuge sludge
12. Fine screening backwash water
13. Sand filter backwash water
14. Sludges from special treatment processes such as the treatment of industrial wastes or combined sewer overflows.

Sludge sampling methods are usually confined to water and wastewater plants, either municipal or industrial. The sampling programs employed are concerned mainly with the following sludges: primary settling tank sludge, return and waste activated sludge, thickened sludge, digester sludge, and the resulting cakes produced by sludge drying methods.

10.2 OBJECTIVES OF SAMPLING PROGRAMS

10.2.1 Process Control

Most sludges are measured for various process control reasons including the following:

1. Optimization of sludge drawoff procedure

2. Determination of the efficiency of a concentration process

3. Determination of the loadings to the process

4. Evaluation of feed material for subsequent sludge conditioning techniques which may vary with changing feed characteristics

5. Control of the activated sludge process, i.e., the mixed liquor suspended solids (MLSS) concentration

6. Control of blanket depths in clarifiers

7. Determination of sludge characteristics that may be detrimental to digester processes

10.2.2 Research

Research projects require specific sampling techniques which are determined by the program.

10.3 PARAMETERS TO ANALYZE

The parameters to analyze will depend on the objective of the process. For example, analysis of total and suspended solids content of the sludge is necessary to determine the efficiency of a sludge thickening process. A guide for parameters to analyze is shown in Figure 10.1. Additional parameters to analyze include: heavy metals, pesticides, and nutrients.

10.4 LOCATION OF SAMPLING POINTS

10.4.1 Flowing Sludges

10.4.1.1 Piping

Collect samples directly from the piping through a sampling cock having a minimum I.D. of 3.8 cm (1.5 in) (1).

10.4.1.2 Channels

Collect samples at the measuring weirs, or at another point where the sludge is well mixed.

10.4.2 Batch Sludges

10.4.2.1 Digesters

Collect samples from a mixed sink which is fed through lines attached at different levels in the digester. Be certain to waste sludge accumulated in the lines prior to sampling (1).

10.4.2.2 Tanks

Mix tank thoroughly and collect samples. Or collect samples at various depths and locations in the tank. Mix samples together prior to analysis.

10.4.3 Specific "In Plant" Locations

The following locations are recommended for sludge sampling at wastewater treatment plants:

1. Primary Sludge - Draw sludge from the settling tank hoppers into a well or pit before pumping, mix well and then collect a representative sample directly from this well. Alternately, collect samples from openings in pipes near the sludge pumps or from the pump itself (4).

2. Activated Sludge - Collect samples at:

   a. the pump suction well
   b. the pump or adjacent piping
   c. the point of discharge of the return sludge to the primary effluent.

   The sample point should be located in a region of good agitation to insure suspension of solids (4).

3. Digested Sludge - Collect samples at the point of the discharge of the digester drawoff pipe to the drying beds or the drying equipment (3).

4. Bed Dried Sludge - Collect equal sized samples at several points within the bed without including sand. Mix thoroughly (4).

5. Filtered Sludge - Collect equal size portions (possibly by using a cookie cutter) at the filter discharge (4).

10.5 FREQUENCY OF SAMPLING

The extreme variability of sludges creates a need for frequent sampling

to achieve accurate results. Each composite sample should be composed of at least 3 individually obtained samples (4). Sample batch operations at the beginning, middle and end of a discharge, or more frequently if high variability is suspected (4). Tapped lines should also be sampled in three separate intervals because of variations in the sludge at the drawoff source (i.e., clarifier, digester, etc.) Minimum frequencies for various sludge processes are included in Figure 10.1.

10.6 NUMBER OF SAMPLES

The number of samples is determined from the frequency and the number to include in the composite. Refer to Figure 10.1 for minimum guidelines.

10.7 TYPE OF SAMPLE

Collect grab samples when analyzing an unstable sludge for a parameter which is affected by the instability, or when analysis is required as soon as possible (e.g., sludge volume index test for activated sludge samples).

Analysis of composite samples is recommmended in all other situations to reduce the effects of sludge variability. Use at least three individual samples to form the composite. Wherever possible, collect frequent discrete samples and composite according to flow rate (5).

10.8 METHOD OF SAMPLING

Automatic samplers are not commonly available for sludge sampling due to the high fouling potential and solids content of the wastewater. Use manual sampling techniques in most situations unless special adaptations can be made.

10.9 VOLUME OF SAMPLE AND CONTAINER TYPE

Use a wide mouth container to sample sludges. The size and material of container depends on the parameters to be analyzed. In general, a clean

	Gravity Thickening		Air Flotation Thickening		Centifugation		Vacuum (pressure) Filtration		Aerobic Digestion		Anaerobic Digestion Primary		Anaerobic Digestion Secondary		Wet Air Oxidation	
	F[1]	L[2]	F	L	F	L	F	L	F	L	F	L	F	L	F	L
Temperature									1/D	1s	Mn	1s	Mn	1s	Mn	1s
pH									1/D	1s	1/D	1s			1/D	S
BOD	2/W	Su	2/W	Su	1/W	C	2/W	F	AD	S			1/W	S	2/D	S
SS	1/D	Su	1/D	Su	1/D	C	1/D	F	AD	S			1/W	S	1/D	S
TS	1/D	1 P	1/D	1 P	1/D	1 P	1/D	1 P	2/W	1 P	1/W	1s	AD	U	1/D	1 U
TVS									2/W	1 P	1/W	1s	AD	U		
Alkalinity											1/D	1s				
Volatile Acids											2/W	1				
Settleable Solids					1/H	C			3/W	1s						

1. F = frequency
2. L = location

Where:

Mn = monitor
H = hour
D = day
W = week

AD = at drawoff
Su = *subnatant*
1 = influent
P = product sludge or cake
C = centrate
F = filtrate
Is = in situ
S = supernatant or decant
U = underflow

Figure 10.1 Recommended minimum sampling programs for municipal wastewater sludge treatment processes (2).

borosilicate glass container is preferable to reduce the possibility of adsorption of organics to the container wall; however, polyethylene can be used for non-organic type analyses. See Chapter 17 for more details.

10.10 PRESERVATION AND HANDLING OF SAMPLES

Preservation methods are discussed in Chapter 17. Be certain to completely mix the sample after a preservative is added to disperse the chemical and allow adequate preservation. Considerable mixing or homogenization is required prior to aliquot removal to insure representative portions are obtained. Further studies on the preservation of sludges appear warranted.

10.11 FLOW MEASUREMENT

For flowing lines do not use flow measuring devices which will be easily fouled by solids (e.g., orifice, venturi meter). Use a permanently installed self-cleaning or non-obstructive device such as a magnetic flow meter.

Batch sludge discharges are not easily quantified in terms of volume discharged. Make estimates from pump capacity, the change in depth in a tank or well and time of pumping or other appropriate methods.

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CHAPTER 11

SUSPENDED SOLIDS SAMPLING

A key water quality parameter is suspended solids since it impacts upon such activities as the design of Wastewater Treatment plants, turbidity removal in drinking water, sediment control in streams, and disinfection. Also, the concentration of other key water quality parameters is related to suspended solids since the solid structure may contain biochemical and chemical oxygen demand materials, trace metals, nutrients, pesticides and toxic-hazardous materials absorbed on the surface. Therefore, it is imperative that representative samples be collected for suspended solids.

11.1 REPRESENTATIVE SAMPLING THEORY

For solids distributed uniformly within a given system and containing the same chemical and physical properties, any sample taken shall be representative. However, most systems in practice contain suspended solids varying in physical and/or chemical properties; the degree of non-uniformity in practice ranges from slight to large and subsequently causes errors in obtaining a representative sample.

11.1.1 Sampling Error

The error in sampling suspended solids in the field or subsampling from a previously collected sample is attributed to two factors: (1) solid segregation effects, and (2) random distribution of solids:

(a) Segregation Effects - Error in sampling due to significant differences

between solid particles in specific gravity, size, and shape.

(b) Random Solid Distribution - Error due to imperfect sampling or homogenization procedures. For example, a mixture of 1,000 green beads and 5,000 yellow beads, color being the only difference, is homogenized as completely as possible, however, a sample of 24 beads will not always contain four green beads but may vary from zero to eight. The magnitude of this type of error depends on the size of the sample being withdrawn.

Segregation effects are more pronounced in field sampling since solids are difficult to mix thoroughly or process through devices that eliminate solid segregation. Random effects are more pronounced in the laboratory since segregation effects can be minimized by homogenization of the wastewater sample.

11.2 SEGREGATION SAMPLING ERROR

Typical waters/wastewaters contain solid particles which vary in size, shape, and specific gravity. All of these properties influence the particle settling rate which must be exceeded to keep the solid suspended and prevent segregation of solids within the water/wastewater system being sampled. The theoretical settling rate of a spherical solid in a quiescent aqueous medium is given by Stokes law:

$$V_s = \frac{D^2 (S_s - S_w) g}{18 \nu}$$

Where: V_s = settling velocity

D = sphere diameter

S_s = specific gravity of solid

S_w = specific gravity of water

ν = kinamatic viscosity of water

11.2.1 Particle Size

Stokes law indicates that the settling velocity increases with increasing particle diameter. The size of solids found in water/wastewater vary as shown in Figure 11.1. Approximately 90% of all solids are less than 1 mm in size.

11.2.2 Specific Gravity of Solids

Stokes law also indicates that the settling rate increases with increasing specific gravity of the solid. The specific gravity of suspended solids found in waters/wastewaters vary from 0.8 to 3.5, some of which are shown below:

Material	Specific Gravity
Oils, other organics	0.95
Flocculated mud particles with 95% water	1.03
Municipal	
(a) Effluents	1.15
(b) Influent	0.8 - 1.6
(c) Grit	1.2 - 1.7
Aluminum Floc	1.18
Iron Floc	1.34
Sand	2.65
Calcium Carbonate Precipitate	2.70

11.2.3 Shape of Solids

The settling velocity formula of Stokes applies to spherical particles, however, most waters/wastewaters contain solids of non-spherical shape. In general solids with irregular shapes tend to settle at lower rates than spherical particles of the same specific gravity (1). Shapes encountered in waters/wastewaters include:

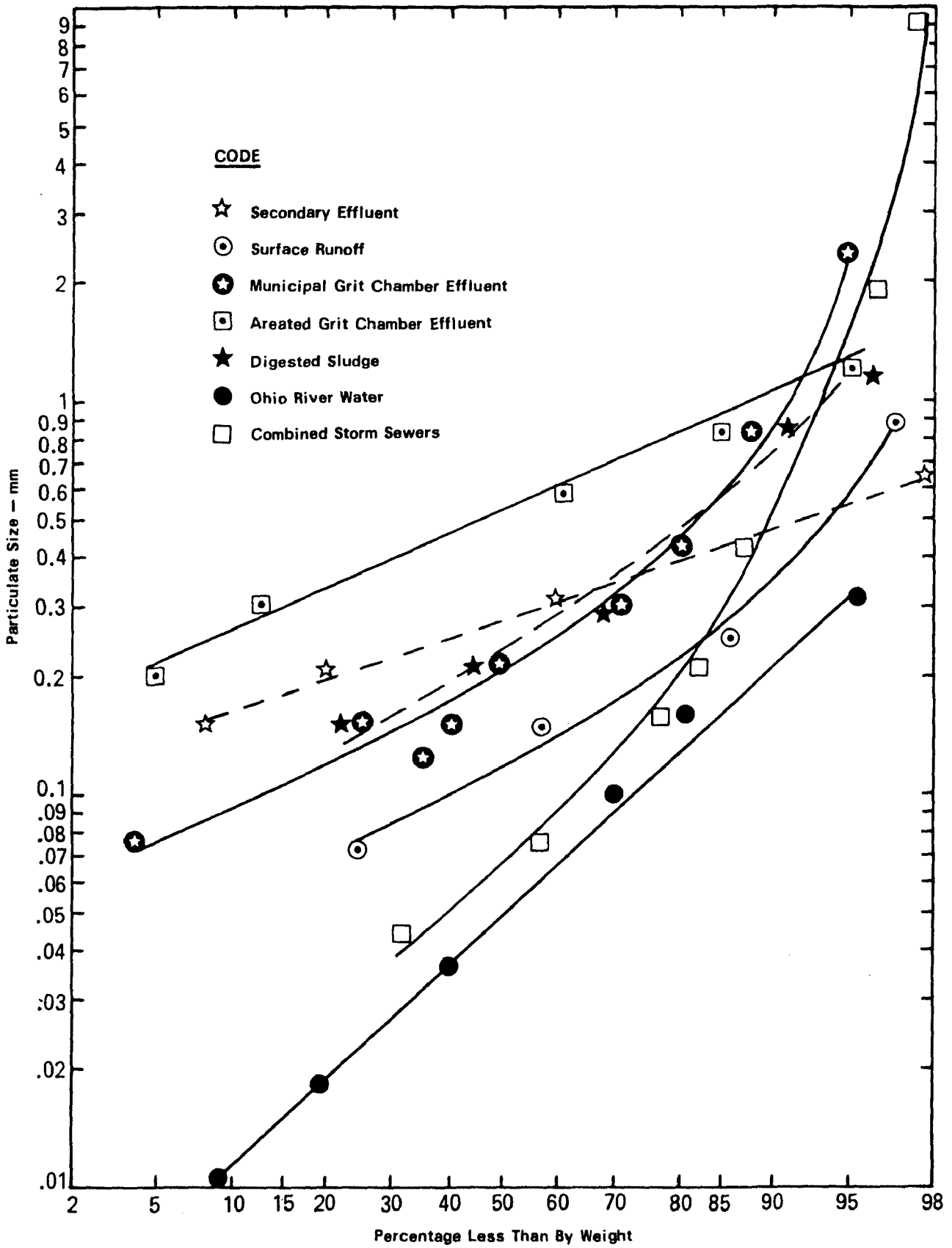


Figure 11.1 Suspended solid particle sizes in various waters/waste waters (2).

Type	Shape
(a) Microbiological and paper scraps	Placoid
(b) Sand grains	Angular
(c) Plastic monomers	Spherical
(d) Fibers - wood, rayon, nylon	Cylindrical-stringy

11.2.4 Settling Velocities

Experimentally determined settling velocities (2) for various solid types are:

(a) Erosion soil run-off - Ranges from .015 - 10.1 cm/sec (.0005 - 0.33 ft/sec).

(b) Grit chamber effluent - Mean of 0.54 cm/sec (.0017 ft/sec).

(c) Primary clarifier design for settable solids removal - .028 - .043 cm/sec (.0009 - .0014 ft/sec).

11.2.5 Scouring Velocity

Sampling of horizontal flowing open channels and pipes for suspended solids must be conducted at velocities which assures adequate mixing. Stratification or segregation of solids are classified as follows:

(a) Bed load - Solids that move by saltation, rolling, or sliding along or near the bottom surface.

(b) Suspended solids or suspended load - solids that are supported by the upward components of turbulent currents and that stay in suspension for appreciable amounts of time. The equation for estimating the velocity (3) to transport solids is:

$$V_s = \frac{8B}{f} (g) (S - 1) Dg = \frac{1.486}{n} R^{1/6} B (S - 1) Dg$$

Where:

V_s = Scouring velocity

S = Specific gravity of the particle

Dg = Diameter of particle

B = 0.04 to start scouring and 0.8 for scouring

f = Friction factor - .03 for concrete

n = Manning roughness factor - See Table 11.1

R = Hydraulic Radius - See Table 11.2

g = 32.2 ft/sec^2.

TABLE 11.1 VALUES OF MANNING'S ROUGHNESS COEFFICIENT n

Glass, plastic, machined metal	0.010
Dressed timber, joints flush	0.011
Sawn timber, joints uneven	0.014
Cement plaster	0.011
Concrete, steel troweled	0.012
Concrete, timber forms, unfinished	0.014
Untreated gunite	0.015-0.017
Brick work or dressed masonry	0.014
Rubble set in cement	0.017
Earth, smooth, no weeds	0.020
Earth, some stones and weeds	0.025
Natural river channels:	
Clean and straight	0.025-0.030
Winding, with pools and shoals	0.033-0.040
Very weedy, winding and overgrown	0.074-0.150
Clean straight alluvial channels	$0.031d^{1/6}$
	d D-75 size in ft.

TABLE 11.2 VALUES OF HYDRAULIC RADIUS R_H FOR VARIOUS CROSS SECTIONS

$R_H = \frac{\text{area of stream cross section}}{\text{wetted perimeter}}$; "equivalent diameter" = $4R_H$

Shape of Cross Section	R_H
Pipes and ducts, running full:	
Circle, diam. = D	$\frac{D}{4}$
Annulus, inner diam. = d. outer diam. = D	$\frac{(D - d)}{4}$
Square, side = D	$\frac{D}{4}$
Rectangle, sides a,b	$\frac{ab}{2(a + b)}$
Ellipse, major axis = 2a, minor axis = 2b	$\frac{ab}{K(a + b)}$*
Open channels or partly filled ducts:	
Rectangle, depth = y, width = b	$\frac{by}{b + 2y}$
Semicircle, free surface on a diam. D	$\frac{D}{4}$
Wide shallow stream on flat plate, depth =	y
Triangular trough, $\angle = 90^\circ$, bisector vertical, depth = y, slant depth = d	$\frac{d}{4} = \frac{y}{2\sqrt{2}}$
Trapezoid (depth = y, bottom width = b): Side Slope 60° from horizontal	$\frac{yb + y/\sqrt{3}}{b + 4y/\sqrt{3}}$
Side slope 45°	$\frac{y^b + y^2}{b + 2\sqrt{2y}}$

(continued)

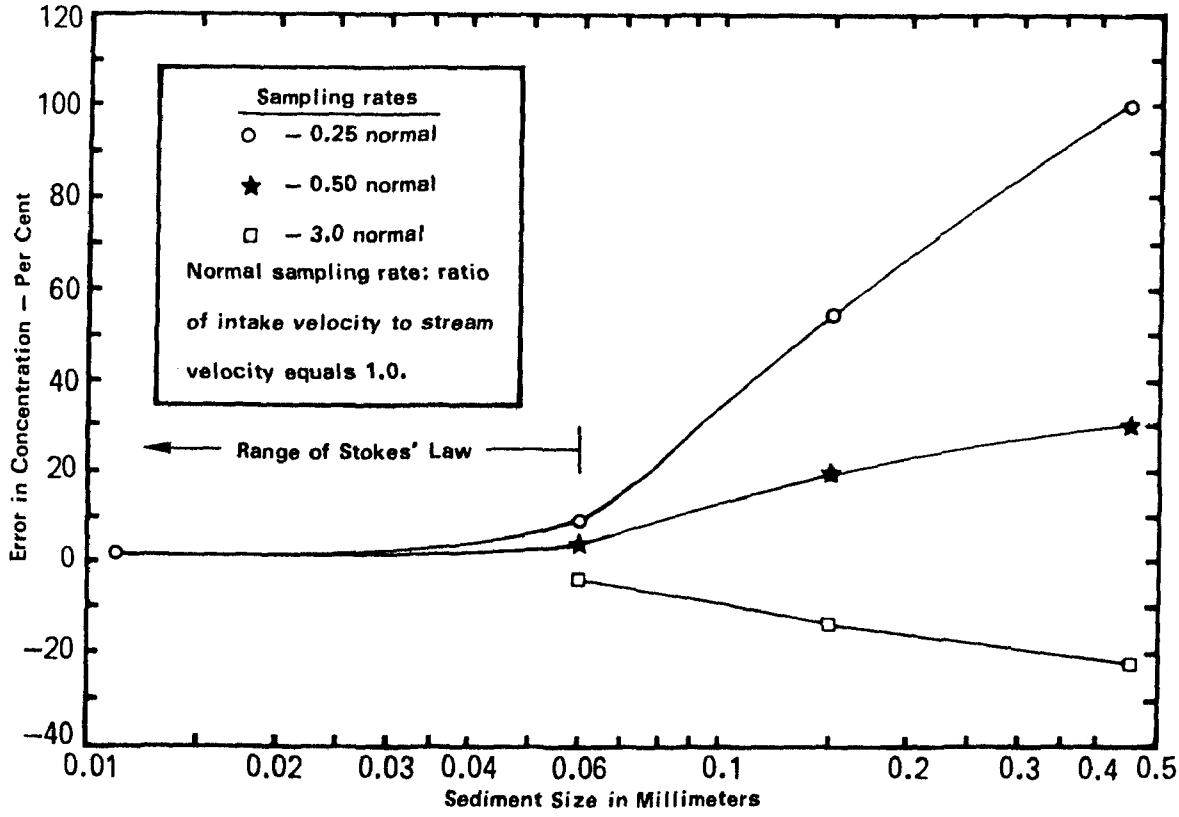


Figure 11.2 Relation of sediment size to errors in sediment concentration.

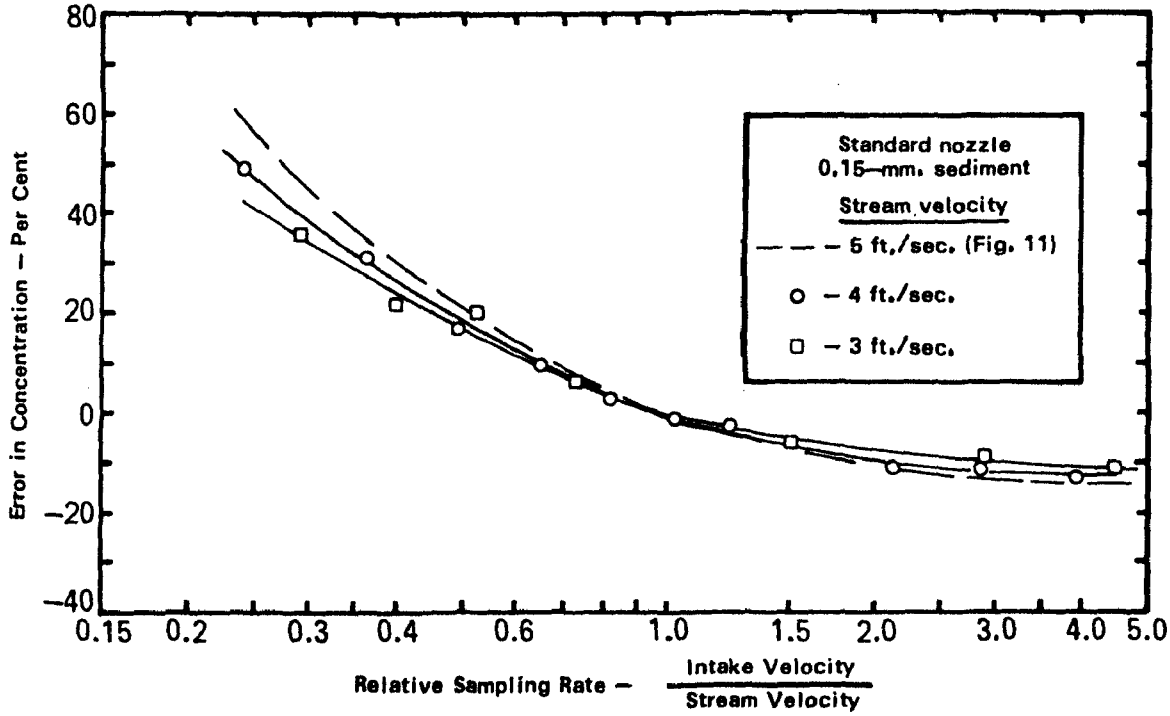


Figure 11.3 Effect of stream velocity on errors in sediment concentration.

TABLE 11.2 (continued)

Film (thickness = t) on wall of vertical wetted wall tower of diameter - D	$t - {}^{t}2/D = t$ (approx.)

