INDUSTRIAL LIQUID WASTE SURVEYS

TRAINING MANUAL

U.S. ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF WATER PROGRAMS

INDUSTRIAL LIQUID WASTE SURVEYS

This course is designed for engineers, chemists, or other professional personnel who will be responsible for planning and conducting industrial liquid wastes surveys.

It is intended that, at the conclusion, the participants will be able to plan, supervise, and evaluate an industrial waste survey which measures or characterizes wastes at outfalls or in-plant locations, or both.

ENVIRONMENTAL PROTECTION AGENCY
Water Programs Operations
TRAINING PROGRAM

January 1973

TRAINING PROGRAM

Through the Water Programs Operations Office, Environmental Protection Agency conducts programs of research, technical assistance, enforcement, and technical training for water pollution control.

The objectives of the Training Program are to provide specialized training in the field of water pollution control which will lead to rapid application of new research findings through updating of skills of technical and professional personnel, and to train new employees recruited from other professional or technical areas in the special skills required. Increasing attention is being given to development of special courses providing an overview of the nature, causes, prevention, and control of water pollution.

Scientists, engineers, and recognized authorities from other Agency programs, from other government agencies, universities, and industry supplement the training staff by serving as guest lecturers. Most training is conducted in the form of short-term courses of one or two weeks' duration. Subject matter includes selected practical features of plant operation and design, and water quality evaluation in field and laboratory. Specialized aspects and recent developments of sanitary engineering, chemistry, aquatic biology, microbiology, and field and laboratory techniques not generally available elsewhere, are included.

The primary role and the responsibility of the states in the training of wastewater treatment plant operators are recognized. Technical support of operator-training programs of the states is available through technical consultations in the planning and development of operator-training courses. Guest appearances of instructors from the Environmental Protection Agency, and the loan of instructional materials such as lesson plans and visual training aids, may be available through special arrangement. These training aids, including reference training manuals, may be reproduced freely by the states for their own training programs. Special categories of training for personnel engaged in treatment plant operations may be developed and made available to the states for their own further production and presentation.

A bulletin of courses is prepared and distributed periodically by the National Training Center. The bulletin includes descriptions of courses, schedules, application blanks, and other appropriate information. Organizations and interested individuals not on the mailing list should request a copy from The National Training Center.

FOREWORD

These manuals are prepared for reference use of students enrolled in scheduled training courses of the Office of Water Programs, Environmental Protection Agency.

Due to the limited availability of the manuals, it is not appropriate to cite them as technical references in bibliographies or other forms of publication.

References to products and manufacturers are for illustration only; such references do not imply product endorsement by the Office of Water Programs, Environmental Protection Agency.

The reference outlines in this manual have been selected and developed with a goal of providing the student with a fund of the best available current information pertinent to the subject matter of the course. Individual instructors may provide additional material to cover special aspects of their own presentations.

This manual will be useful to anyone who has need for information on the subjects covered. However, it should be understood that the manual will have its greatest value as an adjunct to classroom presentations. The inherent advantages of classroom presentation is in the give-and-take discussions and exchange of information between and among students and the instructional staff.

Constructive suggestions for improvement in the coverage, content, and format of the manual are solicited and will be given full consideration.

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I SOURCES AND EFFECTS

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INDUSTRIAL WATER USES

I INTRODUCTION

A A successful industrial waste engineer has a nearly instinctive ability to detect potential sources of liquid waste. This ability develops with experience in analyzing industrial processes and operational procedures.

B This skill is largely based upon intimate familiarity with industrial uses of water and proves valuable in many phases of survey operations -- from selection of sampling points to evaluation of final results.

C This outline is intended to focus attention upon specific industrial water uses. In particular, the information contained herein should expedite selection of sampling locations.

II COOLING WATER

A The bulk of the water withdrawn by all industry is used for cooling -- over 90% of its total supply. The largest portion of this water is used to condense steam in thermal electric power stations. Exclusive of electric utilities, industry employs twice as much water for cooling as for process and other purposes.

B Both conditioning practices and the quantity of water required will depend upon the type of cooling system employed.