* Values of K. If S = (a - b)/(a + b),

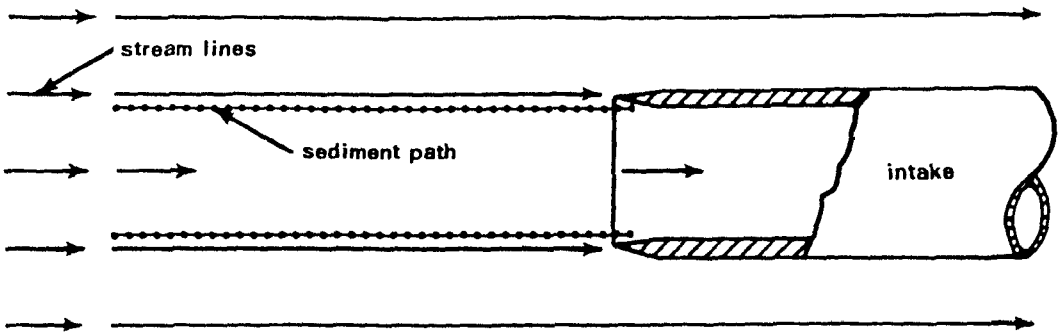
S =	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
K =	1.010	1.023	1.040	1.064	1.092	1.127	1.168	1.216	1.273

11.3 FIELD SAMPLING

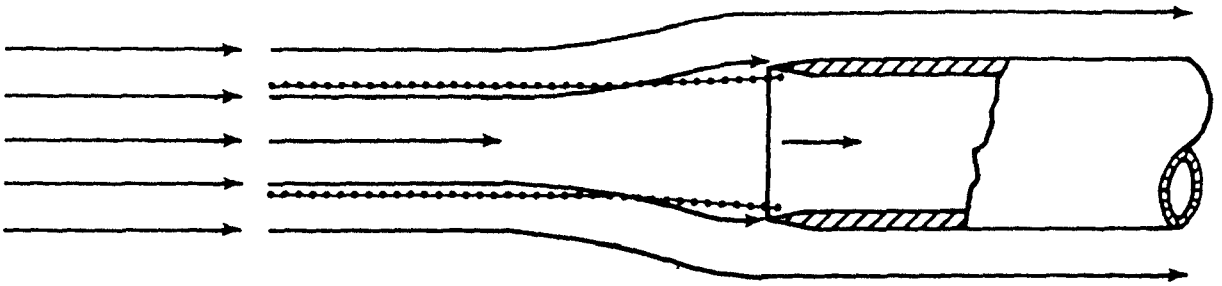
Collection of suspended solids in the field can be performed manually or automatically, however significant differences in results can be expected when sampling non-homogeneous systems such as raw municipal wastewaters as shown in Table 11.3 (4). Also, automatic samplers with high intake velocities, i.e. 2-10 ft/sec., will capture about 1.5 - 2.0 times more solids than manual flow proportional or manual grab sampling methods. However, as the system becomes more homogeneous with respect to solids, i.e., final effluent values in Table 11.3, intake velocities or method of sampling becomes less important in obtaining comparable results.

Intake velocities above or below stream velocities for suspended sediment solids (S.g. 2.65) within Stokes law, i.e., Reynolds number less than 1.0, do not result in any significant error as shown in Figure 11.2 (5). However, as the particle size increases, significant error occurs when the intake/stream velocity ratio varies from 1.0. This relationship, Figure 11.3, between the Relative Sampling Rate Ratio as error in concentration has a negative slope, i.e., when the intake velocity is less than the stream velocity, more solids will be collected and when the intake velocity exceeds the stream velocity, less solids shall be collected.

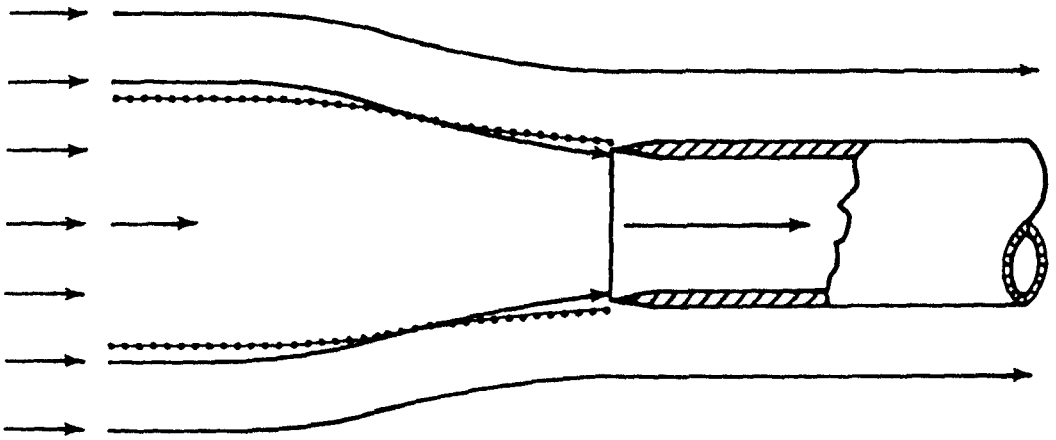
The rationale for this inverse relationship is illustrated in Figure 11.4. Therefore, in order to insure representative sampling, the intake/stream velocity ratio should be unity (isokinetic flow).



a. Normal sampling rate — intake velocity equal to stream velocity.



b. Sampling rate below normal — as illustrated, ratio of intake velocity to stream velocity approximately 1/3.



c. Sampling rate above normal — as illustrated, ratio of intake velocity approximately 3.

Figure 11. 4 Flow patterns at mouth of sampler intake.

TABLE 11.3 RICHARDS-GEBAUR SEWAGE TREATMENT PLANT NFS COMPARISON
RATIO OF SAMPLING METHOD VALUE TO MANUAL FLOW VALUE

Station	Sample Method	Date May 21	May22	May 23	Average	Intake Velocity ft/sec.
Influent	QCEC	2.099	1.155	1.755	1.669	2-5
	ISCO	0.991	0.431	1.406	0.942	2
	Manual Flow	1.0	1.0	2.0	1.0	--
	Manual Grab	1.223	0.697	0.820	0.907	--
Primary Effluent	Hants	3.141	1.537	1.449	2.042	2.5
	Sigmamotor	0.783	0.700	0.968	0.817	0.25
	Manual Flow	1.0	1.0	1.0	1.0	--
	Manual Grab	0.981	0.975	1.170	1.042	--
Final Effluent	Hants	1.354	0.743	1.387	1.161	2.5
	Brailsford	0.822	0.769	1.225	0.939	.02
	Manual Flow	1.0	1.0	1.0	1.0	--
	Manual Grab	0.951	0.794	1.209	0.985	--

11.4 LABORATORY SUBSAMPLING

Subsampling from previously collected field samples may be subject to error resulting from segregation effects, i.e., particle size and specific gravity. As shown in Figure 11.5, the shake and pour technique achieves 93% recovery of solids with specific gravities in the range of 2.2-2.6 and

particle sizes less than 50 microns; magnetic stirring improves percent recoveries.

Subsampling recoveries of 100 percent for solids having specific gravities ranging from 1.05-1.14 can be expected up to 500 microns. Therefore, to insure representative subsampling, the entire sample should be thoroughly blended and as large an aliquot used as possible.

11.5 GUIDELINES FOR SAMPLING OF SUSPENDED SOLIDS

Minimize sampling errors caused by segregation effects by sampling in a well mixed or turbulent zone.

Minimize random sampling errors in the laboratory by homogenizing the sample and using as large a sample aliquot as possible.

Maintain the flow rate in the sample lines to effectively transport suspended solids. For horizontal runs, the velocity must exceed the scouring velocity and in vertical runs, the velocity must exceed the settling velocity of the particle.

For solids falling within the range of Stokes law, consistant representative samples can be obtained at intake/stream ratio either greater or less than 1.0. For solids falling outside Stokes law, an intake/stream ratio of 1.0 is recommended.

The geometry of the intake has little effect upon the representativeness of the sample, however, the intake should face into the stream at no more than 20 degrees from the direction of stream flow.

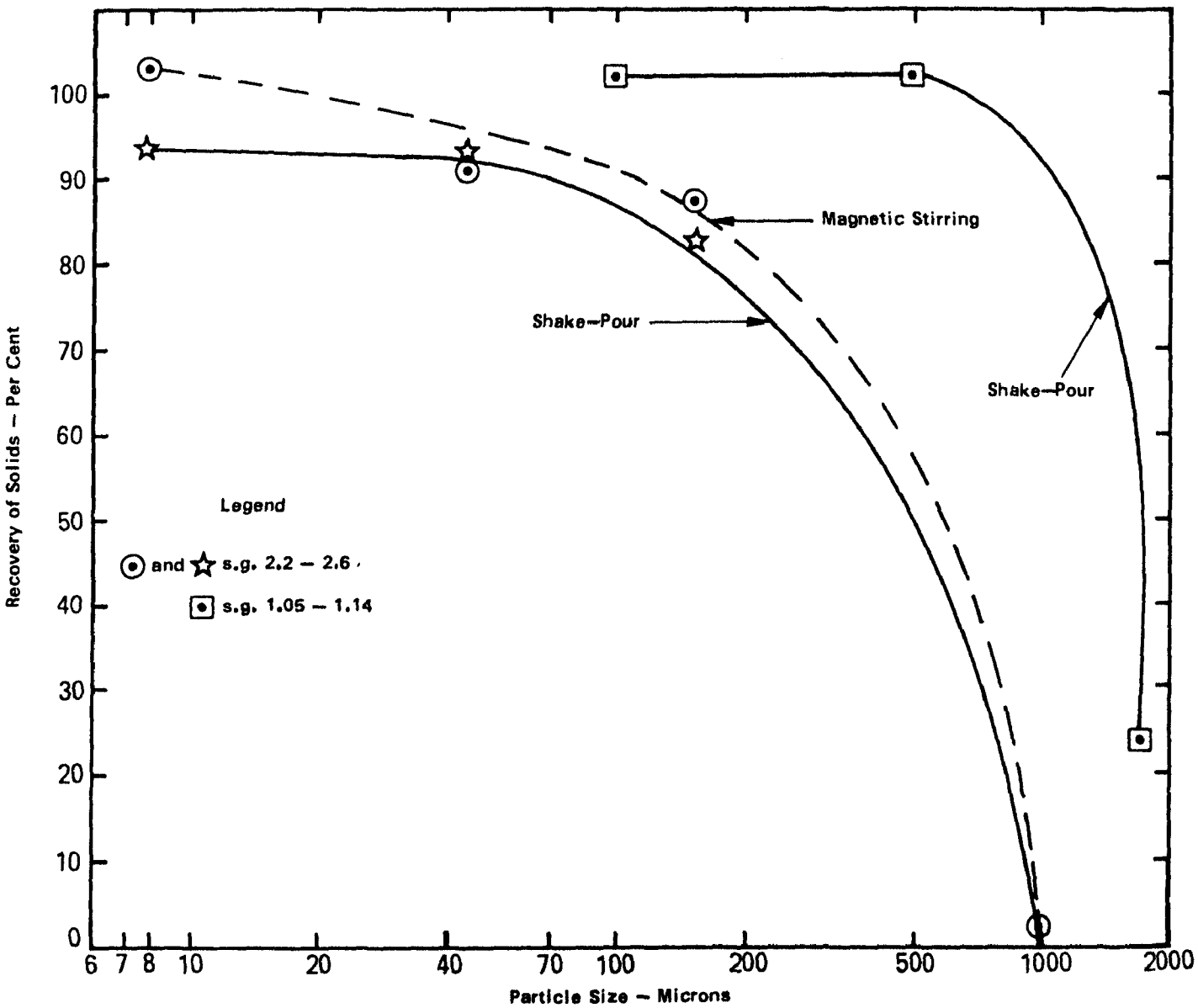


Figure 11.5 Percent recovery vs particle size during subsampling with different mixing techniques

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CHAPTER 12

SAMPLING, PRESERVATION AND STORAGE CONSIDERATIONS FOR TRACE ORGANIC MATERIALS

The presence of organic compounds in water and wastewater is regulated by the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

The SDWA has established maximum contaminant levels (1,2) for the following organic chemicals:

(a) Chlorinated hydrocarbons:

Endrin	Methoxychlor
Lindane	Toxaphene

(b) Chlorophenoxys:

2,4-D	2,4,5-TP (silvex)

(c) Trihalomethanes:

Trichloromethane	Bromodichloromethane
Dibromochloromethane	Tribromomethane

Some chemical indicators of industrial contamination are listed in Table 12.1. This list contains chemicals which have been detected in drinking water supplies and for which the possibility of adverse health effects exists. The presence of these chemicals is indicative of chemical pollution; this list is not exhaustive, but serves merely as a guide (3).

A court settlement agreement involving the Natural Resources Defense Council, et al. and the Environmental Protection Agency (EPA Consent Decree) resulted in EPA publishing a list of 65 compounds and classes of compounds (Table 12.2). The Consent Decree required that EPA regulate these compounds via the Federal Water Pollution Control Act (subsequently amended by the Clean

Water Act). EPA's list of 129 priority pollutants (Table 12.3) is an outgrowth of the Consent Decree's list of 65.

Specific toxic pollutant effluent standards will be promulgated for the 129 priority pollutants, thus far they have been promulgated (4,5,6) for the following:

Aldrin/Dieldrin	Endrin
Benzidine	Toxaphene
DDT (DDD, DDE)	PCB's

Analytical procedures for the identification of organic compounds can be found in a number of publications (7 through 22). However, analytical results are only meaningful if the sample analyzed is truly a representative sample of the media you are testing. Chemical analysis for organics present at trace levels places high demands on sampling techniques.

TABLE 12.1 CHEMICAL INDICATORS OF INDUSTRIAL CONTAMINATION (23)

I. Aliphatic halogenated hydrocarbons:

Methane derivatives:

Dichloromethane	Dichlorodifluoromethane
Trichlorofluoromethane	Carbon tetrachloride

Ethane derivatives:

1,1-dichloroethane	1,1,1-trichloroethane
1,2-dichloroethane	1,1,2-trichloroethane
hexachloroethane	1,1,2,2-tetrachloroethane

Unsaturated hydrocarbons:

Trichloroethylene	1,2-dichloroethene
Tetrachloroethylene	1,3-dichloropropene
Vinyl chloride	Hexachlorobutadiene
1,1-dichloroethene	2-chlorovinyl ether

Other halogenated compounds:

1,2-dichloropropane	Bis(2-chloroethyl) ether
	bis(2-chloroisopropyl) ether

II. Cyclic aliphatic compounds:

Chlorinated hydrocarbons:

Lindane	Kepone
BHC	Toxaphene

Cyclodienes:

Chlordane	Heptachlor
Aldrin	Heptachlor epoxide
Dieldrin	Endrin
	Hexachlorocyclopentadiene

TABLE 12.1 (continued)

III.	Aromatic hydrocarbons:	
	3,4-benzofluoranthene	fluoranthene
	benzo(k)fluoranthene	indeno(1,2,3,c,d)pyrene
	1,12-benzoperylene	benzo(a)pyrene
	Benzenes:	
	Benzene	Ethylbenzene
	Toluene	Propylbenzene
	Xylenes	Styrene
	Halogenated aromatics:	
	Chlorinated naphthalenes	DDE
	Chlorobenzene	DDD
	Dichlorobenzenes	Chlorophenols
	Polychlorinated biphenyls	Trichlorobenzenes
	Pentachlorophenol	4-bromophenylphenyl ether
	Bromobenzene	4-chlorphenylphenyl ether
	DDT	Hexachlorobenzene
	Other aromatic hydrocarbons:	
	Nitrobenzene	Phthalate esters
	Dinitrotoluene	Atrazine

TABLE 12.2 65 TOXIC POLLUTANTS OR CLASSES OF TOXIC POLLUTANTS (21)

Acenaphthene
Acrolein
Acrylonitrile
Aldrin/Dieldrin
Antimony and compounds
Arsenic and compounds
Asbestos
Benzene
Benzidine
Beryllium and compounds
Cadmium and compounds
Carbon tetrachloride
Chlordane (technical mixture and metabolites)
Chlorinated benzenes (other than dichlorobenzenes)
Chlorinated ethanes (including 1,2 dichloroethane 1,1,1-trichloroethane, and hexachloroethane)
Chloroalkyl ethers (chloromethyl, chloroethyl, and mixed ethers)
Chlorinated naphthalene
Chlorinated phenols
Chloroform
2-chlorophenol
Chromium and compounds
Copper and compounds
Cyanides
DDT and metabolites
Dichlorobenzenes (1,2-,1,3- and 1,4-dichlorobenzenes)
Dichlorobenzidine
Dichloroethylenes (1,1- and 1,2-dichloroethylenes)
2,4-dichlorophenol
Dichloropropane and dichloropropene
2,4 Dimethylphenol
Dinitrotoluene
Diphenylhydrazine
Endosulfan and metabolites
Endrin and metabolites
Ethylbenzene
Fluoranthene
Haloethers
Halomethanes
Heptachlor and metabolites
Hexachlorobutadiene
Hexachlorocyclohexane (all isomers)
Hexachlorocyclopentadiene
Isophorone
Lead and compounds
Mercury and compounds
Naphthalene
Nickel and compounds
Nitrobenzene
Nitrophenols (including 2,4-dinitrophenol, dinitrocresol)
Nitrosamines
Pentachlorophenol
Phenol
Phthalate esters
Polychlorinated biphenyls (PCB's)
Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes and indenopyrenes)
Selenium and compounds
Silver and compounds
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
Tetrachloroethylene
Thallium and compounds
Toluene
Toxaphene
Trichloroethylene
Vinyl Chloride
Zinc and compounds

TABLE 12.3 PRIORITY POLLUTANTS

I. Phthalate esters:

Dimethyl phthalate	Di-n-octyl phthalate
Diethyl phthalate	Bis(2-ethylhexyl)phthalate
Di-n-butyl phthalate	Butylbenzyl phthalate

II. Haloethers

Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane
Bis(2-chloroisopropyl)ether	4-chlorophenylphenyl ether
2-chloroethylvinyl ether	4-bromophenylphenyl ether

Bis(chloromethyl)ether

III. Chlorinated hydrocarbons:

Hexachloroethane	1,3-dichlorobenzene
Hexachlorobutadiene	1,4-dichlorobenzene
Hexachlorocyclopentadiene	1,2,4-trichlorobenzene
1,2-dichlorobenzene	Hexachlorobenzene

2-chloronaphthalene

IV. Nitroaromatics and Isophorone:

Nitrobenzene	2,4-dinitrotoluene
2,6-dinitrotoluene	Isophorone

V. Nitrosoamines:

N-nitrosodimethylamine	N-nitrosodipropylamine

N-nitrosodiphenylamine

VI. Dioxin:

2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

VII. Benzidines:

Benzidine	3,3-dichlorobenzidine

1,2-diphenylhydrazine

VIII. Phenols:

Phenol	Pentachlorophenol
2,4-dimethylphenol	4-chloro-3-methylphenol
2-chlorophenol	2-nitrophenol
2,4-dichlorophenol	4-nitrophenol
2,4,6-trichlorophenol	2,4-dinitrophenol

4,6-dinitro-2-methylphenol

TABLE 12.3 (continued)

IX. Polynuclear aromatics:

Acenaphthene	Acenaphthylene
Fluoranthene	Anthracene
Naphthalene	Benzo(g,h,i)perylene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Phenanthrene
Benzo(b)fluoranthene	Dibenzo(a,h)anthracene
Benzo(k)fluoranthene	Indeno(1,2,3-cd)pyrene
Chrysene	Pyrene

X. Pesticides & PCB's:

Aldrin	Heptachlor epoxide
Dieldrin	Alpha-BHC
Chlordane	Beta-BHC
DDD	Delta-BHC
DDE	Gamma-BHC
DDT	Toxaphene
A-endosulfan	Aroclor 1242
B-endosulfan	Aroclor 1254
Endosulfan	Aroclor 1221
Endrin	Aroclor 1232
Endrin aldehyde	Aroclor 1248
Heptachlor	Aroclor 1260
Toxaphene	Aroclor 1016

XI. Purgeables:

Benzene	Chloroform
Chlorobenzene	1,1-dichloroethylene
Toluene	1,2-transdichloroethylene
Ethylbenzene	1,2-dichloropropane
Carbon tetrachloride	1,1-dichloropropylene
1,2-dichloroethane	Methylchloride
1,1,1-trichloroethane	Methylenechloride
1,1-dichloroethane	Methylbromide
1,1,2-trichloroethane	Bromoform
1,1,2,2-tetrachloroethane	Dichlorobromomethane
Chloroethane	Trichlorofluoromethane
Chlorodibromomethane	Trichloroethylene
Tetrachloroethylene	Vinyl chloride
Dichlorodifluoromethane	

XII. Acrolein & Acrylonitrile:

Acrolein	Acrylonitrile

TABLE 12.3 (continued)

XIII. Inorganics:

Antimony	Mercury
Arsenic	Nickel
Beryllium	Selenium
Cadmium	Silver
Chromium	Thallium
Copper	Zinc
Lead	Asbestos

Cyanide

12.1 SAMPLE COLLECTION METHOD

The method of sampling shall be either manual or automatic. Sampling practices, as specified in Chapter 2, should be followed, except as indicated in this chapter.

12.1.1 Manual Sampling

The considerations outlined in Chapter 2 are applicable. However, the sample collector and container material should be borosilicate glass. Collectors and containers constructed of borosilicate glass will minimize sample contamination. Grab samples obtained for analysis involving purgeable organics shall be sealed in such a manner as to eliminate entrapped air(7). This type of sample, collected without headspace, is illustrated in Figure 12.1.

12.1.2 Automatic Sampling

Although continuous automatic sampling is probably the best method for collecting truly representative samples, certain precautions must be taken. Automatic sampling equipment must be free of Tygon and other potential sources of contamination such as plastic, or rubber components (23). Tygon tubing is a potential source of phthalate ester contamination. Teflon is acceptable and may be used in other parts of the sampling system as required.

Automatic samplers used to obtain samples for trace organics analysis may need special design features. An experimental sampler has been developed which is capable of collecting grab samples for purgeable organics analysis and collecting samples on accumulator columns for non-purgeable organics analyses (24). All system components in contact with the sample are either constructed of Teflon or glass; this includes a specially designed Teflon-bellows pump. Various illustrations of this system are shown in Figures 12.2 through 12.6.

Sampling systems utilizing carbon or macroreticular resin in columns have been employed for sampling organics in ground water (25,26,27). The accumulator column in these systems is located between the water to be sampled and the pump, therefore, special Teflon type pumps are not needed. These type systems are illustrated in Figures 12.7 through 12.10.

Automatic samplers can be used to collect grab samples or composited grab samples. EPA's 600 series methods for analyzing non-volatile organic priority pollutants make reference to these types of automatic samplers.