1 A once-through system

2 An open recirculating system

3 A closed recirculating system

C Although most water used for cooling does not suffer any significant deterioration, contaminants may be introduced by:

1 Addition of treatment chemicals

2 The use of direct contact condensers

3 Leakage of process and other equipment

D Blowdown from open recirculating systems may contain considerable hexavalent chromium or other compounds. Chromates and phosphates are used to control corrosion, whereas bromines, chlorine, copper and mercury salts, and quaternary amines are used to inhibit biological growths. Blowdown usually amounts to only 0.5-2.0% of the total amount of water recirculating in the system.

E On the other hand, once-through cooling waters may cause thermal pollution since all of the heat absorbed in the system is discharged to the receiving water.

F In addition to cooling water, steam generating facilities discharge a number of other wastes such as boiler blowoff, chemicals used for cleaning of boilers and other equipment, and exhausted regenerent solutions from demineralizer operations.

III PROCESS WATER

Nearly all industries produce some kind or quantity of liquid waste. However, the myriad wastes produced are all derived from a few specific uses:

A Reactant

A portion of water used as a reactant actually enters a chemical reaction and becomes part of the product. Examples of such use include:

1 Production of acetylene from calcium carbide

2 Manufacture of phosphoric acid

B Reaction Medium

Water may be used as a reaction medium to facilitate mixing and contact of all components. Although a reaction takes place, the water may not be an active agent and may not be included in the product. Examples of this use include:

1 Suspension or emulsion polymerization

2 Chemical pulping as in the Kraft or sulfite processes

3 Metal finishing baths

C Solvent

Industrial use bears witness to water's reputation as the "universal solvent". Water is used as a solvent in a wide variety of applications including:

1 Extraction of sugar from sliced sugar beets

2 Hot water extraction of glues and gelatine from skins and bones after pretreatment

3 Leaching of metallic ores by acid, alkaline, and other aqueous solutions

4 Extraction or removal of inorganic salts from crude oils (referred to as crude oil desalting)

D Cleaning or Washing of Products, Raw Materials, or Intermediates

Batch or continuous washing of raw materials or product at intermediate or final stages of manufacture is common. Examples include:

1 Preliminary washing of fruit and vegetables after harvesting to remove soil and organic materials

2 Washing of sugar beets prior to slicing into thin strips for use in the diffusion battery

3 Pulp washing after digestion to remove spent liquor

4 Pulp washing after bleaching

5 Washing and soaking of salted or cured hides at tanneries to remove dirt, salts, blood, and non-fibrous proteins and restore moisture lost during preservation and storage

E Intermediate and Final Rinsing of Parts

Rinsing is a high volume application of washing, which may occur in a single step. Rinsing is characterized by continuous use, possibly several steps, discharge of considerable effluent to waste, and high volume. Examples include:

1 Water rinsing of parts after plating

2 Water rinsing of parts after pickling

3 Water rinsing of parts after alkaline cleaning, anodizing, bright dipping, and other metal finishing operations.

F Washing of Equipment

In many industries washing of equipment and facilities may produce the majority of the liquid waste. This use is especially common in the food industry. Examples include:

1 Water washing of cans, vats, tanks, process equipment, and facilities in dairies

2 Water washing of pans after each baking to remove grease, flour, and sugar

3 Water washing of equipment, tables, and floors at the end of each day of operation in canneries

G Quenching

Water is commonly used in the metals industries to rapidly cool hot metals and other products to desired temperature. Examples of this use include:

1 Quenching of hot coke

2 Quenching of blast furnace slag

3 Quenching of hot metals

H Scrubbing of Gases

Scrubbers are commonly employed to reduce hazard and air pollution by water absorption. Unfortunately, the absorbed compound may prove equally or more objectionable in liquid form than in the gaseous state. Examples include:

1 Water scrubbing or washing of blast furnace flue gases and exit gases from open hearth and basic oxygen furnaces to remove particles

2 Water scrubbing of off-gases produced during electrolytic smelting of alumina-fluorine salt mixtures

3 Water scrubbing of stack gases from thermal-electric generating plants

I Buoyant Transporting Medium

Use of water to transport reactants, products, and wastes is inherent to most industries. Most large manufacturing plants are equipped with an elaborate network of channels and ditched for this purpose. Examples include:

1 Transporting fibers and chemical additives (sizes, fillers, and pigments) to paper machines

2 Transporting washed raw fruit or vegetables in canneries

J Processing Medium

Use of water as a processing medium does not involve a chemical reaction, as does its use as a reaction medium. Processing is a purely physical action. Examples include:

1 Wet classification

2 Froth flotation of ores

3 Wet grinding

4 Debarking logs or cleaning metal parts with high pressure water jets

5 Use of high pressure water sprays to remove skin and excess caustic from potatoes withdrawn from lye peelers

K Heat Transfer Medium

Water is commonly used to control temperature of critical stages of many industrial processes. Temperature control may be accomplished by either heating or cooling in jacketed kettles or coil heat exchangers. Water is commonly converted to steam for this use. Examples include:

1 Temperature control during nitration of toluene to produce TNT

2 Air conditioning of assembly rooms in electronics plants

IV SUMMARY

The ability to detect potential or actual waste sources expedites all phases of industrial waste surveys, especially selection of sampling points. This ability is largely related to individual familiarity with industrial uses of water. Industry uses water for cooling and a number of process applications including reactant, reaction medium, solvent, cleaning or washing, rinsing, washing of equipment, quenching, scrubbing of gases, and as a transporting, processing, or heat transfer medium.

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SOURCES AND EFFECTS OF INDUSTRIAL WASTES

I INTRODUCTION

As a result of manufacturing every industry produces some kinds and quantities of liquid-borne wastes. These may be detrimental to quality of the receiving waters in many ways: toxicity, oxygen demands, sludge deposits, surface films, thermal effects, etc. Since agriculture is a form of production, the effects of drainage from the land will be considered among the industrial wastes.

II CLASSIFICATION SCHEMES

Classification is one of the most important steps in any water pollution control investigation involving industrial waste discharges.

A There are essentially two approaches to industrial waste classification:

1 Classification according to industry.

2 Classification according to the effects the waste produces in the receiving stream.

B By Industry

Under this scheme industrial wastes are classified as those from the paper and pulp industry, or antibiotic industry, or citrus concentrate industry, etc.

1 As a whole, the manufacture of a specific product will result in similar liquid waste materials. Classifying wastewater by specific industries is very valuable in that it allows for an evaluation of the pollutional load being discharged to a stream no matter where the industry is located. In this regard, calculated waste loadings should be related to plant production, e.g., pounds of BOD per ton of finished product.

2 This classification scheme is based on the assumption that although manufacturing plants within an industry will produce different quantities of waste, the chemical constituents of the wastes will be fairly uniform. Wastewaters from various plants within the same industry will have different effects on water quality when discharged to specific, unique receiving streams.

3 This classification gives no indication of interaction type effects produced by more than one industry within a specified area.

C By Effect

There are many classification schemes for industrial wastes based upon their effects in the receiving water body. This type of classification has more advantages for water quality studies than the previous type, i.e., by industry. Many of the analytical procedures record the effects of the industrial waste (BOD, Bioassay, etc.), rather than the components.

III CLASSIFICATION BY EFFECTS

Classification by effects is based on the supposition that an industrial waste may be characterized by a single predominant effect. In some cases, this may be true, but most industrial wastes exhibit multiple effects. Classification according to one effect may be unduly restrictive. Notwithstanding this problem, classification by effect appears to be the more popular scheme because it is more related to stream conditions and is easily applied.

A Oxygen Depleting Wastes

1 Effect: Low DO levels, due to oxygen demand, may alter the whole balance of the biota of the receiving stream. The natural process of self-purification may be delayed significantly because of the lack of adequate oxygen resources. The demand exerted may be either chemical or biochemical.

2 Typical Wastes: Examples of industrial wastes having significant oxygen demand are:

a Sulfite waste liquors from pulp mills

b Canning plant wash effluents

c Meat packing wastes

d Textile scouring and dyeing effluents

e Milk products wastes

f Fermentation wastes

3 Measurement: Since the primary effect of these materials is a reduction in dissolved oxygen, the BOD test is commonly used to determine the deoxygenation potential of the waste. In conjunction with the BOD, the COD test will yield valuable information.