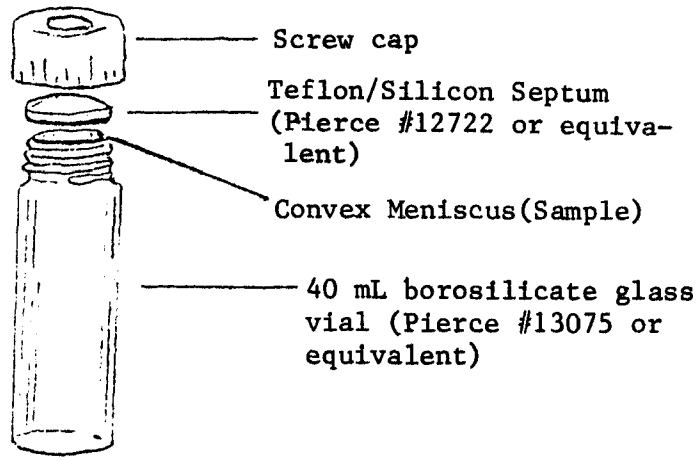

Figure 12.1 Collection Bottle (21,22)

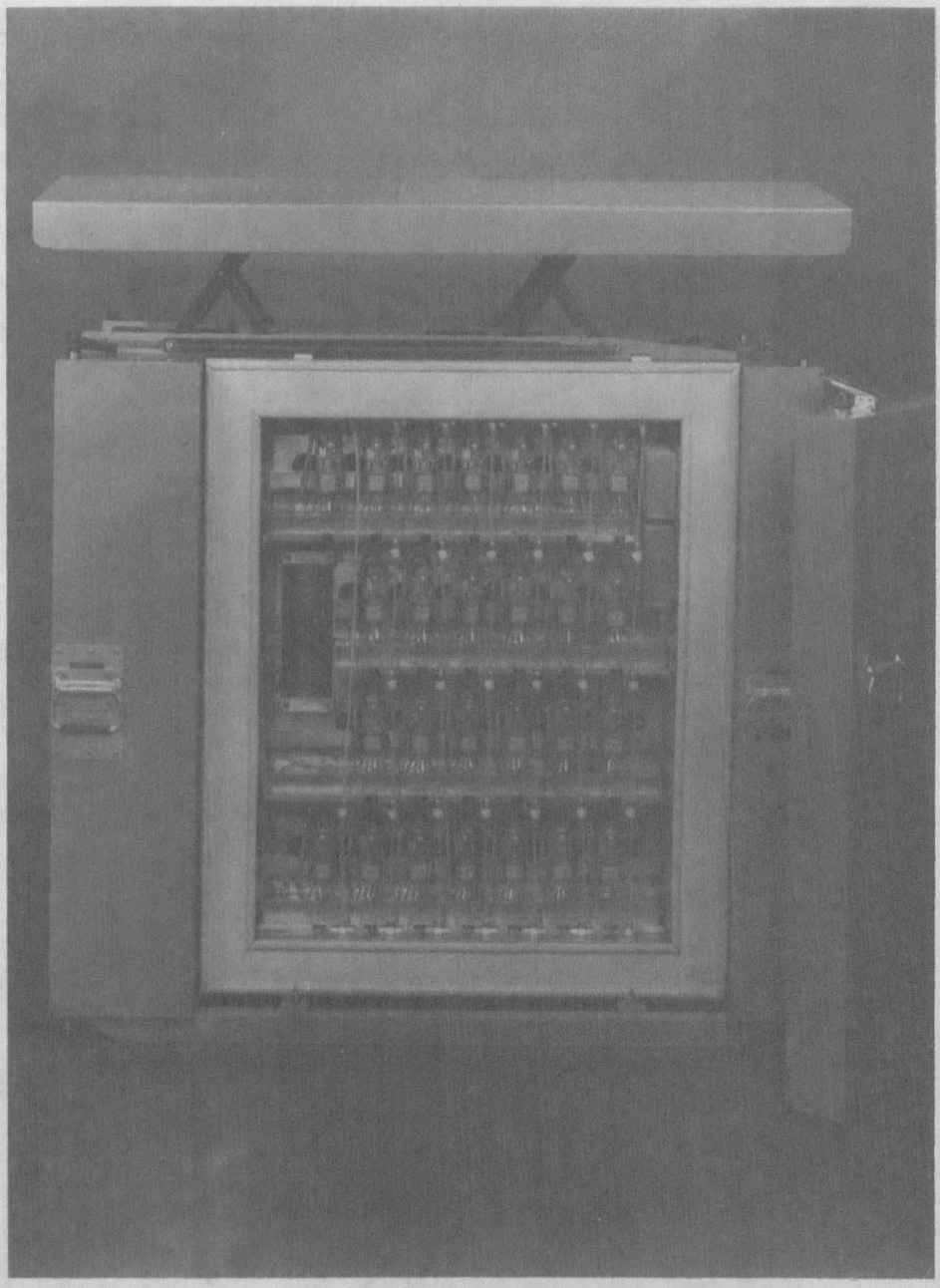

Figure 12.2 Automatic sampler opened to show the 26 purgeable sample bottles in position.

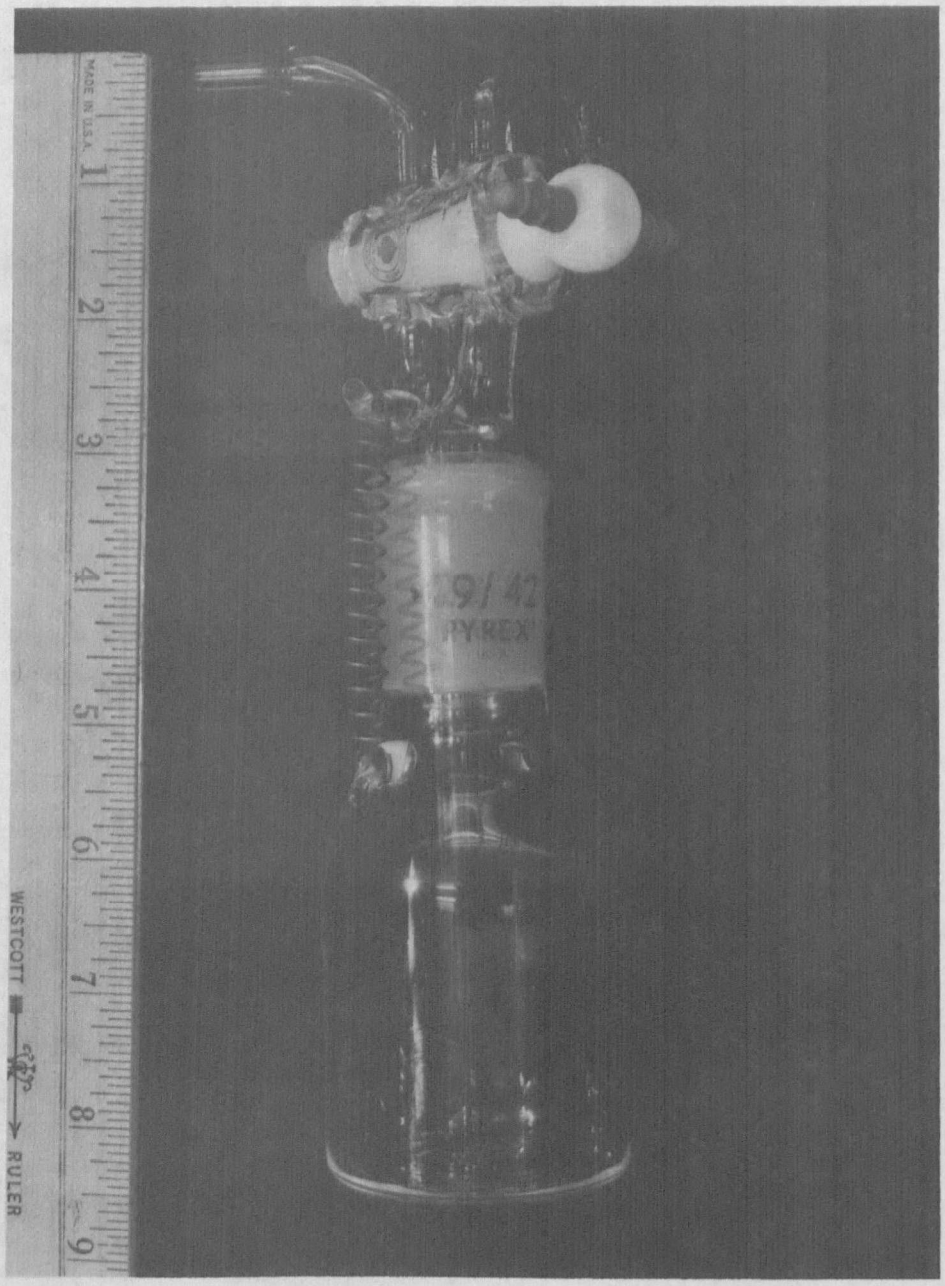

Figure 12.3 A 140 mL purgeable sample bottle for the automatic sampler.

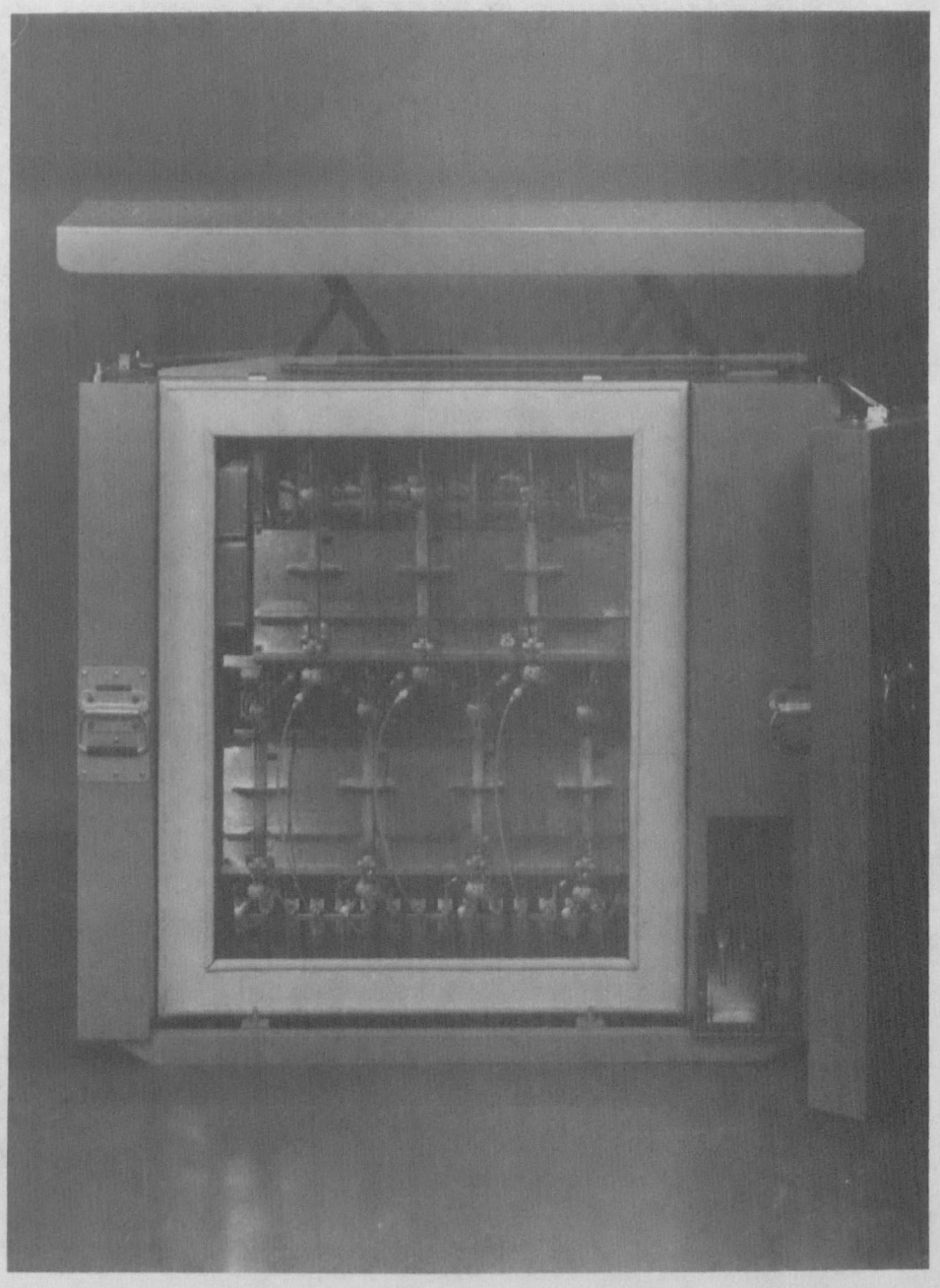

Figure 12.4 Automatic sampler opened to show 7 or the 14 accumulator columns. Another bank of 7 is located behind the visible bank.

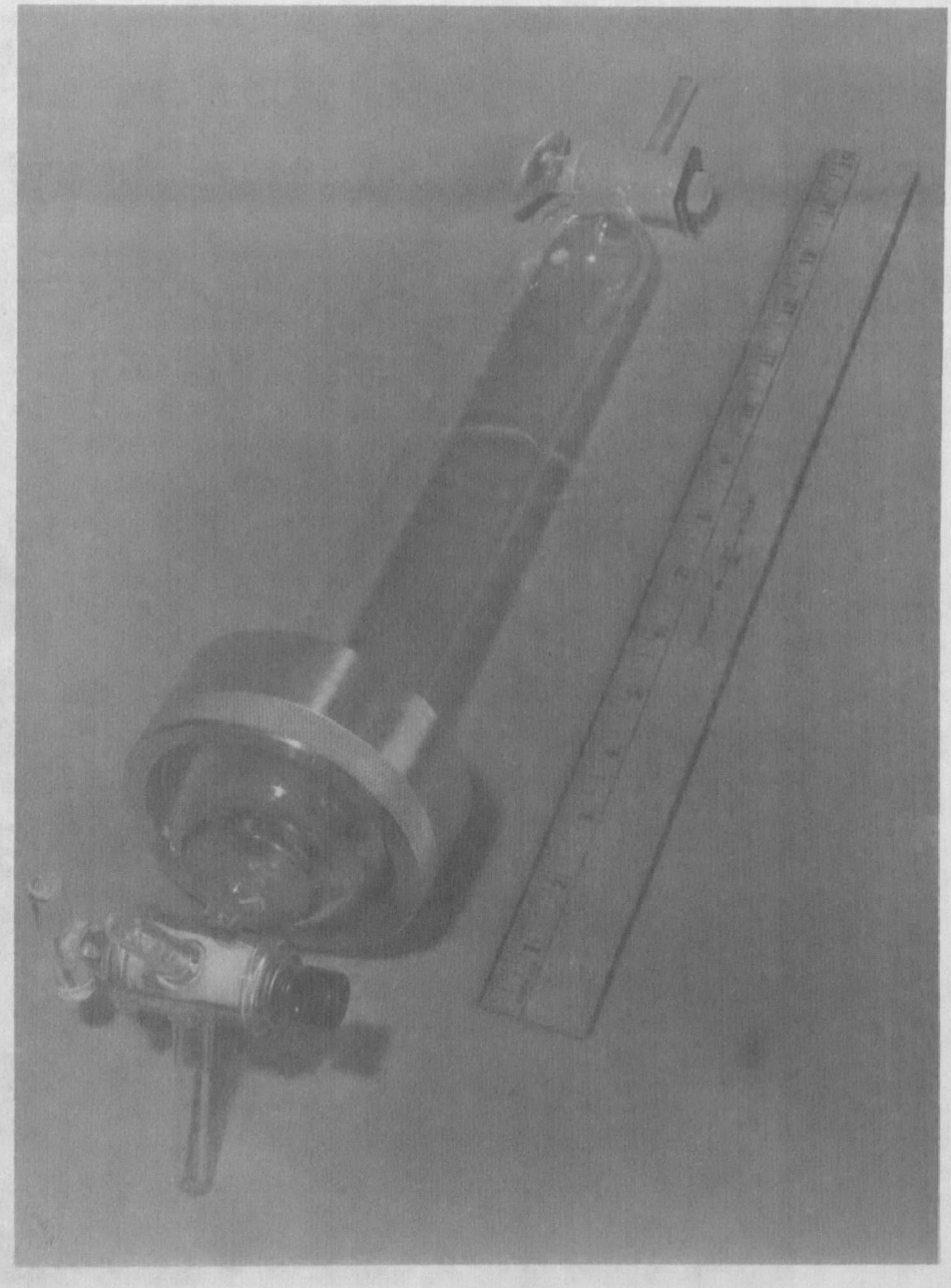

Figure 12.5 A 1.8 x 27 cm empty accumulator column for the automatic sampler.

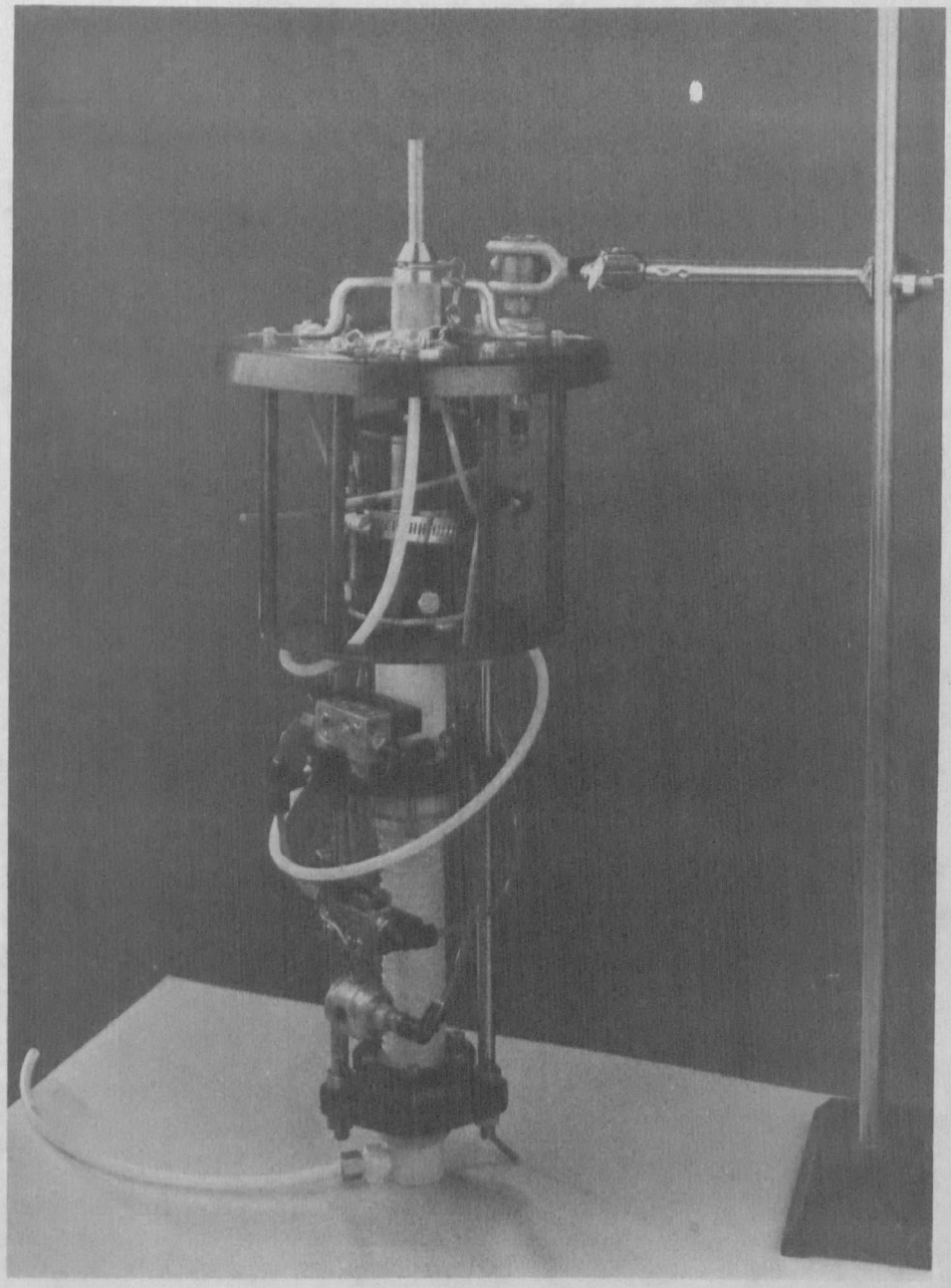

Figure 12.6 Automatic sampler pump with container removed. Teflon bellows are at the bottom.

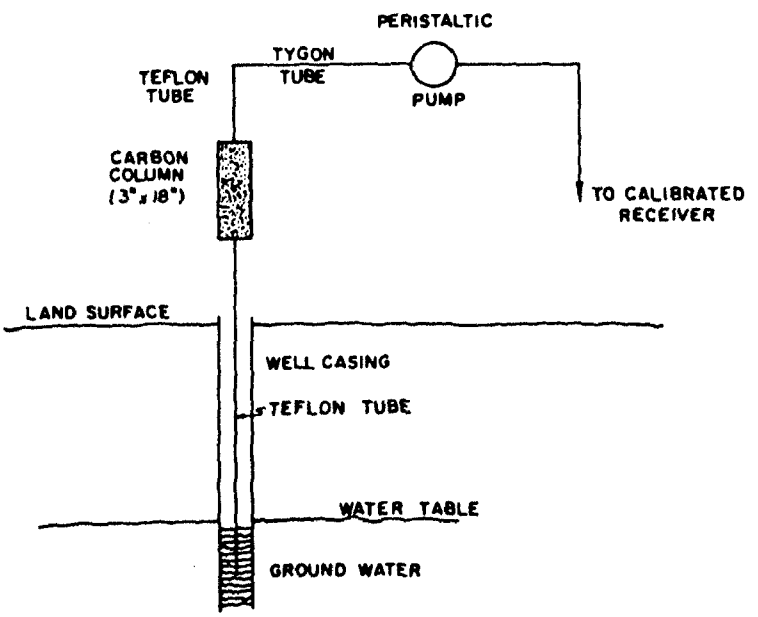

Figure 12.7 Ground water Sampling System (26)

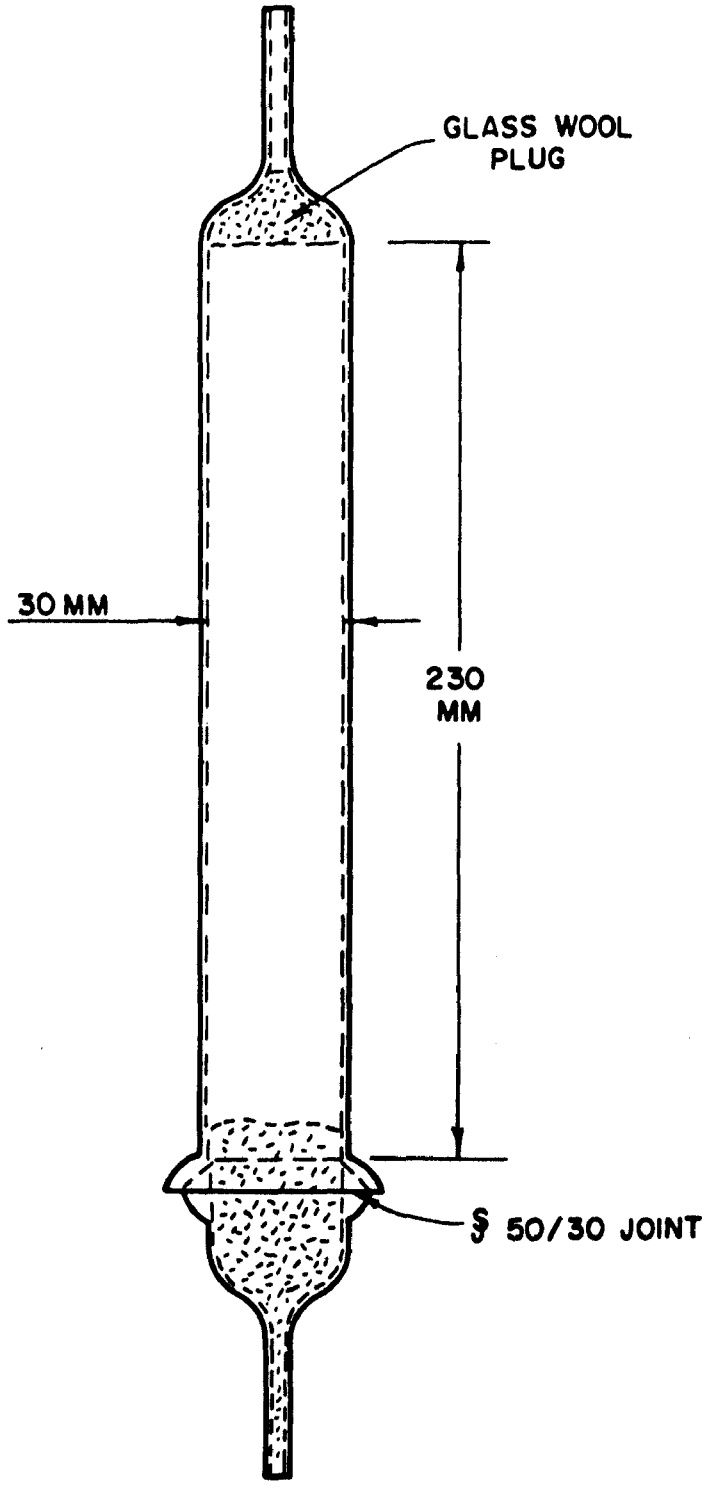

Figure 12.8 Carbon adsorption column (27)

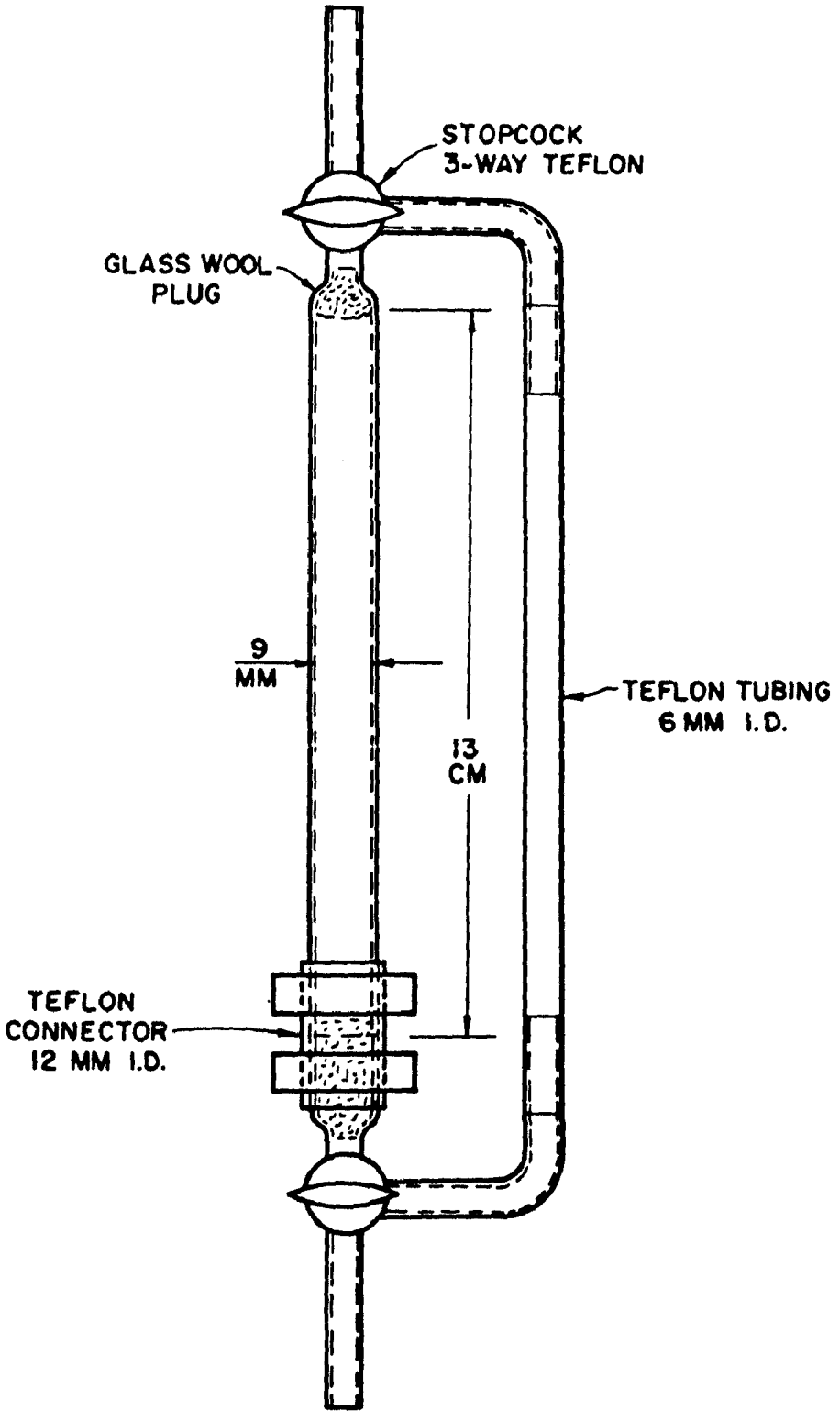

Figure 12.9 Resin adsorption column (27)

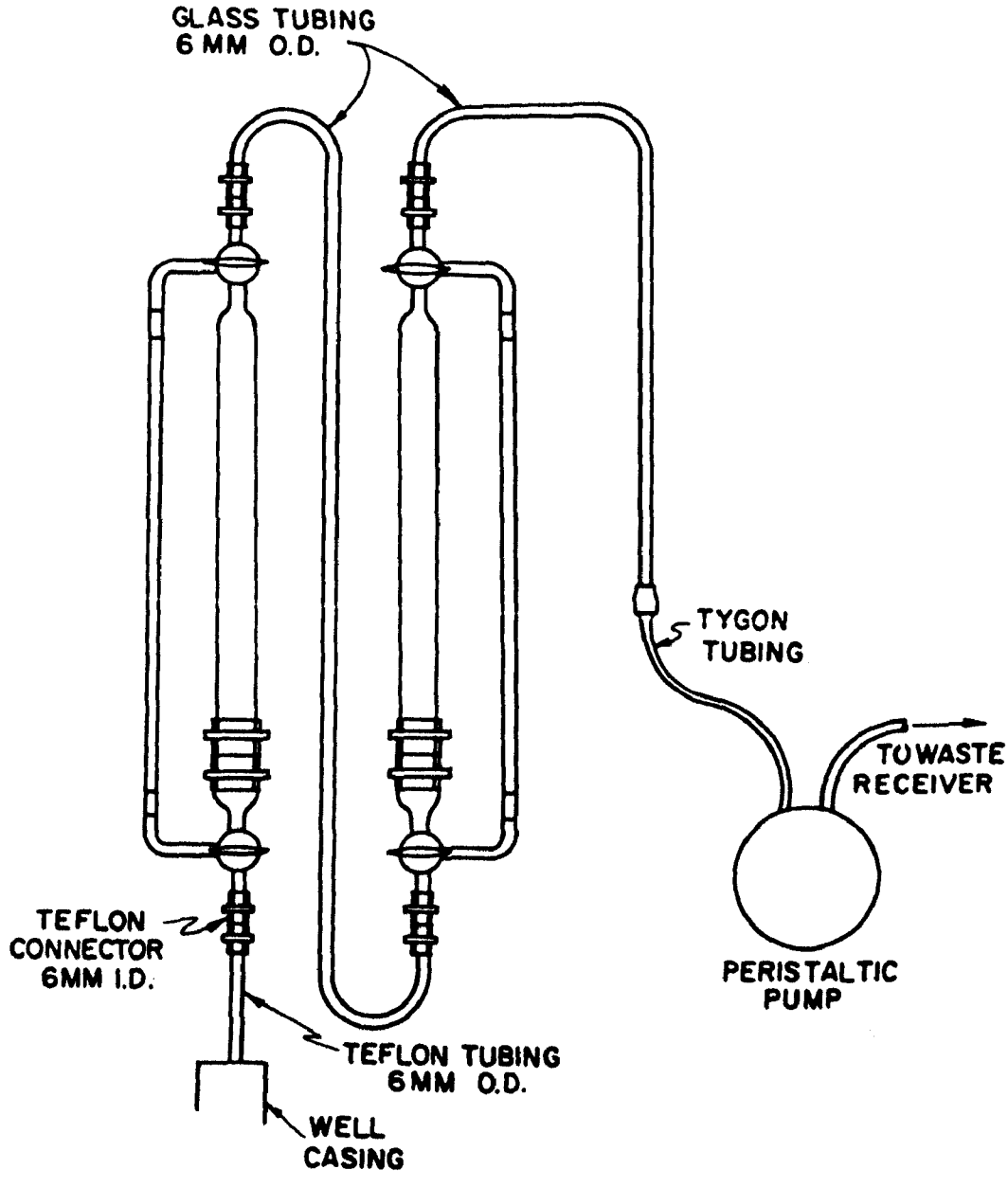

Figure 12.10 Ground-water sampling system (27)

12.2 SEDIMENT SAMPLING

Sediment sampling can be classified into two general categories:

1. Suspended sediments and
2. Bottom sediments

12.2.1 Suspended Sediment Samplers

Suspended sediment samplers should be in accordance with the suspended solids sampling considerations of Chapter 1. When employing any suspended sediment sampler for the collection of samples to be analyzed for organics, all materials such as Neoprene and Tygon must be replaced by inert materials such as teflon. In addition, oil must be eliminated from any valves.

12.2.2 Bottom Sediment Samplers

Bottom sediment samplers are designed to obtain a sample of the sediment mixture of which the stream bed is composed. This should be differentiated from the bed-load. Refer to Chapter 8,Tables 8.4 and 8.5 for a listing of these types of samplers. Replacement of contaminating materials (e.g., Tygon, Neoprene, etc.) with inert materials should be considered.

When replacement of contaminating materials is not possible or not practical, it may be necessary to obtain specially constructed sediment collectors.

12.2.2.1 Sampling Site (28)

The selection of a sampling site when collecting bottom sediments for subsequent organic analysis is extremely important. Bottom sediments, within any river, stream, etc., tend to be heterogeneous, for example, some bottom areas will be composed primarily of sand, while others may be composed primarily of silt and clay. The composition of bottom sediments is extremely important. Organic pollutants tend to be adsorbed on sediments that possess a

large surface-to-volume ratio, therefore, finer sediments such as silts and clays will exhibit higher concentrations of organics, than will coarser sediments such as sands and gravels. Sample sites should, therefore, be selected at depositing areas (these are areas where silt and clay will settle out). Depositing areas are areas where current speeds are low, for example:

- inside of river bends,
- downstream of islands or other obstructions, and
- near the center of water mass in ponds, lakes, and reservoirs.

Do not sample areas that are exposed during low flow or low tide conditions or at points immediately following the confluence of two streams.

Collect representative samples using random sampling techniques and the grid systems specified in Chapter 8. Particle sizes should not exceed 2 mm.

12.2.2.2 Sampling Equipment (28)

Sampling equipment should be designed to minimize disturbance of the top layers of sediments and minimize the loss of low density deposits during the sampling process. Thus, drag buckets and scoops are not recommended for trace organic sampling. All samplers, regardless of type, disturb sediment fines, however, if precautions are taken, the disturbance can be minimized. Recommended sampling equipment and their particular limitations are summarized in Table 12.4.

12.3 SAMPLING LOCATION

The considerations and factors which influence the sampling location should be taken into account as indicated in Chapter 2.

12.4 SAMPLE CONTAINER

The configuration and materials of a container which can be utilized in

the collection and storage of organic containing samples are somewhat varied. However, the following criteria should be met:

1. Non-purgeable samples must be collected in amber glass containers in a liter or quart volume and preferably of French or Boston round design (22,23). Various glass vials have also proved to be adequate (22,27,29,30).
2. Container caps should be threaded to screw onto the container. Caps must be lined with Teflon (22,23). Foil may be substituted if sample is not corrosive (22).
3. Purgeable sample must be collected in 40 mL borosilicate glass vials with screw-caps (Pierce #13075 or equivalent). The septa used must be Teflon faced silicon (Pierce #12722 or equivalent) (22).

TABLE 12.4 SUMMARY OF BOTTOM SAMPLING EQUIPMENT (DEVICES LISTED IN DESCENDING ORDER OF RECOMMENDATION) (28)

Device	Use	Advantages	Disadvantages
Teflon or Glass Tube	Shallow wadeable waters or deep waters if SCUBA available. Soil or semi-consolidated deposits	Preserves layering and permits historical study of sediment deposition. RAPID - samples immediately ready for laboratory shipment. Minimal risk of contamination. Inexpensive.	Small sample size requires repetitive sampling.
Hand Corer with removable Teflon or glass liners.	Same as above except more consolidated sediments can be obtained. Use extended to waters of 4-6 feet by the use of extension rods.	Handles provide for greater ease of substrate penetration.	Requires removal of liners before repetitive sampling. Slight risk of metal contamination from barrel and core cutter.
Eckman or Box-Dredge, line or pole operated.	Soft to semi-soft sediments. Can be used from boat, bridge, or pier in waters of various depths.	Obtains a larger sample with respect to coring tubes. Can be subsampled through box-lid. Pole operated sampler provides greater control and minimizes disturbance of the "fines".	Possible incomplete jaw closure and sample loss. Possible shock wave which may disturb the fines. Metal construction may introduce contaminants.
Gravity corers i.e. Phleger Corer	Deep lakes and rivers. Semi-consolidated sediments	Low risk of sample contamination.	Small sample, requires repetitive operation and removal of liners. Time consuming.
Ponar Grab Sampler	Deep lakes, rivers, and estuaries. Useful on sand, silt, or clay.	Most univerasal grab sampler. Adequate on most substrates. Large sample obtained intact, permitting subsampling.	Shock wave from descent may disturb "fines". Possible incomplete closure of jaws and sample loss. Possible contamination from metal frame construction. Sample must be further prepared for analysis.
BMH-53 Piston Corer	Waters of 4-6 feet deep when used with extension rod. Soft to semi-consolidated deposits.	Piston provides for greater sample retention.	Cores must be extruded on site to other containers - metal barrel introduces risk of metal contamination.
USBMH 60	Sampling moving waters from a fixed platform.	Streamlined configuration allows sampling where other devices could not achieve proper orientation.	Possible contamination from metal construction. Subsampling difficult. Not effective for sampling line sediments.
Peterson Grab Sampler	Deep lakes, rivers, and estuaries. Useful on most substrates	Large sample; can penetrate most substrates.	Heavy, may require winch. No cover lid to permit subsampling. All other disadvantages of Eckman and Ponar.
Orange Peel Grab Smith McIntyre Grab	Deep lakes, rivers, and estuaries. Useful on most substrates.	Not recommended for priority pollutant sampling.	See text
Scoops, drag buckets	Various environmental degrading.	Not recommended for priority pollutant sampling.	See text

12.5 SAMPLING PROCEDURE AND PRETREATMENT OF SAMPLE EQUIPMENT

12.5.1 Pretreatment of Equipment

Sample and storage containers should be pretreated as follows:

1. Wash bottles with hot detergent water.
2. Rinse thoroughly with tap water followed by three or more rinses with organic-free water.
3. Finally, rinse with interference free redistilled solvent such as acetone or methylene chloride and air dry (in contaminant free air) at room temperature. Protect from atmospheric or other sources of contamination. Caps and liners for bottle must also be solvent rinsed as above.

If automatic samplers are to be employed, use the peristaltic pump type with a single 8-10 liter (2.5-3.0 gallons) glass container. Vacuum type automatic samplers can be used if sample containers are glass. The procedure outlined above should be followed for the pretreatment of the containers. In addition all tubing and other parts of the sampling system must be scrubbed with hot detergent water and thoroughly rinsed with tap water and blank water prior to use. Further rinsing with interfence free acetone or methylene chloride is advised when tubing and other parts permit, i.e., are not susceptible to dissolution by the solvent.

12.5.2 Sampling Procedure

Purgeables (22,31)

Grab samples must be collected in glass containers. The procedure for filling and sealing sample containers is a follows: Slowly fill each container to overflowing. Carefully set the container on a level surface. Place the septum (Teflon side down) if applicable, on the

convex sample meniscus. Seal the sample with the screw-cap. To insure that the sample has been properly sealed, invert the sample and lightly tap the lid on a solid surface. The absence of entrapped air bubbles indicates a proper seal. If air bubbles are present, open the bottle, add additional sample, and reseal (in same manner as stated above). The sample must remain hermetically sealed until it is analyzed. Maintain samples at 4°C (39°F) during transport and storage prior to analysis. If the sample is taken from a water tap, turn on the water and permit the system to flush. When the temperature of the water has stabilized, adjust the flow to about 500 mL/minute and collect samples as outlined above.

Non-Purgeables (22)

Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be pre-washed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of Tygon and other potential sources of contamination.

12.6 SAMPLE PRESERVATION AND STORAGE (22)

Samples should be analyzed as soon as possible. Samples, collected to be analyzed via EPA's 600 Method Series, should be preserved and stored as described below:

Method 601 - Purgeable Halocarbons

The samples must be iced or refrigerated from the time of collection until extraction. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL will suffice for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site, fill with sample just to overflowing, seal the bottle, and

shake vigorously for 1 minute.

All samples must be analyzed within 14 days of collection.

Method 602 - Purgeable Aromatics

Collect about 500 mL sample in a clean container. Adjust the pH of the sample to about 2 by adding 1:1 diluted HCl while stirring vigorously. If the sample contains free or combined chlorine, add 35 mg of sodium thiosulfate per part per million of free chlorine per liter of sample. Fill a 40 mL sample bottle (see: Section 12.5.2; Purgeables).

The samples must be iced or refrigerated from the time of collection until extraction.

All samples must be analyzed within 7 days of collection.

Method 604 - Phenols

The samples must be iced or refrigerated from the time of collection until extraction. At the sampling location fill the glass container with sample. Add 35 mg of sodium thiosulfate per part per million free chlorine per liter. Adjust the sample pH to approximately 2, as measured by pH paper, using appropriate sulfuric acid solution or 10N sodium hydroxide. Record the volume of acid used on the sample identification tag so the sample volume can be corrected later.

All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

Method 605 - Benzidines

The samples must be iced or refrigerated from the time of collection to extraction. Benzidine and dichlorobenzidine are easily oxidized by materials such as free chlorine. For chlorinated wastes, immediately

add 35 mg sodium thiosulfate per part per million of free chlorine per liter.

If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4 ± 0.2 units to prevent rearrangement to benzidine. Otherwise, if the samples will not be extracted within 48 hours of collection, the sample pH should be adjusted to 2-3 with sodium hydroxide or sulfuric acid.

All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

Method 606 - Phthalate Esters

The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

Method 607 - Nitrosamines

The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they must be preserved as follows:

Add 35 mg of sodium thiosulfate per part per million of free chlorine per liter of sample.

Adjust the pH of the water sample to pH 7 to 10 using sodium

hydroxide or sulfuric acid. Record the volume of acid or base added.

All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

Method 608 - Organochlorine Pesticides and PCB's

The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

Method 609 - Nitroaromatics and Isophorone

The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

Method 611 Haloethers

The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the

field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

Method 612 - Chlorinated Hydrocarbons

The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hyroxide or sulfuric acid.

All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

Method 613 - 2,3,7,8-Tetrachlorodibenzo-p-dioxin

The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

Method 624 - Purgeables (GC/MS)

The samples must be iced or refrigerated from the time of collection until extraction. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 µg/40 mL) to the empty sample bottles just prior to shipping to the sample site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.
All samples must be analyzed within 7 days of collection.

Method 625 - Base/Neutrals, Acids and Pesticides (GC/MS)

The sample must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they must be preserved as follows:

If the sample contains residual chlorine, add 35 mg of sodium thiosulfate per 1 ppm of free chlorine per liter of sample. Adjust the pH of the water sample to a pH of 7 to 10 using sodium hydroxide or sulfuric acid. Record the volume of acid or base used.

All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

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CHAPTER 13

SAMPLING RADIOACTIVE MATERIALS

13.1 BACKGROUND

Radioactivity in the environment results from the decay processes of individual radionuclides, which are the unstable isotopes of the various chemical elements. Radioactive isotopes possess the same chemical properties as the stable isotopes of a given element. The rules and precautions to be observed for collecting, handling and preserving samples of a specific element or compound apply likewise to its radioactive forms. Guidance given elsewhere in this manual should be reviewed when sampling for radioactive material.

Radioactive waste originates from such diverse nuclear facilities as uranium and thorium mines and mills, fuel enrichment and fabrication plants, nuclear power plants, test reactors, fuel reprocessing plants, waste burial sites, hospitals with nuclear medicine laboratories, nuclear weapons sites, radiochemical producers, research and test laboratories, and manufacturers of products incorporating radioactive substances. Routine gaseous or liquid discharges from nuclear facilities to unrestricted areas contain relatively low concentrations of radioactive material; high level wastes are condensed, sealed and stored on site or transported to radioactive waste disposal sites. The types and amounts of discharged radionuclides vary widely with facility.

The Nuclear Regulatory Commission (NRC) regulates the discharge of radioactive material from nuclear facilities. Concentrations of radionuclides permitted in releases to unrestricted areas are specified in Section 20.106 of

10 CFR 20 (1). The EPA has established permissible concentrations of biologically significant radionuclides in drinking water (2). These levels are lower than those given in 10 CFR 20 since the EPA limits allow for radionuclide uptake from food.

The pathways through which radionuclides in water reach man are shown in Figure 13.1 (3). The drinking water pathway is usually the one that contributes the most dose. Others of significance include consumption of plants and animals that live in water or are fed by irrigation. Less important generally is the external dose received during work or recreational activity from radioactivity in nearby surface water, sediment deposited near shorelines, or irrigated fields (4).

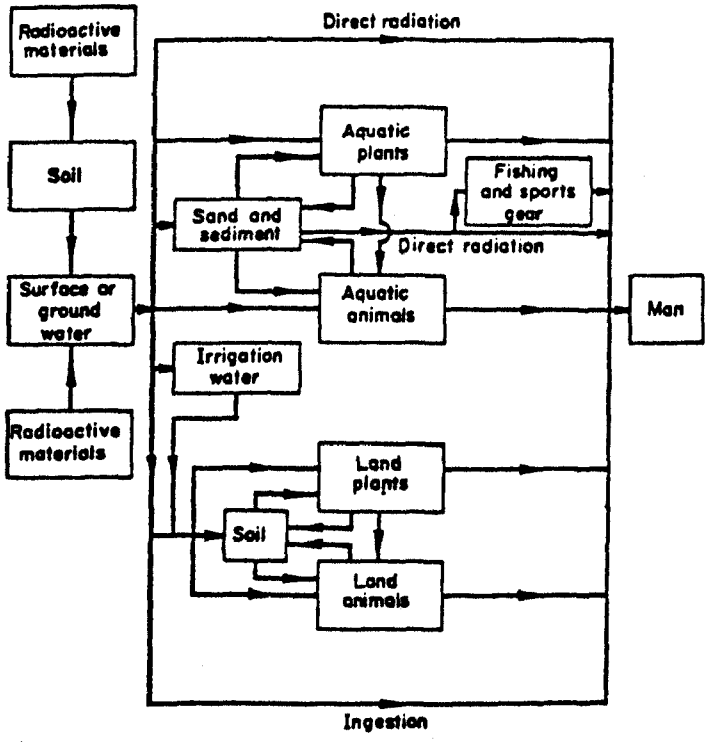

Figure 13.1 (3)

Simplified pathways between radioactive materials released to ground or surface waters (including oceans) and man

13.2 GENERAL CONSIDERATIONS

13.2.1 Background Radioactivity

Many naturally-occurring radionuclides exist in soil, water, air and living matter (5). In addition, man-made radionuclides have become widespread in the natural environment during the past few decades. Due to their presence, background radioactivity at sampling locations must be assessed to determine the actual amount contributed by a nuclear facility to the environment. Control samples taken upstream of the liquid discharge point provide data on the types and amounts of background radionuclides.

In addition, natural and artificial radionuclides occur as impurities in many materials used for sample containers, radiation detection equipment and shields, and chemical reagents (6). For example; glass contains natural ^{40}K, natural water contains uranium, thorium,and their decay products. Cerium compounds contain thorium. Since these contaminants can produce interferences in radionuclide analyses, their effects must be evaluated before sampling.