4 Treatment: All of the methods for the treatment of oxygen depleting wastes involve satisfying all or part of the oxygen demand before discharge to the stream. This usually involves some type of secondary treatment either chemical or biological.

B Toxic Wastes

1 Effects: For the purpose of classification, toxicity is considered as a direct lethal effect on biological forms, as contrasted to the indirect effects of oxygen deficiency or smothering.

2 Typical Wastes: Among the many wastes having toxic effects on stream biota are:

a Spent plating solutions containing heavy metals and cyanides.

b Acid wastes from pickling operations, chemical manufacture, and mine drainage.

c Organic materials such as strong phenolics, antibiotics, pharmaceuticals and petro-chemical wastes, and pesticides.

d Textile dyes

3 Measurement: Traditionally, toxic wastes are evaluated by chemical analysis of the waste to determine the concentration of the offending compound. Unfortunately, suitable analytical methods are not available for some of the newer, more complex materials. The bioassay is rapidly assuming a key place in the evaluation of toxic wastes.

4 Treatment: Removal of the toxic agent is essential to adequate treatment. Heavy metals are precipitated from plating solutions, cyanide is oxidized by chlorination, acids are neutralized, and organic compounds are oxidized biochemically by the use of acclimatized flora.

C Wastes Causing Physical Damage

1 Effects: Certain industrial wastes cause damage to the stream by physical actions rather than chemical or biochemical reaction. These materials create an unfavorable environment because of the specific physical properties which they possess.

2 Typical Wastes: Physical damage may be associated with the following:

a Wastes from lumbering and mining operations, which contribute large amounts of silt, sawdust, and other insoluble deposits.

b Power plant discharges, raising the temperature of the stream in the vicinity of the outfall.

c Petroleum refinery wastes, which contribute oils and other immiscible liquids, color, and sludge.

d Dyeing operations, which might possibly contribute large amounts of color to receiving streams.

3 Measurement: Wastes which create insoluble deposits in the stream are evaluated in terms of the settleable and total solids tests. Special techniques are required for other wastes, e.g., thermal, oil, and industrial color.

4 Treatment: As in the case of the other types of wastes, changing the properties which cause damage is the accepted method of treatment. Settling basins and ponds, cooling systems, oil separators, and similar devices satisfactorily remove the objectionable property.

D Wastes Producing Tastes and Odors

1 Effects: Many industrial effluents contain substances which are capable of imparting disagreeable tastes to water supplies. Even very minute amounts of these materials may cause public reaction. Often the undesirable tastes are increased by chlorination.

2 Typical Wastes: The following contribute tastes and odors to water supplies.

a Petroleum and petro-chemical wastes, even when present in extremely small concentrations.

b By-product coke plants discharges (phenolics) which are rendered very objectionable by chlorination.

c Liquid wastes from the manufacture of synthetic rubber are often implicated where offensive odors are present.

3 Measurement: Because of the small amounts of materials involved, special concentrating techniques, such as the carbon filter, are required. Identification of the compounds by means of infrared spectroscopy and gas chromatography are utilized. Threshold odor testing also yields valuable information.

4 Treatment: Most of the compounds which produce tastes and odors are organic and lend themselves to biological treatment. Certain wastes (those from synthetic rubber manufacturer for example) are resistant to attack and require special treatment processes.

E Waste Containing Inorganic Dissolved Solids

1 Many industrial effluents contribute large amounts of cations (Na, K, Ca, Mg, Fe) which may cause some distress to the stream biota.

2 Typical wastes: Tannery wastes and irrigation waters.

3 Measurement: These wastes are usually evaluated by chemical analysis for the specific cation.

4 Treatment: chemical treatment, coagulation and ion exchange. Irrigation waters pose a special problem as far as treatment is concerned and no adequate treatment technique has been developed.

F Radioactive Waste

1 Effects: Contamination of water environment, destruction of aquatic life.

2 Typical Wastes: nuclear reactor cooling water, uranium ore mining and refining.

3 Measurement and Treatment: Special techniques due to the nature of the contaminant. Types of treatment, ion exchange, storage, coagulation and storage.

G Corrosive Wastes

1 Effects: Highly acidic or basic wastes, although also toxic, deserve special attention as corrosive wastes. Such wastes seriously damage piping systems and may even corrode ships' hulls and bridge piers.