13.2.2 Radioactive Decay

The half-lives of sampled radionuclides relative to the interval between sampling and measurement must be considered for determining analytical priority. Those with short (less than one week) half-lives need immediate measurement.

Radionuclide concentrations are reported at levels occurring at the time of sampling. This requires that the times of sampling and analyses be carefully recorded for accurate decay corrections. Note, however, that many naturally-occurring radionuclides possess long half-lives which eliminates the need for correction.

References 7, 8 and 9 list half-life values as well as radiation emission

data. Reference 9, although comparatively old, provides comprehensive radionuclide data. Many chemistry handbooks provide data pertaining to common radionuclides. Use recent editions since research to obtain more accurate values continues. For this reason, the data used in an analysis must be recorded since the advent of more accurate values may require revision of earlier calculations.

13.2.3 Detection Capability

The ability to identify and measure very low concentrations of radionuclides depends on the types of counting instrumentation on hand and their sensitivity. An important element affecting detection capability is the instrument background level that results from radioactivity ambient in the counting facility and present in the detector shield and the detection equipment itself. Counting equipment presently available together with proper background control provides sufficient sensitivity to measure radionuclides at levels below regulatory standards.

Knowledge of detection capabilities aids in designing the sampling program, such as, necessary sample volume.

Minimum detectable levels for radionuclides frequently observed in water and analyzed by routine techniques are given in Table 13.1. In some cases, several detection limits are listed to show how they vary with method. Gross alpha and beta counting are preferred by some because the instruments are relatively inexpensive and sufficiently sensitive to determine compliance with certain standards such as those for drinking water. Effective use of gross measurements, however, requires knowledge of radionuclide composition.

TABLE 13.1 RADIONUCLIDE DETECTION CAPABILITIES

Radionuclide	Physical Half-life	Sample Size, liters	Minimal Detectable Level, pCi/liter*	Method
^{3}H	12.4y	0.008	200	LSC
^{14}C	5730y	0.2	30	LSC
^{60}Co	5.27y	0.4	10	γ-spect (Ge)
		3.5	10	γ-spect (NaI)
^{89}Sr	50.5d	1.0	0.5	CS and LBBC
^{90}Sr	28.5y	1.0	0.2	CS and LBBC
^{131}I	8.04d	2.0	0.2	CS and LBBC
		10.0	0.4	IOR, γ-spect
		0.4	10	γ-spect (Ge)
^{137}Cs	30.0y	0.4	10	γ-spect (Ge)
		1.0	0.3	CS and LBBC
		3.5	10	γ-spect (NaI)
^{226}Ra	1600y	1.0	0.02	RE
^{228}Ra	5.75y	2.0	0.1	CS and LBBC
Ra (total)	--	2.0	0.06	CS and IPC
Gross alpha	--	0.1	0.5	IPC
		0.5	0.1	IPC
Gross beta	--	0.1	2.0	LBBC
		0.5	0.5	LBBC

* Calculated at the 99.7 percent (three-sigma) confidence level, based on 1000-minute counting intervals and typical counting efficiencies and instrument background levels.

Methods:

CS	Chemical separation technique (10)
IOR	Ion-exchange resin
IPC	Internal proportional counter
LBBC	Low background beta counter
LSC	Liquid scintillation counter
RE	Radon emanation and counting by alpha scintillation cell (10)
γ-spect	Gamma-ray spectroscopy, "NaI" denotes a 10cm X 10cm NaI (Tl) detector and "Ge" an 85cm^3 Ge (Li) detector

13.3 FREQUENCY OF SAMPLING

13.3.1 Regulatory

As specified in : 1) license or regulations issued by the NRC or NRC Agreement State, 2) EPA drinking water standards, or 3) permits from other governmental agencies.

13.3.2 Surveillance

Frequency of sampling must be based on an evaluation of:

1) types, amounts and potential hazards of radionuclides discharged,
2) their behavior in the environment,
3) waste discharge practices,
4) nature of use of local environment, and
5) the distribution and habits of potentially affected populations (5).

A minimum grab sampling program for surveillance of nuclear power reactors (4) that may be applicable to other types of facilities recommends the following minimum frequencies:

1. Surface water - monthly.
2. Ground water, from sources likely to be affected - quarterly.
3. Drinking water supplies - sample at the water intake with a continous flow proportional sampler. If impracticable, obtain a monthly grab sample at the reservoir when its holding time exceeds one month; if less, make sampling frequency equal to reservoir holding time.
4. Sediment - semiannually.

13.3.3 Other (e.g. testing effectiveness of waste treatment or control methods)

Frequency determined by objectives of investigation.

13.4 LOCATION OF SAMPLING

Unless specified in regulatory licenses, requirements or permits, selection of proper sampling locations is based on judgment (see Section 13.3.2). As a guide, the EPA recommends for surveillance of light-water reactor sites (4):

1. Surface water - At streams receiving liquid waste, collect one sample both upstream and downstream of the discharge point. Obtain downstream sample outside of the restricted area at a location no closer than 10 times the stream width to allow for mixing and dilution. At facility sites on lakes or large bodies of water, sample near but beyond the turbulent area caused by discharge. The upstream sample provides data on background radioactivity. Collect the background sample just above but beyond any influence by the discharge. Record the discharge flow rate at the time of sampling.
2. Drinking water - sample all water supplies with intakes downstream and within 10 miles of a nuclear facility. If none exists, sample the first water supply within 100 miles.
3. Ground water - necessary when a facility discharges radioactive waste to pits or trenches. When local ground water is used for drinking or irrigation, at a minimum, sample the nearest affected well. Subsurface movement of most radionuclides is retarded by the filtering and ion-exchange capacity of soil; tritium, however, moves more rapidly with seepage.
4. Sediment - samples to detect accumulation of undissolved or adsorbed radionuclides in beds of streams or other bodies of water receiving liquid effluents from nuclear facilities are collected: 1) downstream near the discharge outfall but beyond the turbulent area, 2) down-

stream of the discharge at locations where sediment is observed to accumulate, e.g. at bends of streams or dam impoundments, and 3) upstream near the discharge outfall but beyond its influence, to determine background radionuclides.

See also Section 8.4 of this manual for additional guidance in selecting proper sample locations.

13.5 SAMPLE VOLUME

Determining necessary sample volume depends on the types and number of analyses to be performed and the sensitivity of available analytical instruments. For surveillance purposes, obtain the following minimum volumes:

Measurement	Volume, liters
Gamma-ray spectroscopy (NaI detector)	3.5*
Gamma-ray spectroscopy (GeLi detector)	0.4
Gross alpha or beta only	0.1
Liquid scintillation - tritium only	0.01

*Water can be subsequently used for analyses requiring chemical separations (e.g., ^{89}Sr, ^{90}Sr).

Sediment analyses usually require 1 kg. of sample (5).

Obtain larger volumes or weights when sample splitting or replicate analyses is required for quality control purposes.

13.6 SAMPLE CONTAINERS

Use sample containers constructed of material that minimizes radionuclide losses by adsorption or other processes during collection and storage. Containers made of fluorinated hydrocarbon material (e.g. Teflon) are preferred because of their resistivity to adsorption. Polyethylene and polyvinyl chlo-

ride are also recommended (11). Glass and metal containers tend to retain radionuclides (12). Glass bottles also are more subject to breakage during handling.

When adsorption problems persist, try: 1) washing container and sampling apparatus with HCl or HNO_3 before sampling or 2) flushing the container and apparatus with the liquid to be collected before final sampling (13). Test for adsorption by analyzing used containers by gamma-ray spectroscopy when this type of radionuclide emission is present. For other emitters, use successive acid leachings with hot aqua regia and analyze the leachate (12).

Use caps or container covers that seal tightly to prevent handling losses and maintain preservation.

Discard container after use to eliminate possibility of cross-contamination through re-usage. If for economic reasons the more expensive containers are to be used again, test for adsorbed contamination as described above.

13.7 SAMPLE FILTRATION

Filter water and wastewater sample when the radionuclide contents in either or both the suspended solids and dissolved matter fractions are to be determined. Filter as soon as practicable after collection to assure that no redistribution occurs during storage before analysis (12). Use membrane or glass fiber filters since these types resist adsorption effects (11). Filter before adding preservative or other substances to the sample since they can effect changes in distribution (14).

13.8 SAMPLE PRESERVATION

Radionuclides at very low concentrations (parts per billion, or less), typical of most environmental water samples, are subject to many little understood chemical and physical processes (11, 12, 15). Variations in

original sample concentration or homogeneity can result from: 1) adsorption on sampling apparatus, container walls or solid material in the sample (5), 2) co-precipitation of radionuclides due to precipitation of Fe and Mn in ground water samples exposed to air (15), 3) ionic exchange with components of glass containers (12), 4) uptake by bacteria, algae or other biological matter in the sample (13), and 5) formation of colloids (12). Many of these problems are thought to occur because the amounts of stable isotopes are insufficient for carrying the radioactive nuclides of the same element (11).

The standard preservation technique for radionuclides in water and wastewater samples consists of adding concentrated HCl or HNO_3 to obtain a pH of <2 (14,15). Several exceptions exist:

1. Tritium - add no acid; begin analysis immediately upon return to the laboratory (10).
2. Carbon 14 - see tritium
3. Radiocesiums - use HCl only
4. Radioiodines - see tritium: acid oxidizes iodides to iodines which are rapidly lost through volatilization (12). For samples containing ^{3}H, ^{14}C or ^{131}I along with radionuclides requiring preservatives, obtain duplicate samples and add acid to only one.

Add acid preservative after sample collection (but not before filtration-see Section 13.7) or as soon as practicable but do not delay beyond 5 days (14).

When acid preservation is not desirable: 1) add isotopic carriers of the same elements as the radionuclides (12), 2) refrigerate samples at or near their freezing temperature to retard chemical reaction rates and to inhibit bacterial growth (16).

Samples of bottom sediments require no preservation additive (13).

13.9 GENERAL SAMPLING PROCEDURE - WATER AND WASTEWATER

The following procedure summarizes the elements of good practice for collecting and preserving samples of water and wastewater for radionuclide measurements. These guidances apply to the situation where no unusual circumstances exist:

1. Flush sample lines, equipment or other apparatus and sample container with sample medium to minimize adsorption effects. Use type of containers recommended in Section 13.6.
2. Avoid floating debris and bottom sediments when sampling surface waters. When aliquoting large samples containing significant amounts of suspended solids, vigorously shake or mix to assure representative subsamples.
3. Wash sampling apparatus with distilled water to minimize contamination of subsequent samples.
4. Filter sample as soon as practicable after collection when radionuclide distribution in soluble and/or insoluble phases is to be determined (See Section 13.7). Use membrane or glass fiber filters.
5. Add preservative of the required type to liquid samples (see Section 13.8). When concentrated HCl or HNO_3 is the indicated type, add to obtain a pH of <2. In cases of mixtures of radio nuclides, for some (^{3}H, ^{14}C, ^{131}I) of which acid preservation is not recommended, collect replicate samples and treat only one with acid.
6. Seal sample container tightly. Complete sample data label including time of collection for decay corrections.

7. Analyze samples containing short-lived radionuclides as soon as possible.
8. Discard sample containers after use or test for contamination if expensive types of containers are to be used again.

13.10 RADIATION SAFETY

Storage of large numbers or volumes of samples containing radioactivity is a potential source of exposure to workers occupying the area. However, this is unlikely with environmental samples due to low radionuclide content. If in doubt, survey the area periodically with a beta-gamma survey instrument, e.g., a Geiger-Mueller (GM) meter. Note that sample containers reduce all alpha-particle and much beta-particle radiation. If levels above instrument background occur at work stations, consult a radiation safety specialist for procedures to reduce levels and for proper disposal techniques when samples are no longer needed.

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CHAPTER 14

COLLECTING AND HANDLING MICROBIOLOGICAL SAMPLES

14.1 BACKGROUND

Fecal contamination from warm-blooded animals and man is present in certain industrial effluents and in urban and rural runoff municipal wastewaters, and can cause serious diseases and other health problems in drinking water supplies, in waters used for recreation, agriculture, or in the food, dairy and beverage industries. Consequently, the Federal Water Pollution Control Act Amendments (Clean Water Act), the Marine Protection, Research, and Sanctuaries Act (Ocean Dumping), and the Safe Drinking Water Act require monitoring of water supplies, ambient waters and wastewater effluents for compliance with bacterial limits (1, 2 and 3).

In order to control pathogens discharged into these waters, selected groups of microorganisms are monitored as indicators of the sanitary quality of a stream or water supply. These include "total" bacteria (standard plate count), total coliform bacteria, fecal coliform bacteria, and fecal streptococci, as well as the pathogens themselves: Salmonella, Shigella, Giardia, Pseudomonas, Klebsiella, Pneumoniae, Clostridium spp, Viruses, etc.

14.2 ANALYTICAL METHODOLOGY

The bacterial parameters: Standard Plate Count, Total Coliform, Fecal Coliform, Fecal Streptococci and Salmonella will be discussed.

For a more detailed description of the methodologies see Standard Methods and the EPA Manual (4,5).

14.2.1 Standard Plate Count

The Standard Plate Count (SPC) Method is a direct quantitative measurement of the viable aerobic and facultative anaerobic bacteria in a water environment that are capable of growth on plating medium. This test is usually performed by suspension and growth of the sample in agar (pour plate) but may be done as surface growth on a spread plate or membrane filter procedure. Although no one set of plate count conditions can enumerate all organisms present, the Standard Plate Count Method provides the uniform technique required for comparative testing and for monitoring water quality in selected applications.

This simple technique is a useful tool for determining the bacterial density of potable waters for quality control studies of water treatment processes. The Standard Plate Count provides a method for monitoring changes in the bacteriological quality of finished water throughout a distribution system to indicate the effectiveness of chlorine in the system as well as the possible existence of cross-connections, sediment accumulations and other problems within the distribution lines. The procedure may also be used to monitor quality changes in bottled water or emergency water supplies.

14.2.2 Coliforms

The coliform or total coliform group includes all of the aerobic and facultative anaerobic, gram-negative, nonspore-forming, rod-shaped bacteria that ferment lactose in 24-48 hours at 35°C in a multiple-tube most probable number (MPN) procedure or that produce a golden-green metallic sheen within 24 hours at 35°C in the membrane filter (MF) procedure. The definition includes the genera: Escherichia, Citrobacter, Enterobacter, and Klebsiella.

The coliform group may be subdivided into the two following categories:

1. Coliforms normally of fecal origin (primarily Escherichia coli types).
2. Coliforms usually associated with vegetation and soils (Citrobacter, Enterobacter, Klebsiella, and Escherichia spp), which may occur in fecal matter but in smaller numbers than E. coli.

The two analytical techniques recommended by EPA and Standard Methods for enumeration of coliforms are the MPN and the Single-Step, Two-Step and Delayed Incubation MF Methods (4,5)

Although microbiological standard for public water supplies and drinking waters are based on total coliform numbers which include coliform from sources other than human and animal feces, the trend in recent years is to provide a more accurate estimate of the sanitary quality of the water tested by conducting fecal coliform analyses.

14.2.3 Fecal Coliform Methods

The fecal coliforms are part of the total coliform group. They are defined as gram-negative nonspore-forming rods that ferment lactose in 24 ± 2 hours at 44.5 ± 0.2°C with the production of gas in the multiple-tube procedure or produce acidity with blue colonies in the membrane filter procedure.

The major species in the fecal coliform group is Escherichia coli, a species indicative of fecal pollution and the possible presence of enteric pathogens. No method is presently available which distinguishes human fecal coliforms from those of other warm-blooded animals.

The analytical techniques for identifying fecal coliforms in water are the direct MF, the delayed-incubation MF and the multiple-tube, MPN methods.

The test is applicable to the examination of lakes and reservoirs, wells

and springs, public water supplies, natural bathing waters, secondary non-chlorinated effluents from sewage treatment plants, farm ponds, storm-water runoff, raw municipal sewage, and feedlot runoff. The MF test has been used with varied success in marine waters.

14.2.4 Fecal Streptococci

The term, fecal streptococci, is used to describe the streptococci which indicate the sanitary quality of water and wastewater. The fecal streptococci group includes the serological groups D and Q: *Streptococcus faecalis*, *S. faecalis* subsp. *liquifaciens*, *S. faecalis* subsp. *zymogenes*, *S. faecium*, *S. bovis*, *S. equinus*, and *S. avium*.

The MF, MPN and direct pour plate procedures can be used to enumerate and identify fecal streptococci in water and wastewater.

Fecal streptococci data verify fecal pollution and may provide additional information concerning the recency and probable origin of pollution. In combination with data on coliform bacteria, fecal streptococci are used as a supplement to fecal coliform analyses when a more precise determination of sources of contamination is necessary. The occurrence of fecal streptococci in water indicates fecal contamination by warm-blooded animals. They are not known to multiply in the environment.

Further identification of streptococcal types present in the sample may be obtained by biochemical characterization. Such information is useful for source investigations. For example, *S.bovis* and *S. equinus* are host specific and are associated with the fecal excrement of non-human warm-blooded animals. High numbers of these organisms are associated with pollution from meat processing plants, dairy wastes, and run-off from feedlots and farmlands. Because of limited survival time outside the animal intesti-

nal tract, their presence indicates very recent contamination from farm animals.

14.2.5 Salmonella

The genus Salmonella is comprised of a large number of serologically related, gram-negative, nonspore-forming bacilli that are pathogenic for warm-blooded animals including man, and which are found in reptiles, amphibians and mammals. They cause enteritis and enteric fevers via contaminated water, food or food products. Because Salmonella are responsible for many outbreaks of waterborne disease, increased efforts have been made to identify and enumerate them.

Generally the numbers of Salmonella present are small, so that a larger sample volume (> a liter) is required to isolate this pathogen than for coliform and fecal coliform analyses. Since negative result does not assure absence of Salmonella or other pathogens, analyses for indicator organisms are usually run concurrently, to measure the potential health risk.

Recommended methods for recovery of Salmonella from water and wastewater and their subsequent identification are presented in Standard Methods and the EPA Manual (4,5). The methods are particularly useful for recreational and shellfish-harvesting waters. No single method of recovery and identification of these organisms from waters and wastewaters is appropriate for all sampling situations. Rather the method is selected based on the characteristics of the sample and the microbiologist's experience with the procedures. Multiple option techniques are described for sample concentration, enrichment, isolation and identification.

14.2.6 Enteric Viruses (4)

Viruses excreted by animal and man also pollute waters. These

viruses are present in domestic sewage even after waste treatment and enter streams and lakes that serve as the source of water for many communities. Viruses are excreted much lower in numbers than coliform bacteria, and do not multiply outside of the animal or man host. Dilution in ambient waters, sewage treatment, and water treatment further reduce viral numbers in the environment. However it has been demonstrated that infection can be produced by a few viral units.

Sample concentration is needed to demonstrate and quantitate viruses in clean or potable waters because the numbers are quite low. For clean waters, 400 liters or more of water must be sampled to detect viruses. The most promising method for concentrating small quantities of viruses from those waters is adsorption onto a microporous filter. Viruses are removed from the filter with a protein eluant or glycine buffer at a controlled pH. Viruses may be reconcentrated a second time.

Measuring viruses in wastewaters and natural waters is even more difficult because of suspended solids. For such samples, the aqueous polymer two-phase separation technic may be used directly for virus recovery but the sample size is limited to 2 to 4 liters.

After concentration of viruses and elution, the eluate is analyzed by cell culture or whole animal assay.

At this time, the routine examination of the waters and wastewaters for enteric viruses is not recommended. However, for special needs such as wastewater reuse, disease control, or special studies, virus testing can be done but only by competent virologists with proper facilities.

14.3 SAMPLE BOTTLE PREPARATION (4,5)

Sample bottles must be resistant to sterilizing conditions and the

solvent action of the water. Wide-mouth, screw-cap or ground-glass stoppered glass bottles, or heat-resistant plastic bottles (preferably polypropylene) may be used if they can be sterilized without producing toxic materials. Screw capped bottles must be equipped with neoprene rubber liners or other materials that do not produce bacteriostatic or nutritive compounds upon sterilization.

14.3.1 Selection and Cleansing of Bottles

Select bottles of sufficient capacity to provide a volume necessary for all analyses anticipated. Use at least a 125 mL bottle for a minimum sample volume of 100 mL and to provide adequate mixing space. Discard bottles which have chips, cracks, and etched surfaces. Bottle closure must be capable of creating a water-tight seal. Before use, thoroughly clean bottles and closures with detergent and hot water and rinse with hot water to remove all traces of detergent. Then rinse three times with a good quality laboratory pure water. A test for bacteriostatic or inhibitory residues on glassware is described in Standard Methods and in EPA's Manual (4,5).

14.3.2 Use of Dechlorinating and Chelating Agents

Use a dechlorinating agent in the sample bottle when water and wastewater samples containing residual chlorine are anticipated. Add 0.1 mL of a 10 percent solution of sodium thiosulfate to each 125 mL (4 oz) sample bottle prior to sterilization.

Use a chelating agent when waters are suspected of containing more than 0.01 mg/L concentration of heavy metals such as copper, nickel, zinc, etc. Add 0.3 mL of a 15 percent solution ethylene diamine tetra-acetic acid, tetra sodium salt (EDTA), to each 125 mL (4 oz.) sample bottle prior to sterilization (6,7).

14.3.3 Wrapping of Bottles

Protect the tops and necks of glass stopper bottles from contamination by covering them with aluminum foil or kraft paper before sterilization. Screw-cap closures do not require a cover.

14.3.4 Sterilization of Bottles

Autoclave glass or heat-resistant polypropylene plastic bottles at 121°C for 15 minutes. Glassware may be sterilized in a hot air oven at 170°C for two hours. Ethylene oxide gas sterilization is acceptable for plastic containers that are not heat resistant. Before use, store sample bottles sterilized by gas overnight to allow the last traces of gas to dissipate.

14.4 SAMPLING METHODS AND EQUIPMENT (5)

These methods are applicable for sampling potable water, streams and rivers, recreational waters such as bathing beaches and swimming pools, lakes and reservoirs, marine and estuarine waters, shellfish harvesting waters, and domestic and industrial waste discharges.

In no case should a composite sample be collected for microbiological examination. Data from individual samples show a range of values which composite samples will not display. Individual results give information about industrial process variations. Also, one or more portions that make up a composite sample may contain toxic or nutritive material and cause erroneous results.

Collect samples by hand if possible. If depth samples are required or if the sampling sites are difficult to access such as bridges or banks adjacent to surface waters use a sampling device.

Do not rinse bottle with sample, but fill it directly to within 2.5-5 cm (1-2 in.) from the top for proper mixing of the sample before analysis. Use caution to avoid contaminating the sample with fingers, gloves or other materials.

Locate and then carefully identify the sampling site on a field log sheet and on a chain of custody tag, if this is required, and on a label. (See Chapter 15).

14.4.1 Tap Sampling

Do not collect samples from spigots that leak or that contain aeration devices or screens. In sampling direct connections to water main, flush the spigot for five minutes to clear the service line. For wells equipped with hand or mechanical pumps, run the water to waste for five minutes before the sample is collected. Remove the cap aseptically from the sample bottle. Hold the sample bottle upright near the base while it is being filled. Avoid splashing. Replace bottle closure and hood covering.

14.4.2 Surface Sampling by Hand

Collect a grab sample directly into a sample bottle prepared as described in Section 14.3. Remove the bottle top cover and closure and protect them from contamination. Avoid touching the inside of the closure. Grasp the bottle securely at the base with one hand and plunge it mouth down into the water, avoiding surface scum. Position the bottle towards the current flow and away from the hand of the collector, the shore, the side of the sampling platform, or boat. The sampling depth should be 15 to 30 cm (6-12 in.) below the water surface. If the water body is static, an artificial current can be created by moving the bottle horizontally in the direction it is pointed and away from the sampler. Tip the bottle slightly upwards to

allow air to exit and the bottle to fill. After removal of the bottle from the stream, tightly stopper and label the bottle.

14.4.3 Surface and Well Sampling by Weighted Bottle Frame

When sampling from a bridge or other structure above a body of water, Place the bottle in a weighted frame that holds the bottle securely. Remove the cover and lower the device to the water. It is preferable to use nylon rope which does not absorb water and will not rot. Aim the bottle mouth upstream by swinging the sampling device first downstream, and then allow it to drop into the water, without slack in the rope. Pull the sample device rapidly upstream and out of the water, simulating the scooping motion of grab sampling. Take care not to dislodge dirt or other material from the sampling platform.

If sampling a well that does not have pumping machinery, use a weighted sterilized sample bottle. Avoid contaminating the sample with surface scum or dislodged material from the sides of the well.

14.4.4 Depth Sampling

Several additional devices are needed for collection of depth samples from lakes, reservoirs, estuaries and the oceans. These depth samplers require lowering the sample device and/or container to the desired depth, then opening, filling, and closing the container and returning the device to the surface. Although depth measurements are best made with a pre-marked steel cable, the sample depths can be determined by premeasuring and marking a nylon rope at intervals with non-smearing ink, paint, or fingernail polish. The following list of depth samplers is not inclusive but can serve as a guide: The ZoBell J-Z, the Niskin, the New York Dept. of Health, and the

Kemmerer samplers.

14.4.5 Sediments and Sludge Sampling

Microorganisms attach to particles and artifacts in water and are found in large numbers at the bottom sediment/interfaces in any body of water. Sewage solids in treated domestic wastewaters and sludges contain very large numbers of microorganisms which pass into receiving streams, lakes and oceans and then settle into the bottom sediments. This is a particular concern in the ocean dumping program because of the concentrated disposal of very large amounts of sludge in selected ocean dump sites. Microorganisms in these materials are periodically released into the overlying waters as the bottoms are disturbed.

Sediments and bottom materials are difficlt to sample because of the variable composition, size, density and shape of particles and the lack of homogeneity. They vary from light, fluffy particles to compacted high density, solid layers.

Grab samples are not usually satisfactory for quantitative bottom sampling because they may contain material which is not representative. However, they give an indication of the processes that occur.

Corers are used in quantitative work though none is entirely satisfactory. The Eckman corer is used when sampling from small boats. The Wildlife Co. (Saginaw, Michigan) coring device is used in shallow water (15 meters or more). In extremely shallow water a lucite tube can be inserted into the sediment by hand, and capped by a stopper. The Van Donsel-Geldreich sampler can be used to collect soft sediments or muds in relatively deep waters. It uses a sterile plastic bag in a weighted frame to collect the sample and then closes the bag with a wire loop.

14.5 SAMPLE FREQUENCY AND SITE SELECTION (5)

14.5.1 Frequency of Sampling

The frequency of sampling depends upon the type of pollution that is to be measured. Cyclic pollution and its duration are measured as frequently as practical immediately downstream from the source. Uniform pollution loads are measured at greater distances downstream from the source and at less frequent time intervals than cyclic pollution. A common approach for short-term studies is to collect samples from each site daily and advance the sampling intervals one hour during each 24-hour period to obtain data for a 7-10 day study.

Often the numbers of samples to be collected are specified by NPDES permits, drinking water regulations, or by State requirements. Some standards require a minimum number of samples to be collected each month. Other standards are less explicit and simply indicate that the geometric mean coliform density shall not exceed a certain level each month, with no more than 10%, 20%, etc. of samples exceeding a certain value. Where the number of samples required is undetermined, a sufficient number should be collected to measure the variations in conditions.

14.5.2 Raw Water Supplies

Reservoirs, and lakes used as water supplies, are sampled at inlets, other possible sources of pollution, the draw-off point, the quarter point intervals around the draw-off point at about the same depth, and the reservoir outlet.

14.5.3 Potable Water Supplies

Coliform standards for potable water supplies established by Public

Health Service Act of 1962 were amended by the Safe Drinking Water Act of 1974 (SWDA) and its amendments (8). The levels for the 1962 PHS Standards were retained in the SDWA but were redefined as Maximum Contaminant Levels (MCLs). As with the previous standards, the MCLs emphasize the importance of collecting samples at regular intervals, in numbers proportionate to the population served, and at points representative of conditions in the distribution system. A set protocol was established for repeat sampling when positive coliform results occur. For application of the MCLs, the frequency of sampling and the location of sampling points is established jointly by the utility, the Reporting Agency, and the Certifying Authority.

The SDWA also specifies that any laboratory generating data for public water supplies, as required under the Act, must be certified according to the procedures and criteria in the Laboratory Certification Manual (9). The laboratory facility, personnel, equipment and instrumentation, sampling methodology, quality control, data reporting and necessary action responses are specified.

14.5.4 Distribution Systems

Sample locations should be representative of the distribution system and include sites such as municipal buildings, public schools, airports and parks, hydrants, restaurants, theaters, gas stations, industrial plants and private residences. A systematic coverage of such points in the distribution system should detect contamination from breaks in water lines, loss of pressure, or cross-connections. The sampling program should also include special sampling locations such as dead-end distribution lines that are sources of bacterial contamination, and far reaches of the distribution lines where chlorine residual may have dissipated.

The minimum number of samples which must be collected and examined each month is based upon the population density served by the distribution system. Samples should be collected at evenly spaced time intervals throughout the month. In the event of an unsatisfactory sample, repetitive samples must be collected until two consecutive samples yield satisfactory quality water. Check samples from any single point or special purpose samples must not be counted in the overall total of monthly samples.

Standard Sample: The standards for microbiological quality are based upon the number of organisms allowable in a standard sample. A standard sample for the membrane filter technique is at least 100 mL. For the MPN test, a standard sample consists of five standard portions of either 10 mL or 100 mL.

14.5.5 Lakes and Impoundments

Sampling points in a recreational impoundment or lake should include inlets, sources of pollution, grids or transects across the long axis of the water body, bathing areas and outlets.

14.5.6 Stream Sampling

The objectives of the initial survey dictate the location, frequency and number of samples to be collected.

A. Selection of Sampling Sites: A typical stream sampling program includes sampling locations upstream of the area of concern, upstream and downstream of waste discharges, upstream and downstream from tributary. Downstream sites should be located far enough below entry of discharge or tributary to allow thorough mixing. For more complex situations, where several waste discharges are involved, sampling includes sites upstream and downstream from the combined discharge area and samples taken directly from each industrial or muni-

cipal waste discharge. Using available bacteriological, chemical and discharge rate data, the contribution of each pollution source can be determined.

B. Small Streams: Small streams should be sampled at background stations upstream of the pollution sources and at stations downstream from pollution sources. Additional sampling sites should be located downstream to delineate the zones of pollution. Avoid sampling areas where stagnation may occur (backwater of a tributary) and areas located near the inside bank of a curve in the stream which may not be representative of the main channel.

C. Large Streams and Rivers: Large streams are usually not well mixed laterally for long distances downstream from the pollution sources. Sampling sites below point source pollution should be established to provide desired downstream travel time and dispersal as determined by flow rate measurements. Particular care must be taken to establish the proper sampling points at: the upper reach control station, non-point sources of pollution, waste discharges as they enter the stream, quarter-point samples below the pollution sources to detect channeling, tributaries, and downstream from tributaries after mixing. Occasionally, depth samples are necessary to determine vertical mixing patterns.

14.5.7 Recreational Waters

A. Selection of Sampling Sites: Select sampling sites which reflect the quality of water throughout the recreational area. Boat marinas, waste drainage from dry well restrooms and other public buildings, any upstream flows from impounded rivers or drainages into lakes, reservoirs or impounded streams, as well as the lake or body

of water itself should be sampled.

Sampling sites at bathing beaches or other recreational areas should include upstream or peripheral areas and locations adjacent to natural drains that would discharge stormwater, or run-off areas draining septic wastes from restaurants, marinas, or garbage collection areas.

Swimming pool water should be monitored at least daily during maximum use periods, preferably at the overflow. It is important to test swimming pool samples for neutralization of residual chlorine at pool side to assure that the dechlorinating agent was effective.

B. Depths: Sampling in bathing areas should be standardized at 1 foot for shallow depths and at 3 feet for swimming depths.

C. Frequency and Time: Collect samples daily during high-use seasons. Select high use days (Fridays, weekends and holidays) and sample during peak period of the day, generally in the afternoons. Sample estuarine waters at high tide, low tide and ebb tide to obtain a measure of the cyclic changes in water quality.

14.5.8 Domestic and Industrial Waste Discharges

When it is often necessary to sample secondary and tertiary wastes from municipal waste treatment plants and various industrial waste treatment operations, sampling must be adjusted to meet the specific situation. If plant treatment efficiency varies considerably, collect grab samples around the clock at selected intervals for a three to five day period. If it is known that the process displays little variation, fewer samples are needed. The NPDES has established treatment plant effluent limits for wastewater dischargers. These are often based on maximum and mean values. A sufficient number

of samples must be collected to satisfy the permit and/or provide statistically sound data and give a fair representation of the bacteriological quality of the discharge (10).

14.5.9 Marine and Estuarine Sampling

Sampling marine and estuarine waters requires the consideration of other factors in addition to those usually recognized in fresh water sampling. They include tidal cycles, current patterns, bottom currents and counter-currents, stratification,climatic conditions, seasonal fluctuations, dispersion of discharges and multi-depth samplings.

The frequency of sampling varies with the objectives. When a sampling program is started, it may be necessary to sample every hour around the clock to establish pollutional loads and dispersion patterns. The sewage discharges may occur continuously or intermittently.

When the sampling strategy for a survey is planned, data may be available from previous hydrological studies done by Coast Guard, Corps of Engineers, National Oceanic and Atmospheric Administration (NOAA), U.S. Geological Survey, or university and private research investigations. In a survey, float studies and dye studies are often used to determine surface and undercurrents. Initially depth samples are taken on the bottom and at five feet increments between surface and bottom. A random grid pattern for selecting sampling sites is established statistically.

A. Marine Sampling: In ocean studies, the environmental conditions are most diverse along the coast where shore, atmosphere and the surf are strong influences. The shallow coastal waters are particularly susceptible to daily fluctuations in temperature and seasonal changes. Sampling during the entire tidal cycle or during a half

cycle may be required. Many ocean studies such as sampling over the continental shelf involve huge areas where no two areas are the same. Selection of sampling sites and depths are most critical in marine waters. In winter, cooling of coastal waters can result in water layers which approach 0°C. In summer, the shallow waters warm much faster than the deeper waters. Despite the higher temperature, oxygen concentrations are higher in shallow than in deeper waters due to greater water movement, surf action and photosynthetic activity from macrophytes and the plankton.

Moving from the shallow waters to the intermediate depths, one observes a moderation of these shallow water characteristics. In the deeper waters, there is a marked stabilization of conditions. Water temperatures are lower and more stable. Deep waters have limited turbulence, little penetration of light, sparse vegetation, and a layer of silt and sediment covering the ocean floor.

B. Estuarine Sampling: When a survey is made on an estuary, samples are often taken from a boat, ususally making an end to end traverse of the estuary. Another method involves taking samples throughout a tidal cycle, every hour or two hours from a bridge, or from a boat anchored at a number of fixed points.

In a large bay or estuary where many square miles of area are involved, a grid or series of stations may be necessary. Two sets of samples are usually taken from an area on a given day, one at ebb or flood slack water, and the other three hours earlier, or later, at the half tide interval. Sampling is scheduled so that the mid-sampling time of each run coincides with the calculated occurrence of the tidal condition.

In locating sampling sites, one must consider points at which tributary waters enter the main stream or estuary, location of shellfish beds, and bathing beaches. The sampling stations can be adjusted as data accumulate. For example, if a series of stations one-half mile apart consistently show similar values, some stations may be dropped and others added in areas where data shows more variability.

Considerable stratification can occur between the ocean's salt water and fresh river water. It is essential when starting a survey of an unknown estuary to find out whether there is any marked stratification. This can be done by chloride determinations at different locations and depths. It is possible for stratification to occur in one part of an estuary and not in another.

On a flood-tide, the more dense salt water pushes up into the less dense fresh river water causing an overlapping, with the fresh water flowing on top and forming the phenomenon called a salt water wedge. As a result, stratification occurs. If the discharge of pollution is in the salt water layer, the contamination will be concentrated near the bottom at the flood tide. The flow or velocity of the fresh water will influence the degree of stratification which occurs. If one is sampling only at the surface, it is possible that the data will not show the polluted underflowing water which was contaminated at a point below the fresh water river. Therefore, where stratification is suspected, samples at different depths will be needed to measure vertical distribution.

C. Shellfish-Harvesting Waters: Water overlying shellfish-harvesting areas should be sampled during periods of most unfavorable hydro-

graphic conditions, usually at low tide after heavy precipitation. However, shellfish beds are sometimes exposed during low tide and must be sampled during other tidal conditions. Procedures for sampling of shellfish and water in shellfish growing areas are governed by the National Shellfish Sanitation Program's Manual of Operations (11).

14.6 PRESERVATION AND TRANSIT OF SAMPLES (4,5)

The adherence to sample preservation and holding time limits is critical to the production of valid data. Samples exceeding these limits should not be analyzed. The following rules must be observed.

14.6.1 Storage Temperature and Handling Conditions

Bacteriological samples should be iced or refrigerated at a temperature of 1-4^{o}C during transit to the laboratory. Insulated containers are preferable to assure proper maintenance of storage temperature. Care should be taken that sample bottles are not totally immersed in water during transit or storage.

14.6.2 Holding Time Limitations

Although samples should be examined as soon as possible after collection, they should not be held longer than six hours between collection and initiation of analyses (12). This limit is applied to fresh waters, seawaters and shellfish-bed waters. The exception is water supply samples mailed in from water treament systems. Current regulations permit these samples to he held up to 30 hours.

Although a holding time of six hours is permitted sewage samples, organically-rich wastes and marine waters are particularly susceptible to rapid

increases or die-away and should be held for the shortest time possible, to minimize change.

If the specified holding time limits cannot be observed the following alternatives should be considered:

A. Temporary Field Laboratories: In situations where it is impossible to meet the six hour maximum holding time between collection and processing of samples, consider the use of temporary field laboratories located near the collection site.

B. Delayed Incubation Procedure: If sampling and transit conditions require more than six hours, and the use of field laboratories is impossible, consider the delayed incubation procedures for total and fecal coliforms and fecal streptococci.

C. Public Transportation: Occasionally, commercial forms of transit such as airlines, buslines or couriers are used to transport samples contained in ice chests to the laboratory. These should be considered only when storage time, temperature requirements and the proper disposition of the samples can be assured.

14.7 REFERENCES

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CHAPTER 15

SAMPLE IDENTIFICATION AND CHAIN OF CUSTODY PROCEDURES

The successful implementation of a monitoring program depends on the capability to produce valid data and to demonstrate such validity (1). In addition to proper sample collection, preservation, storage and handling appropriate sample identification and chain of custody procedures are necessary to help insure the validity of the data.

15.1 SAMPLE IDENTIFICATION

15.1.1 Sample Number

Assign each sample container a unique number for identification in the field and laboratory. The identification number should have as few digits as possible to discourage abbreviation. The following guidelines should facilitate proper identification:

1. Use preprinted rolls of peel back labels assigned from the laboratory to a sampling crew.
2. For relatively small numbers of samples use sequential numbering and affix a label to each bottle. When the sample is placed in two or more containers, assign two or more numbers to that sample. For large numbers of samples such as encountered in river, lake, or estuary sampling, use a five digit number, the first two numbers indicating the week of the year. When a sample is split into two or more parts, use one sample number and apply a color coded label to each sample which indicates the type of preservative added.

Therefore, once the type of preservative has been indicated, the general group of parameters to be analyzed on that sample is established. For example, a blue label indicates that nitric acid has been added, therefore, the analyst could obtain an aliquot from this sample for metal analysis.

3. Note the date and preservative on the label.
4. Note additional information in the field notebook.

15.2 CHAIN OF CUSTODY (2)

15.2.1 General

The regulatory body must be able to demonstrate the reliability of its evidence in pollution cases by proving the chain of possession and custody of any samples which are offered for evidence or which form the basis of analytical results introduced into evidence in any water pollution case. Therefore, it is imperative that each regulatory body and its laboratory prepare written procedures to be followed whenever evidence samples are collected, transferred, stored, analyzed, or destroyed. The primary objective of these procedures is to create an accurate written record which can be used to trace the possession of the sample from the moment of its collection through its introduction into evidence. The following guidelines on the chain of custody procedures are provided. However, in those cases where state chain of custody procedures apply, follow the procedures which satisfy state rules or laws for the introduction of evidence into enforcement or judicial proceedings.

A sample is in custody if it is:

1. In actual physical possession, or
2. In view, after being in physical possession, or

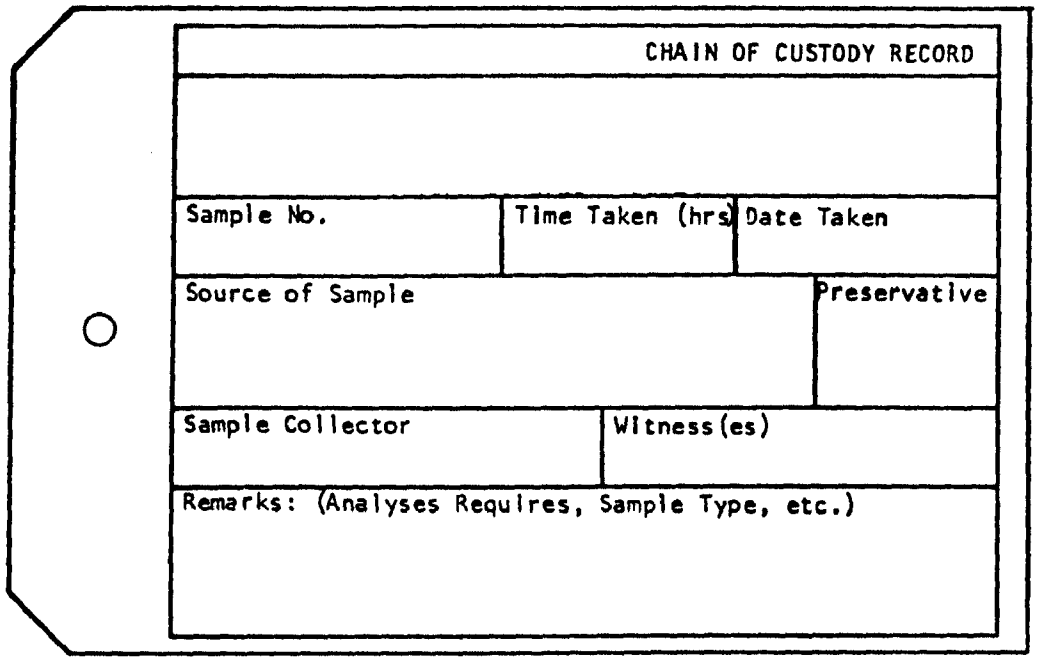
3. In physical possession and locked up so that no one could tamper with it.

15.2.2 Sample Collection

1. Limit handling the sample to as few people as possible.
2. Obtain samples using the guidelines in this handbook.
3. Attach sample tags, (Figure 15.1), securely to the sample container at the time the sample is collected. The tag should contain as a minimum: station number and location, date, time taken, type of sample, sequence number (first sample of the day-sequence No. 1, second sample-sequence No. 2 etc.), analyses required and the name of the person taking the sample. The tag must be filled out legibly in waterproof ink.
4. Record field measurements and other pertinent information in a bound field notebook to refresh the memory of the sampling personnel in the event that a witness is required at an enforcement proceeding. A separate set of field notebooks should be maintained for each survey and stored in a safe place where they can be protected and accounted for at all times. Establish a field data record format (Figure 15.2) to minimize field entries or possible omissions. The following information should be included:

date	field measurements such as:
time	temperature
survey name	conductivity
type of samples taken	DO
volume of each sample	pH
type of analyses	flow
sample numbers	other pertinent information
sample location	or observation

(FRONT SIDE)



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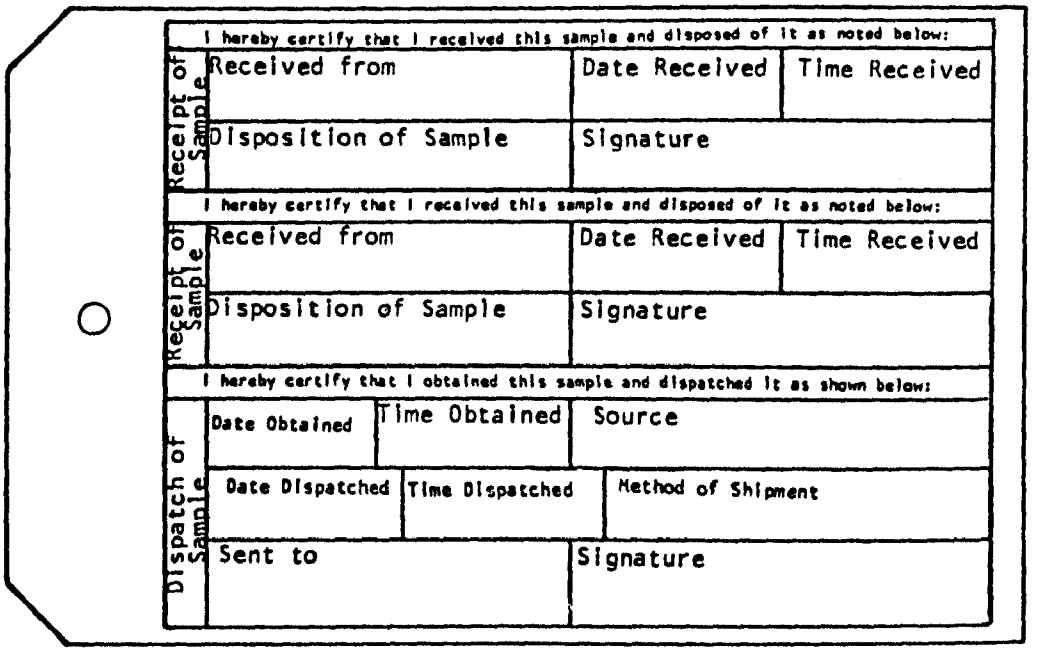

Figure 15.1 Chain of Custody Record Tag

Samplers: _____

FIELD DATA RECORD

Station	Sample Number	Date of Collection	Time		pH	Temperature	Other Parameters		
			Sample Taken	Sample Received					

Figure 15.2 Sample - Field Data Record

The entries should be signed by the person taking the sample. Assign a survey coordinator or designated representative the responsibility for preparing and retaining field notebooks during and after the survey.

5. The sample collector is responsible for the collected samples until they are properly dispatched to a receiving laboratory or turned over to an assigned custodian. He must assure that each container is in his possession or view at all times or is stored in a locked place where no one can tamper with it.
6. Take color slides or photographs of the outfall sample location and any visible water pollution. Document in writing on the back of the photo the following information: signature of the photographer, time, date, and site location. Photographs of this nature should be handled according to the established Chain of Custody procedures to prevent alteration.

15.2.3 Transfer of Custody and Shipment

In transfer of custody, each custodian of samples must sign, record and date the transfer. Regulatory agencies may develop their chain of custody procedures tailored to their needs. These procedures may vary in format and language but should contain the same essential elements regarding sample identification and chain of custody procedures. Historically, sample transfer under chain of custody has been on a sample by sample basis which is awkward and time-consuming. However, EPA's National Enforcement Investigation Center (NEIC), Denver, has set a precedent with its bulk transfer of samples. Bulk transfer is speedier, reduces paperwork and the number of sample custodians. The following description of chain of custody is similar to that of NEIC - Denver (3).

1. Samples must be accompanied by a Chain of Custody Record which includes the name of the survey, collector's signature, station number, station location, date, time, type of sample, sequence number, number of containers and analyses required (Figure 15.3) When turning over the possession of samples, the transferor and transferee must sign, date, and record time on the sheet. This record sheet allows transfer of a group of samples in the field to the mobile laboratory or to other designated laboratories. When a custodian transfers a portion of the samples identified on the sheet to the field mobile laboratory, the individual samples must be noted in the column with the signature of the person relinquishing the samples. The field laboratory person receiving the samples should acknowledge the receipt by signing in the appropriate column.
2. If a custodian has not been assigned, the field custodian or the sample collector has the responsibility for packaging and dispatching the samples to the laboratory for analysis. The "Dispatch" portion of the Chain of Custody Record must be filled out, dated, and signed.
3. Samples must be carefully packed in shipment containers such as ice chests, to avoid breakage. The shipping containers must be locked for shipment to the receiving laboratory.
4. Packages must be accompanied by the Chain of Custody Record showing identification of the contents. The original must accompany the shipment. A copy is retained by the survey coordinator.
5. If samples are delivered to the laboratory when appropriate personnel are not there to receive them, the samples must be locked in a

designated area within the laboratory in a manner so that no one can tamper with them. The same person must then return to the laboratory and unlock the samples and deliver custody to the appropriate custodian.

15.2.4 Laboratory Custody Procedures

1. The laboratory must designate a "sample custodian" and an alternate to act in his absence. In addition, the laboratory must set aside as a "sample storage security area" an isolated room with sufficient refrigerator space, which can be secured locked from the outside.
2. Samples should be handled by the minimum number of people.
3. The custodian should receive the incoming samples and indicate receipt by signing the Chain of Custody Record Sheet accompanying the samples and retaining the sheet as a permanent record. Couriers picking up samples at the airport, post office, etc. must sign jointly with the laboratory custodian.
4. Immediately upon receipt, the custodian must place samples in the sample room which should be locked at all times except when samples are removed or replaced by the custodian. To the maximum extent possible, only the custodian should be permitted in the sample room.
5. The custodian shall maintain the intergity of the sample by appropriate storage.
6. The custodian must distribute samples to the personnel who are to perform tests.
7. The analyst must record information in his laboratory notebook or analytical work sheet, that describes the samples, the procedures performed and the results of the tests. The notes must be retained

CHAIN OF CUSTODY RECORD

Survey

Samplers: (Signature)

Station Number	Station Location	Date	Time	Sample Type			Seq. No.	No. of Containers	Analysis Required
				Water		Air			
				Comp.	Grab				

Relinquished by: (Signature)	Received by: (Signature)	Date/Time
Relinquished by: (Signature)	Received by: (Signature)	Date/Time
Relinquished by: (Signature)	Received by: (Signature)	Date/Time
Relinquished by: (Signature)	Received by: (Signature)	Date/Time
Dispatched by: (Signature) Date/Time	Received for Laboratory by:	Date/Time

Method of Shipment:

Distribution: Original - Accompany Shipment
1 copy - Survey Coordinator Field Files

Figure 15.3 Sample - Chain of Custody Record

as a permanent record in the laboratory and should include any abnormalities which occurred during the testing procedure. In the event that the person who performed the tests is not available as a witness at the time of the trial, the regulatory agency may be able to introduce the notes in evidence under the Federal Business Records Act.

8. Standard methods of laboratory analyses must be used as described in the "Guidelines Establishing Test Procedures for Analysis of Pollutants," 38 F. R. 28758, October 16, 1973. If laboratory personnel deviate from standard procedures, they should be prepared to justify their decision during cross-examination.
9. Laboratory personnel must be responsible for the care and custody of a sample once it is handed over to them and should be prepared to testify that the sample was in their possession and viewed or secured in the laboratory at all times from the moment it was received from the custodian until the tests were run.
10. Once the sample testing is completed, the unused portion of the sample together with all identifying tags, the laboratory records, and other documentation of work must be returned to the custodian.
11. Samples, tags and laboratory records of tests may be destroyed only upon the order of the Laboratory Director, who will first confer with the Chief, Enforcement Specialist Office, to make certain that the information is no longer required.

15.3 REFERENCES

1. Crim, R. L., Editor. Model State Water Monitoring Program. EPA-440/9-74-002, U.S. Environmental Protection Agency, Washington, D.C. 1974, pp.

2. In Press. Microbiological Methods for Monitoring the Environment/Water and Wastewater, U.S. Environmental Protection Agency, Cincinnati, Ohio. 1976.

3. Anon. Compliance Monitoring Procedures. U.S. Environmental Protection Agency, Denver, Colorado, 1975. 61 pp.

CHAPTER 16

QUALITY ASSURANCE

Quality assurance is an integral part of all sampling programs. The objectives of quality asssurance are to assure that the data generated is:

1. Meaningful
2. Representative
3. Complete
4. Precise
5. Accurate
6. Comparable

Data must be representative of the condition being monitored. To enable comparison with different data and with stated program objectives, data must be presented in standard units. Quality assurance for a sampling program should address all elements from sample collection to data reporting while permitting operational flexibility. A quality assurance plan should include, as an essential part, a continuing education and training program for the personnel involved in the monitoring program. This will enhance quality assurance capabilities and aid in keeping pace with the scientific advancement occuring in the field.

16.1 OBJECTIVES

For the implementation of an effective and meaningful quality assurance program it is imperative that its objectives are well defined, documented and cover all activities that affect the quality of the data. Such written objectives are needed to assure:

1. Effective participation in the quality assurance program by various

personnel in different organizations involved in a sampling program.

2. Uniform thinking and rationale among the personnel participating in a sampling program.
3. Appropriate action at all levels among participating organizations.
4. Integrated and planned course of action.
5. Performance evaluation against stated objectives.

To meet the above objectives, one individual within the organization should be designated the Quality Assurance (QA) Coordinator. The QA Coordinator should undertake activities such as quality planning, auditing, and reliability. The QA Coordinator should also have the responsibility for coordinating all quality assurance activity so that complete integration of the quality assurance plan is achieved.

16.2 ELEMENTS OF A QUALITY ASSURANCE PLAN (1)

The quality assurance plan will contain the following elements:

1. A policy to establish parameter analytical criteria (accuracy, precision, detection limit) for monitoring activities. Field, sample handling, and test procedures are best established only after establishment of criteria.
2. A systematic policy for selection and use of measurement and sampling methodology. Where available, approved methodology must be used. Where alternate methodology is necessary or where approved methodology does not exist, the quality assurance plan should state how the alternate or new methodology will be documented, justified, and approved for agency use.
3. Documentation of operating procedures. The QA Coordinator should establish the format for the procedures and see that the documentation

is done.

4. Intra-office quality assurance audits or acceptance criteria.

   The QA Coordinator as part of the documented methodology or operating procedures will approve or specify the intra-office audits. Detailed quality assurance procedures are necessary for:

   Personnel selection.

   Sample site selection.

   Sample collection, handling and preservation.

   Calibration and maintenance of instruments and equipment (field and laboratory).

   Intra-office audits (field and laboratory) for data acceptance with documentation for agency data credibility.

   Review and approval of data before they are released.

   Scheduled intra-office audits (field and laboratory) through the QA Coordinator to assess the accuracy of field and laboratory methodology.

   An audit by the QA Coordinator on a systematic basis to see that all the above activities are being done.

16.3 PERSONNEL TRAINING (1)

Successful implementation of a quality assurance plan ultimately depends upon the competence of the monitoring personnel. All personnel involved in any function affecting data quality (sample collection, analysis, data reduction and quality assurance) should have sufficient training in their appointed jobs to contribute to the reporting of complete and high quality data. The quality assurance plan should therefore provide for periodic assessment of training needs and should describe the manner in which training is to be accomplished. This will include both in-house and external training and education.

Several methods of training are available to promote achievement of the desired level of knowledge and skill required. The following are the training methods most commonly used in the pollution control field:

16.3.1 On the Job Training (OJT)

An effective OJT program could consist of the following:

Observe experienced professionals perform the different tasks in the measurement process.

Perform tasks under direct supervision of an experienced professional.

Perform tasks independently but with adequate quality assurance checks.

16.3.2 Short-term Course Training

A number of short-term courses (normally two weeks or less) are available that provide knowledge and skills to more effectively implement the NPDES monitoring program. Course schedules can be obtained from the EPA Training Centers.

16.3.3 Long-term Course Training

Numerous universities, colleges, and technical schools provide long-term (quarters or semester length) academic courses in wastewater treatment, analytical chemistry, environmental engineering, and other disciplines.

16.3.4 Training Evaluation

The quality assurance plan needs to address training evaluation.

Training should be evaluated in terms of (1) the level of knowledge and skill achieved by the operator from the training, and (2), the overall effectiveness of the training (including determination of training areas that need improvement).

A good means of measuring skill improvement is to assign the trainee a work task. Accuracy and/or completeness are commonly used indicators to asses

the trainee's proficiency. The tasks should be similar to the following forms:

1. Sample Collection. Trainee would be asked to list or preferably perform all steps in a sample collection for a hypothetical or real case. This would include selection of sample site, duration and frequency of sampling, type of samples collected(grab or composite), sampling and flow measuring equipment that would provide the highest quality data. In addition, the trainee would be asked to perform selected calculations. Proficiency would be judged in terms of completeness and accuracy.
2. Analysis. Trainee would be provided unknown samples for analysis normally measured in the field. As defined here, an unknown is a sample whose concentrations are known to the work supervisor (OJT) or the training instructor (short-term course training) but unknown to the trainee. Proficiency would be judged in terms of accuracy.

16.4 QUALITY ASSURANCE IN SAMPLING

As a first step for quality assurance in sample collection the sampling program should delineate the details on sampling locations, sample type, sample frequency, number of samples, duration of sampling, sample volume, sample collection methods, equipment to be used for the sample collection, sample containers, pretreatment of containers, type and amount of preservative to be used blanks, duplicates/triplicates, spiked samples, replicates, chain of custody procedures, and any other pertinent matter which will have a bearing on the quality assurance in sample collection and handling. Guidelines on the above can be found in this manual.

Despite a well defined sampling program, appropriate sampling and field

TABLE 16.1 QUALITY ASSURANCE PROCEDURES FOR FIELD ANALYSIS AND EQUIPMENT (1)

Parameter	General	Daily	Quarterly
1. Dissolved Oxygen			
Membrane Electrode	Enter the make, model, serial and/or ID number for each meter in a log book.	1. Calibrate meter using manufacturere's instructions or Winkler-Azide method. 2. Check membrane for air bubbles and holes. Change membrane and KCl if necessary. 3. Check leads, switch contacts etc. for corrosion and shorts if meter pointer remains off scale.	Check instrument calibration and linearity using a series of at least three dissolved oxygen standards.
Winkler-Azide Method	Record data to nearest 0.1 mg/l.	Duplicate analysis should be run to check the precision of the analyst. Duplicate values should agree within ±0.2 mg/l.	
2. pH			
Electrode Method	Enter the make, model serial and/or ID number for each meter in a log book.	1. Calibrate the system against standard buffer solutions of known pH value at the start of a sampling run.	Take all meters to the laboratory for maintenance, calibration and quality control checks.

TABLE 16.1 (continued)

Parameter	General	Daily	Quarterly
2. pH (continued)			
		2. Periodically check the buffers during the sample run and record the data in the log sheet or book. 3. Be on the alert for erratic meter response arising from weak batteries, cracked electrode, fouling etc. 4. Check response and linearity following highly acidic or alkaline samples. Allow additional time for equilibration. 4. Check against the closest reference solution each time a violation is found. 5. Rinse electrodes thoroughly between samples and after calibration.	
3. Conductivity			
	Enter the make, model, serial and/or ID number for each meter in a log book.	1. Standardize with KCl standards having similar specific conductance values to those anticipated in the samples. Calculate the cell constant using two different standards	1. Take all meters to lab for maintenance, calibration and quality control checks. 2. Check temperature compensation. 3. Check date of last platinizing and replatinize if necessary.

(continued)

TABLE 16.1 (continued)

Parameter	General	Daily	Quarterly
3. Conductivity (continued)		(continued) Cell Constant = Standard Value / Actual Value Specific Conductance = Reading multiplied by Cell Constant 2. Rinse cell after each sample to prevent carry-over.	4. Analyze NBS or EPA reference standard and record actual vs. observed readings in the log.
4. Residual Chlorine			
Amperometric Titration	Enter the make, model, ID and/or serial number of each titration apparatus in a log book. Report results to nearest 0.01 mg/l	Refer to instrument manufacturer's instructions for proper operation and calibration procedures.	Return instrument to lab for maintenance and addition of fresh, standardized reagents†

† Biweekly

TABLE 16.1 (continued)

Parameter	General	Daily	Quarterly
5. Temperature			
Manual	Enter the make, model, serial number and/or ID number and temperature range for each thermometer. All standardization shall be against an NBS or NBS calibrated thermometer. Readings should agree within 1°C. If enforcement action is anticipated, calibrate the thermometer before and after analysis. All data shall be read to the nearest 1°. Report data between 0°-9°C (32°-48°F) to one significant figure; between 10°-99°C (50°-210°F) to two significant figures.	1. Check for air spaces or bubbles in the column, cracks, etc. Compare with a known source if available.	Check at two temperatures against an NBS or equivalent thermometer. Enter data in a log book. Temperature readings shall agree within 1°C or the thermometer shall be replaced or recalibrated. Accuracy shall be determined throughout the expected working range 0° to 50°C (32°to 120°F) A minimum of three temperatures within the range should be used to verify accuracy. Preferable ranges are: 5°-10°, 15°-25°, 35°-45°C.*(41°-50°, 59°-77°, 95°-113°F)
Thermistors: thermographs etc.	Enter the make, model, serial and/or ID number of the instrument in a log book. All standardization shall be against an NBS or NBS calibrated thermometer. Reading should agree within 1°C.	Check thermistor or sensing device for response and operation according to the manufacturer's instructions.	Accuracy shall be determined throughout the expected working range of 0° to 50°C (32° to 120°F) A minimum of three temperatures within the range should be used to verify the accuracy.

* Initially and Bi-annually

(continued)

TABLE 16.1 (continued)

Parameter	General	Daily	Quarterly
5. Temperature (continued)			
Thermistors; Thermographs etc. (cont.)	If enforcement action is anticipated refer to the procedure listed in Manual above.	Record actual vs. standard temperature in log book.	Preferable ranges are: 5^{o}-10^{o}, 15^{o}-25^{o}, 35^{o}-45^{o}C. (41^{o}-50^{o}, 59^{o}- 77^{o}, 45^{o}-113^{o}F)*
6. Flow Measurement	Enter the make, model, serial and/or ID number of each flow measurement instrument in a log book.	Install the device in accordance with the manufacturer's instructions and with the procedures given in this manual.	Affix record of calibration by NBS, manufacturer or other, to the instrument log.§
7. Automatic Samplers	Enter the make, model serial and/or ID number of each sampler in a log book.		Check intake velocity vs. head (minimum of three samples) and clock time setting vs. actual time interval.

* Initially and Bi-annually

§ Annually

testing procedures, errors crop up due to equipment malfunction which adversely affects the quality. Therefore, as a second step for quality assurance, procedures should be developed for routine testing, maintenance and calibration of the equipment. Manufacturer's instructions are appropriate guides on these procedures. These procedures should establish routine maintenance, testing and calibration intervals, set up written procedures for maintenance, testing and calibration, list the required calibration standards, determine the environmental conditions requiring calibration, and generate a documentation record system. Equipment should be labeled to indicate the calibration data and when the calibration or maintenance expires. Table 16.1 contains a listing of quality assurance guidelines for field analysis, equipment calibration and documentation. (1)

As a third step in quality assurance, random control checks should be performed to make sure that appropriate sampling guidelines on sample collection, handling and chain of custody are followed by the field personnel; and deviations, if any, are rectified. Analytical quality control as an aid to quality assurance can be performed through duplicate, split, and spiked samples; sample preservative blanks, precision, accuracy and control charts. For more details on analytical quality control refer to EPA's "Handbook for Analytical Quality Control in Water and Wastewater" (2).

16.5 REFERENCES

1. U.S. EPA, NPDES Compliance Sampling Manual, Compliance Branch, (Draft), May,4, 1977.

2. U.S. EPA Handbook for Analytical Quality Control in Water and Wastewater Laboratories. Technology Transfer, June 1972.

CHAPTER 17

SAMPLE PRESERVATION

Immediate analysis at the sampling site will preclude the need for sample preservation, however this procedure is not practical in most situations. Therefore, sample preservation and other related aspects of sample handling should be established to maintain the representativeness of the sample until analysis.

Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that take place in a sample after the sample is removed from the parent source. To maintain the integrity of the sample,appropriate selection of containers, pretreatment of containers if necessary and the holding times form the integral part of the sample preservation program.

17. 1 METHODS OF PRESERVATION

Methods of preservation are relatively limited and are intended generally to:

1. Retard biological action.
2. Retard hydrolysis of chemical compounds and complexes.
3. Reduce volatility of constituents.

Preservation methods are generally limited to chemical addition, pH control, refrigeration, and freezing. Combinations of these methods are of-

ten used for the preservation of the sample.

17.1.1 Chemical Addition

The most convenient preservative is a chemical which can be added to a sample bottle prior to sampling. When the sample is added, the preservative disperses immediately, stabilizing the parameter(s) of concern for long periods of time. When a preservative added to preserve some of the parameters interferes with other parameters, collect additional samples for those parameters. For example, concentrated nitric acid added for the preservation of some of the metals would interfere with BOD, so an additional sample must be collected for BOD.

17.1.1.1 pH Control

pH control to preserve the sample is dependent upon chemical addition. As an example, to keep metal ions in a dissolved state concentrated nitric acid is added to lower the pH to less than 2.

17.1.2 Freezing

Freezing has been the subject of many preservation studies (1-16). It is felt by some that freezing would be a method for increasing the holding time and allowing collection of a single sample for all analysis. However, the residue solids components (filterable and nonfilterable) of the sample change with freezing and thawing (8). Therefore, return to equilibrium and then high speed homogenization is necessary before any analysis can be run. This method may be acceptable for certain analysis but not as a general preservation method.

17.1.3 Refrigeration

Refrigeration (or icing) has also been studied with various results (10-12, 17-21). This is a common method used in field work and has no detrimental

effect on sample composition. Although it does not maintain integrity for all parameters, it does not interfere with any analytical methods.

17.1.4 Preservation Guidelines

For NPDES samples, the permit holder must use sample preservation and holding times for different parameters (organic and inorganic) as per the proposed guidelines published in the Federal Register(22) and shown in Table 17.1. Use of alternative preservation methods is permissible if the preservation effectiveness is demonstrated by supporting data.

Table 17.2 provides additional references and furnishes data on preservation methods, storage and holding times for different parameters found in various literature sources. However, for a specific application of the data, reference to the original publication should be made.

17.1.5 Alternative Preservation Methods

Alternative preservation methods with specific preservatives can be used if the preservation effectiveness of the parameters can be demonstrated by supporting data. One way of obtaining the supporting data is through preservation studies. Such preservation studies must include details on the following:

1. Type of water/wastewater used as a sample in the experiment
2. Type of containers used.
3. Pretreatment of the container and the glassware used.
4. Preservation methods used.
5. Specific temperatures or temperature range used.
6. Duration of storage.
7. Stored in light or darkness.

TABLE 17.1 CONTAINERS, PRESERVATION, AND HOLDING TIMES

	Measurement[a]	Container[b]	Preservative[c]	Maximum Holding Time[d]
1	Acidity	P,G	Cool 4°C	14 days
2	Alkalinity	P,G	Cool 4°C	14 days
3	Ammonia	P,G	Cool 4°C H_2SO_4 to pH<2	20 days
	BACTERIA			
4-7	Coliform, fecal	P,G	Cool 4°C 0.008% $Na_2S_2O_3$ [g]	6 hours
8	Fecal streptococci	P,G	Cool 4°C 0.008% $Na_2S_2O_3$ [g]	6 hours
9	Biochemical oxygen demand	P,G	Cool 4°C	48 hours
10	Biochemical oxygen demand Carbonaceous	P,G	Cool 4°C	48 hours
11	Bromide	P,G	None Required	28 days
12	Chemical oxygen demand	P,G	Cool 4°C H_2SO_4 to pH<2	28 days
13	Chloride	P,G	None Required	28 days
14	Chlorinated organic compounds	G,teflon-lined cap	Cool 4°C 0.008% $Na_2S_2O_3$ [g]	48 hours(until extraction) 30 days(after extraction)

(Continued)

TABLE 17.1 (cont'd)

Measurement[a]	Container[b]	Preservative[c]	Maximum Holding Time[d]
15 Chlorine, total residual	P,G	Determined on site	2 hours
16 Color	P,G	Cool, 4°C	48 hours
17-18 Cyanide, total and amendable to chlorination	P,G P,G	Cool, 4°C NaCH to pH>12 0.008% $Na_2S_2O_3$	14 days
19 Dissolved oxygen			
Probe	G bottle & top	Determine on site	1 hour
Winkler	G bottle & top	Fix on site	8 hour
20 Fluoride	P	None Required	28 days
21 Hardness	P,G	HNO_3 to pH<2	6 months
22 Hydrogen ion (pH)	P,G	Determine on site	2 hours
23 & 92 Kjeldahl and organic nitrogen	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
METALS[e]			
40-41 Chromium VI	P,G	Cool, 4°C	48 hours
58-59 Mercury	P,G	HNO_3 to pH<2 0.05% $K_2Cr_2O_7$	28 days
24-87 Metals	P,G	HNO_3 to pH<2	6 months
88 Nitrate	P,G	Cool, 4°C	48 hours

(Continued)

TABLE 17.1 (Cont'd)

Measurements[a]	Container[b]	Preservative[c]	Maximum Holding Time[d]
88(a)[h] Nitrate-nitrate	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
89 Nitrite	P,G	Cool, 4°C	48 hours
90 Oil and Grease	G	Cool, 4°C	28 days
91 Organic Carbon	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
93-206 ORGANIC COMPOUNDS[f]			
Extractables (including phthalates, nitrosamines organochlorine pesticides, PCB's, nitroaromatics, isophorone, polynuclear aromatic hydrocarbons, haloethers, chlorinated hydrocarbons and TCDD)	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[g]	7 days(until extraction) 30 days(after extraction)
Extractables (phenols)	G, teflon-lined cap	Cool, 4°C H_2SO_4 to pH<2 0.008% $Na_2S_2O_3$[g]	7 days(until extraction) 30 days(after extraction)
Purgeables (Halocarbons and Aromatics)	G,teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$	14 days
Purgeables (Acrolein and Acrylonitrite)	G,teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$[g]	3 days

(Continued)

TABLE 17.1 (Cont'd)

Measurement[a]	Container[b]	Preservative[c]	Maximum Holding Time[d]
207 Orthophosphate	P,G	Filter on site Cool, 4°C	48 hours
208 Pesticides	G,teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[g]	7 days(until extraction) 30 days(after extraction)
209 Phenols	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
210 Phosphorus (elemental)	G	Cool, 4°C	48 hours
211 Phosphorus	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
RADIOLOGICAL			
212-216 Alpha, Beta and Radium	P,G	HNO_3 to pH<2	6 months
217 Residue, total	P,G	Cool, 4°C	14 days
218 Residue, Filterable	P,G	Cool, 4°C	14 days
219 Residue, nonfilterable	P,G	cool, 4°C	7 days
220 Residue, settleable	P,G	Cool, 4°C	7 days
221 Residue, volatile	P,G	Cool, 4°C	7 days
73 Silica	P	Cool, 4°C	28 days
222 Specific conductance	P,G	Cool, 4°C	28 days

(Continued)

TABLE 17.1 (Cont'd)

Measurement[a]	Container[b]	Preservative[c]	Maximum Holding Times[d]
223 Sulfate	P,G	Cool, 4°C	28 days
224 Sulfide	P,G	Cool, 4°C Zinc Acetate	28 days
225 Sulfite	P,G	Cool, 4°C	48 hours
226 Surfactants	P,G	Cool, 4°C	48 hours
227 Temperature	P,G	Determine on site	immediately
228 Turbidity	P,G	Cool, 4°C	48 hours

a Parameter numbers refer to Table I

b Polyethylene (P) or Glass (G)

c Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When use of an automatic sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

d Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time.

Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample stability.

e Samples should be filtered immediately on-site before adding preservative for dissolved metals.

f Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific organic compounds.

g Should only be used in the presence of residual chlorine.

h Not available in Table I

8. Quality Control Samples: Spikes, duplicates.

9. Blanks; controls.

10. Number of samples analyzed, and results.

11. Statistical analysis, precision and accuracy.

17.2 CONTAINERS

A variety of factors affect the choice of containers and cap material. These include resistance to breakage, size, weight, interference with constituents, cost and availability. There are also various procedures for cleaning and preparing bottles depending upon the analyses to be performed on the sample.

17.2.1 Container Material

The two major types of container materials are plastic and glass (23).

Glass:

1. Kimax or Pyrex brand (borosilicate)
2. Vycor
3. Corning
4. Ray-Sorbor Low-Actinic
5. Corex

Plastic:

1. Conventional polyethylene
2. Linear polyethylene
3. Polypropylene
4. Polycarbonate
5. Rigid polyvinyl chloride
6. Teflon

All these materials have various advantages and disadvantages. Kimax or Pyrex brand borosilicate glass is inert to most materials and is recommended where glass containers are used. Conventional polyethylene is to be used when plastic is acceptable because of reasonable cost and less absorption of metal ions. The specific situation will determine the use of glass or plastic. However, use glass containers for pesticides, oil and grease, and other organics. Table 17.3 summarizes the advantages and

TABLE 17.2 INFORMATION ON PRESERVATION AND STORAGE OF PARAMETERS IN VARIOUS WATERS AND WASTEWATERS

Parameters	Sample type	Preservation method	Container Material	Temperature	Holding Time
DEMAND PARAMETERS					
Biochemical Oxygen Demand (BOD)	Raw sewage	N.S.	Glass	37°C 10°-24°C 1°C	6-12 hours (21) 12-24 hours (21) 6 days (21)
	Raw sewage	N.S.	N.S.	4°C	Up to 1 day in composite sampling systems (10)
	Raw semi-treated or fully treated domestic sewage	Frozen in a mixture of acetone and dry ice or finely ground dry ice	Polyethylene	Approximately -5°C	6 months; on thawing either with warm water or at room temperature, analyze using seeded technique (5)
	Raw waste water	Freezing	Polyethylene coated milk cartons	-15°C	236 days, analyze using seeded technique (8)
	1:4 settled sewage to water from a natural stream	60-80 mg/l $HgCl_2$	Plastic	Room temperature	18 days (23)
	Raw sewage	890 mg/l $HgCl_2$	Plastic	Room temperature	43 days (25)

N.S.-Not Stated. (continued)

TABLE 17.2 (continued)

Parameters	Sample type	Preservation method	Container Material	Temperature	Holding Time
DEMAND PARAMETERS					
Chemical Oxygen Demand (COD)	1:4 settled sewage to water from a natural stream	60-80 mg/l $HgCl_2$	Plastic	Room temperature	18 days (23)
	Raw sewage	890 mg/l $HgCl_2$	Plastic	Room temperature	43 days (25)
	Raw sewage	N.S.	Glass	37°C 10°-24°C 1°C	6-12 hours (21) 12-24 hours (21) 6 days (21)
	Raw sewage	N.S.	N.S.	4°C	Several days (10)
Dissolved oxygen (DO)	Sea water	0.5 % chloroform + 0.5% phenol	Glass	22°C	20 days (24)
	Sea water	Acidulating water to pH 1.5 with 2.5 ml H_2SO_4 ; 5 ml HCl per liter of sample	Glass	22°C	22 days (24)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
DEMAND PARAMETER					
Total Organic Carbon (TOC)	Settled sewage, biological filter effluent	1 ml saturated Ag_2SO_4 solution (i.e. 4 mg of Ag+) to a liter of sample	Glass	Refrigerate at 4°C	3 days (26)
METALS:					
Aluminum	Waters in the zone of mixing of river and sea waters in estuaries	Samples frozen rather than acidified	Polyethylene	-20°C	In dark, 14 days (27)
	Natural fresh water	1 ml of 4M H_2SO_4 per 100 ml sample and filtered through glass-fiber filters	Polyethylene	Room temperature	4 weeks (28)
Cadmium	Stock aqueous solutions prepared in laboratory	Acidification to pH 2 with HNO_3	Polyethylene and borosilicate glass	N.S.	32 days (29)
Lead	Stock aqueous solutions prepared in laboratory	Acidification to pH 2 with HNO_3	Borosilicate glass	N.S.	24 days (29)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
METALS: cont.					
Mercury	Distilled water solutions containing 0.1-10.0	Acidified with 5% (v/v) HNO_3 + .05% $Cr_2O_7^{2-}$	Polyethylene	N.S.	10 days (30)
	Distilled water solutions containing 0.1-10.0	Acidified with 5% (v/v) HNO_3 + .01% $Cr_2O_7^{2-}$	Glass	N.S.	5 months (30)
Potassium	1:4 settled sewage and natural stream water	Approx. 1.5 ml saturated $HgCl_2$ per liter of sample (60-80 mg/l $HgCl_2$)	Plastic	Room Temperature	18 days (23)
Silver	Stock aqueous solutions prepared in laboratory	Acidification to pH 2 with HNO_3	Polyethylene	Room temperature	36 days (29)
Sodium	1:4 settled sewage and natural stream water	Approx. 1.5 ml saturated $HgCl_2$ per liter of sample (60-80 mg/l $HgCl_2$)	Plastic	Room temperature	18 days (23)
Zinc	Stock aqueous solutions prepared in laboratory	Acidification to pH 2 with HNO_3	Polyethylene preferred over borosilicate glass	N.S.	60 days (29)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
METALS: cont.					
Cadmium	Natural lake water	Acidified to pH 1	Pyrex glass and polyethylene	-15°C	184 days (31)
Copper	Natural lake water	Acidified to pH 1	Pyrex glass and polyethylene	-15°C	184 days (31)
		.25 ml 3.5 N nitric acid after arrival at the laboratory	25 ml glass vials with polyethylene snap-caps	Room temperature	1 year (32)
Manganese	Natural lake water	Acidified to pH 1	Pyrex glass and polyethylene	-15°C	184 days (31)
Zinc	Natural lake water	Acidified to pH 1	Pyrex glass and polyethylene	-15°C	184 days (31)
		.25 ml 3.5 N nitric acid after arrival at the laboratory	25 ml glass vials with polyethylene snap-caps	Room temperature	1 year (32)

(continued)

TABLE 17.2 (continued)

Parameters	Sample type	Preservation method	Container Material	Temperature	Holding Time
NUTRIENTS:					
Ammonia Nitrogen	Relatively unpolluted bay waters	40 mg Hg^{+2} per liter of sample	Plastic	4°C	30 days (12)
	Sea waters (off shore)	0.4 g phenol per 100 ml of sample	Glass	N.S.	2 weeks (14)
		Slow freezing	Polyethylene	Frozen	20 days (14)
	Near shore and estuarine waters (filtered and fortified samples)	Freezing	Glass tubes polyseal caps	-23°C	3 months (7)
	Synthetic fresh water, unpolluted fresh water, (filtered) chemically treated domestic sewage, polluted sea water (filtered)	Unpreserved	Polyethylene	4°C	1-3 days (33)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
NUTRIENTS:					
Ammonia Nitrogen	Strongly polluted water	Approx. 1.5 ml saturated $HgCl_2$ per liter (75 mg/l)	Plastic	Room Temperature	18 days (23)
	Strongly polluted water	Approx. 3.0 ml of 40% formalin solution per liter of sample (890 mg/l)	Plastic	Room Temperature	18 days (23)
	Raw Sewage	890 mg/l $HgCl_2$	N.S.	N.S.	43 days (25)
Ammonia (soluble)	Surface runoff	Freezing	Plastic	-20°C	In dark, 12 wks.
		Refrigeration	Plastic	4°C	In dark, 12 wks. (34)
		Phenylmercuric acetate (PMA): 20 mg PMA per liter of sample	Plastic	4°C	In dark, 12 wks. (34)
	Amended and unamended river water	40 mg $HgCl_2$ per liter of sample	Plastic	4°C	In dark, 12 wks. (34)
		Freezing	Plastic	-20°C	In dark, 12 wks. (34)
		Phenylmercuric acetate (PMA): 20 mg PMA per liter of sample	Plastic	4°C or 23°C	In dark, 12 wks. (34)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
NUTRIENTS: cont.					
Ammonia (soluble) cont.	Tile drainage water	Freezing	Plastic	-20°C	In dark, 12 wks. (34)
		Phenylmercuric acetate (PMA): (20 mg PMA per liter of sample)	Plastic	4°C	In dark, 12 wks. (34)
		40 mg $HgCl_2$ per liter of sample	Plastic	4°C	In dark, 12 wks. (34)
Kjeldahl nitrogen	Relatively unpolluted bay waters	40 mg Hg+2 per liter of sample	Plastic	4°C	7 days (12)
	Synthetic fresh water, unpolluted fresh water, chemically treated domestic sewage and polluted sea water	Unpreserved	Polyethylene	4°C	Up to 3 days (35)
		1 ml of 0.02% mercury (II) chloride per 100 ml of sample	Polyethylene	4°C	Up to 3 days (35)
	Strongly polluted water	Approx. 1.5 ml of saturated $HgCl_2$ per liter (75 mg/l)	Plastic	Room Temp.	18 days (23)
	Raw manure slurries, oxidation ditch mixed liquor	Freezing and fast thawing or slow thawing	Whirl pack bags	N.S.	5 weeks (36)
		Refrigeration	Whirl pack bags	6-10°C	5 weeks (36)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
NUTRIENTS: cont.					
Kjeldahl nitrogen cont.		Acidification with conc H_2SO_4 to a pH of 2	Whirl pack bags	6-10°C 6-10°C	5 weeks (36) 5 weeks (36)
Nitrate Nitrogen	Relatively unpolluted fresh water (filtered), chemically treated domestic sewage, polluted sea water (filtered)	40 mg Hg^{+2}	Plastic	4°C	Up to 3 days (35)
		1 ml of 0.02% mercury (II) chloride per liter of sample	Polyethylene	4°C	28 days (35)
	4 to 1 mixture of surface water and settled sewage	22 or 66 mg of mercury (II) chloride per liter of sample	Glass	22±2°C	3 weeks (37)
		Conc. H_2SO_4 0.8 ml per liter of sample	Glass	22±2°C	3 weeks (37)
	Strongly polluted water sample	Approx. 1.5 ml of saturated mercury (II) chloride solution per liter of sample (i.e. 60-80 mg/l of mercury (II) chloride)	Plastic	Room Temp.	18 days (23)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
NUTRIENTS: cont.					
Nitrate Nitrogen Cont.		Approx. 3.0 ml of 40% formalin solution per liter of sample (890 mg/l)	Plastic	Room Temp.	18 days (23)
	Surface runoff, tile drainage water, river water	Freezing	Plastic	-20°C	In dark, 12 wks. (34)
		20 mg PMA per liter of sample	Plastic	4°C or 23°C	In dark, 12 wks. (34)
	Surface runoff	40 mg $HgCl_2$ per liter of sample	Plastic	4°C	In dark, 3 wks. (34)
Nitrite Nitrogen	Strongly polluted water	Approx. 1.5 ml of saturated mercuric chloride solution per liter of sample (i.e. 60-80 mg/l of mercuric chloride)	Plastic	Room Temp.	18 days (23)
		Approx. 3.0 ml of 40% formalin solution per liter of sample (890 mg/l)	Plastic	Room Temp.	18 days (23)
	Sea water (filtered) and nitrate enriched	Freezing	Pyrex glass	-18°C	220 days (4)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
NUTRIENTS: cont.					
Nitrite Nitrogen cont.					
	Lake water (unenriched)	1 ml saturated mercuric chloride per liter of sample	Glass	Refrigerated at 6°C	11 days (20)
	Lake water (enriched with nitrite)	1 ml saturated mercuric chloride solution per 300 ml of sample	Glass	Refrigerated at 6°C	6 days (20) 6 days (20)
	Relatively unpolluted bay waters	40 mg Hg^{+2} per liter of sample	Plastic	4°C	7 days (12)
	4 to 1 mixture of surface water and settled sewage	66 mg of mercury (II) chloride per liter of sample	Glass	22±2°C	45 days (37)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
NUTRIENTS: cont.					
Orthphosphate or total phosphate	Waters containing algae	Refrigeration	N.S.	3-5°C	Overnight (11)
	Polluted fresh water, polluted sea water, strongly polluted sea water, biologically treated sewage	1 ml of 8N sulfuric acid per 100 ml of filtered sample	Polyethylene	N.S.	For samples that cannot be analyzed within 8 hrs. (38)
	Estuarine waters	40 mg Hg^{2+} per liter of sample	Glass	-10°C	One month (12)
		40 mg Hg^{2+} per liter of sample	Glass	4°C	Few days (12)
	Strongly polluted waters	Approx. 1.5 ml saturated $HgCl_2$ per liter (75 mg/l)	Plastic	Room Temp.	18 days (23)
Soluble Inorganic Phosphorus (SIP)	Surface runoff	N.S.	N.S.	2°C	3 days (38)
	Slow freezing and sediment removed by centrifugation	N.S.	N.S.	-20°C	3 days (38)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
NUTRIENTS: cont.					
Soluble Inorganic Phosphate	Surface runoff, tile drainage	Freezing	Plastic	-20°C	In dark, 12 wks. (34)
		Phenylmercuric acetate (PMA) 20 mg PMA per liter of sample	Plastic	4°C	In dark, 6 wks. (34)
		40 mg $HgCl_2$ per liter of sample	Plastic	4°C	In dark, 6 wks. (34)
	Ammended river water (45 ml river water + 5 ml of solution containing 100 ppm NH_4-N, 100 ppm of NO_3-N and 5 ppm of ortho phosphate), and natural rainwater	Freezing	Plastic	-20°C	In dark, 12 wks. (34)
		40 mg $HgCl_2$ per liter of sample	Plastic	4°C	In dark, 12 wks. (34)
	Seawater	Addition of Chloroform (0.6-0.8% v/v) before freezing	Polyethylene	-5 to -10°C	Stored until thawed for analysis (39)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time	
PHYSICAL/MINERAL						
Alkalinity	1:4 settled sewage to natural stream water	Approx. 1.5 ml of saturated mercuric chloride solution per liter of sample (60-80 mg/l $HgCl_2$)	Plastic	Room temp. (Not in dark)	18 days	(23)
Chloride	1:4 settled sewage and natural stream water	Approx. 1.5 ml of saturated mercuric chloride solution per liter of sample (60-80 mg/l $HgCl_2$)	Plastic	Room temp. (Not in dark)	18 days	(23)
	Raw sewage	890 mg/l $HgCl_2$	N.S.	N.S.	43 days	(25)
Conductivity	1:4 settled sewage and natural stream water	Approx. 1.5 ml of saturated mercuric chloride solution per liter of sample (60-80 mg/l $HgCl_2$)	Plastic	Room temp. (Not in dark)	18 days	(23)
	Raw sewage	890 mg/l $HgCl_2$	N.S.	N.S.	43 days	(25)
Total hardness	1:4 settled sewage and natural stream water	Approx. 1.5 ml of saturated mercuric chloride solution per liter of sample (60-80 mg/l $HgCl_2$)	Plastic	Room temp. (Not in dark)	18 days	(23)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
PHYSICAL/MINERAL cont.					
Magnesium hardness	raw sewage	890 mg/1 $HgCl_2$	N.S.	N.S.	43 days (25)
Phenols	All types of water and waste waters	1.5 ml of 1N NaOH per liter	N.S.	N.S.	(40)
	All types of water and waste waters	N.S.	Stoppered glass bottles	N.S.	preferably to analyze shortly after collection (19)
		3 ml 10% $CuSO_4$ solution per liter of sample	Stoppered glass bottles	Refrigeration	Analyze within 2 days (19)
Sulfate	1:4 settled sewage and natural stream water	Approx. 1.5 ml saturated mercuric chloride solution per liter of sample (60-80 mg/1 $HgCl_2$)	Plastic	Room Temp. (Not in dark)	18 days (23)
	Raw sewage	890 mg/1 $HgCl_2$	N.S.	N.S.	43 days (25)

disadvantages of these materials.

TABLE 17.3 COMPARISON OF GLASS AND PLASTIC CONTAINERS

	Borosilicate Glass	Conventional Polyethylene
Interference with sample	Inert to all constituents except strong alkali	Good for all constituents except pesticides and oil and grease
Weight	Heavy	Light
Resistance to breakage	Very fragile	Durable
Cleaning	Easy to clean	Some difficulty in removing adsorbed components
Sterilizable	Yes	In some instances
Space	Takes up considerable space	Substantial space savings during extended field studies.

17.2.2 Container Caps

There are two main types of plastic container caps: polyethylene and bakelite with liners. Use polyethylene caps (ease of cleaning) except if these caps do not fit tightly to the container or if pesticides or oil and grease analyses are to be performed. Teflon liners should be used for pesticides and oil and grease samples. There are three liner types available and the advantages/disadvantages are listed in Table 17.4.

17.2.3 Container Structure

Use a wide mouth container in most instances. This structure will permit

easy filling and sample removal. It is also easily cleaned, quickly dried, and can be stored inverted. Use a narrow neck bottle when interaction with the cap liner or outside environment is to be minimized. Use a cleaned solvent container for pesticide sample collection (24).

TABLE 17.4 COMPARISON OF CAP LINERS

Liner Type	Advantages	Disadvantages
Wax coated paper	Generally applicable to most samples	Must be inspected prior to each use because of deterioration
	Inexpensive	Cannot use with organics
Neoprene	Same as wax coated paper	Same as wax coated paper
Teflon	Applicable for all analyses	High cost
	Minimizes container/ sample interaction	

17.2.4 Disposable Containers

Use disposable containers when the cost of cleaning is high. These containers should be precleaned and sterile. The most commonly used disposable container of this type is the molded polyethylene cubitainer shipped nested and sterile to the buyer. However since their cubic shape and flexible sides make them almost impossible to clean thoroughly, use these containers only once.

17.2.5 Container Washing

The following procedure should be followed to wash containers and caps for inorganic and general parameters:

1. Wash containers and caps with a non-phosphate detergent and

scrub strongly with a brush (if possible wash liners and caps separately).

2. Rinse with tap water, then distilled water.
3. Invert to drain and dry.
4. Visually inspect for any contamination prior to storage.
5. If the container requires additional cleaning, rinse with a chromic acid solution (35 mL of saturated sodium dichromate solution in 1 liter of sulfuric acid - this solution can be reused). Then rinse with tap water and distilled water and dry as indicated above.

17.2.6 Container Preparation

For certain parameters, a special cleaning procedure is needed to avoid adsorption or contamination due to interaction with container walls. These procedures are outlined below.

1. Metals: If metals are to be analyzed, rinse the container with a solution of one part nitric acid to four parts water, then with distilled water. If phosphorus is to be analyzed, rinse the container with a solution of one part hydrochloric acid to one part water,followed by distilled water.
2. Organics: If Oil and Grease or Pesticides are to be analyzed, rinse the sample container with methylene chloride, followed by acetone. For Pesticide analysis, use pesticide grade hexane or acetone. The container should have been previously cleaned with chromic acid solution as described in Section 17.2.5. Treat the container caps similarly.

3. Sterilization: For microbiological analyses, sterilize the container and its stopper/cap by autoclaving at 121°C for 15 minutes or by dry heat at 180°C for two hours. Heat-sensitive plastic bottles may be sterilized with ethylene oxide at low temperatures. Wrap bottles in kraft paper or cover with aluminum foil before sterilization to protect against contamination. An acceptable alternative for emergency or field use is sterilization of containers by boiling in water for 15 minutes.

17.3 HOLDING TIME

Holding time is the time interval between collection and analysis. In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results.

It is impossible to state exactly how much time may be allowed to elapse between collection of a sample and its analysis; this depends on the character of the sample, particular analysis to be made, and the conditions of the storage

For NPDES purposes, in accordance with Federal Register, part 136 guidelines follow the recommendations given in Table 1, pp. xvi - xix, Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency, 1979.

For information purposes, however, data relating to holding times for general and inorganic parameters was collected from various literature sources and is tabulated in Table 17.2.

17.4 SAMPLE VOLUME

The volume of sample collected should be sufficient to perform all the required analyses plus an additional amount to provide for any quality control needs, split samples or repeat examination. Although the volume of sample required depends on the analyses to be performed, the amount required for a fairly complete analysis is normally about 8 liters, (about 2 gallons). The laboratory receiving the sample should be consulted for any specific volume requirements. Individual portions of a composite sample should be at least 100 milliliters in order to minimize sampler solids bias. Depending on the sampling frequency and sample volume, the total composited sample should be a minimum of 8 liters (about 2 gallons). Refer to EPA's "Methods for Chemical Analysis of Water and Wastes 1979" for the sample volumes required for specific types of pollutant analyses.

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Appendix A - Population Parameters

I. Populations and Samples (1,3)

Most sampling is done on a non-continuous basis, and so the data gathered give an incomplete picture of the true condition of a water or wastewater. If monitoring were done continuously, the data would be presented as a curve (f(t), where f is the function which gives the value of the parameter at time t) rather than as a discrete set of points (numbers). Therefore, the definitions of mean and variance given in Section 4.1.1 could not be applied. This continuous function defines a "population" from which the samples are taken. This population has a mean and a variance of which the the sample mean and sample variance (which are the mean and variance defined in Section 4.1.1) are only estimators. This is why it is best to take as many samples as possible -- more data reveals more information about the population.

The Population Mean

The population mean, μ_X , is defined by

$$\mu_X = E(X) = \int_{-\infty}^{\infty} x f_X(x)\, dx$$

where E(X) is another expression for the mean and is read "the expected value (or expectation) of X."

$f_X(x)$ is the density function of X, which is a function defining the distribution of X.

The Population Variance

The variance, σ_X^2, of the population is defined by

$$\sigma_X^2 = \text{Var } (X) = E\left((X-\mu_X)^2\right) = \int_{-\infty}^{\infty} (x-\mu_X)^2 f_X(x)\ dx$$

As with the sample standard deviation, the population standard deviation is just the square root of the population variance ($\sigma_X = \sqrt{\sigma_X^2}$).

Appendix B

Areas under the Normal Curve (1,3)

The graph of the probability density function of the standard normal distribution,

$$f_X(x) = \frac{1}{\sqrt{2\pi}} \exp(-x^2/2),$$

is shown in Figure 4.6. It is the familiar bell-shaped curve. For any point z, the area under the curve to the left of z is determined by

$$\int_{-\infty}^{z} f_X(t)dt$$

which we have seen to be $P(Z \leq z)$, where $Z \sim N(0,1)$. We also know that the area to the right of z is $P(Z>z)$. The normal distributions is symmetric about its mean, and so $P(Z>\mu_z + c) = P(Z<\mu_z - c)$ for any constant c, which in the case of the standard normal distribution, in which the mean is zero, reduces to $P(Z>c) = P(Z<-c)$.

There is a property of probabilities which says that, under certain conditions which are not discussed here, $P(Z>c \text{ or } Z<-c) = P(Z>c) + P(Z<-c) = 2P(Z>c)$ and so if $P(Z>c \text{ or } Z<-c) = \alpha$ then $P(Z>c) = \alpha/2$ (which is the area of the shaded region in Figure 4.8).

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