2 Typical Wastes: Examples of corrosive wastes are:

a Spent pickling solutions

b Alkali discharges produced during manufacture of soap.

H Pathogenic Wastes

1 These wastes may contain organisms pathogenic to man or plants.

2 Typical Wastes

a Livestock production (cattle, poultry, swine, laboratory animals)

b Tanneries

c Pharmaceutical manufacture

d Food processing

3 Treatment: Disinfection with chlorine or other active agent.

IV CLIMATOLOGICAL CONDITIONS

Many effects of industrial wastes may be diminished or enhanced by climatological conditions. Some of these to be evaluated are:

A Amount and Frequency of Rainfall

B Amount and Pattern of Run-off

C Stages and Pattern of Stream Flow

D Temperature Patterns - Stream and Air

E Sunlight Patterns

F Wind Patterns

V MISCELLANEOUS FEATURES OF RECEIVING STREAM

A Physical features of stream - cross-sections, profiles, turbulence, etc.

B Past pollution history of stream most important in evaluating present effect of any new industrial waste.

VI SUMMARY

Before any industrial waste can be adequately treated, some idea of the wastes characteristics must be known. The most common procedure is to evaluate the wastewater in light of the condition of the receiving water and the uses to which the receiving water will be put by downstream users. Therefore, approaching the problem based upon the detrimental effects the wastewater produces in the stream and eliminating the causitive agent is the most logical method of attack.

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PHYSICAL AND CHEMICAL EFFECTS OF WATER TEMPERATURE

I INTRODUCTION

A With but a few exceptions, the physical and chemical effects of temperature change on water quality are more subtle than, or subordinate to, the more direct and dramatic biological effects. The important direct effects, moreover, usually are not significant in themselves to water use, but, rather, as they affect in secondary or tertiary sequence some other water property or phenomena.

B The more important primary and secondary effects are:

1 Density on stratification and density currents, and the whole array of impacts stratification and density currents have on water quality and its management.

2 Density and viscosity on sediment transport and the array of impacts this sediment transport mechanism has on movement and deposition of particulate matter.

3 Vapor pressure on evaporation rate and its impact on cooling processes and water loss.

4 Partial pressure of gases on gas solubility (particularly oxygen) and its impact on reaeration.

5 Microbial reaction rate on deoxygenation by organic matter and its impact on the oxygen sag.

II PHYSICAL EFFECTS OF WATER TEMPERATURE

A Temperature affects many physical properties of water. Of these, the most significant to water quality are density, viscosity, vapor pressure and solubility of dissolved gases. Table 1 shows the effect of incremental changes in temperature on these properties for fresh water.

B Very slight differences in density are sufficient to cause thermal stratification in quiescent water bodies, but stratification stability also depends on water movement and depth.

1 While the stratification process in reservoirs and lakes is well known, the resulting changes in water quality are not. The changes are becoming increasingly important because of the growth of complex water resource systems.

2 At the end of a winter season, the impounded water is usually of a fairly uniform quality and has a relatively low temperature. At the onset of higher atmospheric temperatures, the surface water and the incoming water temperatures are raised and this lighter water tends to "float" on the colder and denser water already in the lake.

3 Three definite strata may be formed, the surface stratum or epilimnion, the lower stratum or hypolimnion, and a transition zone called the thermocline, where the maximum rate of change of temperature with depth occurs.

4 Stratification may exist until autumn, when the lake begins to lose heat more quickly than it is absorbed. As the water becomes cooler and more dense, the thermocline sinks, unstable conditions occur and the reservoir mixes or overturns. In climates where the water temperature goes below 4° C, two turnovers may occur per year.

5 Many impounded waters circulate completely but some circulate only partially, these lakes being called meromictic by limnologists. This stable, lower layer can be caused by either an accumulation of dissolved or suspended solids in the water and may render this lower portion of the lake unsuitable for a water supply.

TABLE 1

WATER PROPERTIES

Temperature (°C)	(°F)	Density (gm/cm^3)	Abs. Viscosity (centipoises)	Pressure (mm Hg)	Dissolved Oxygen Saturation (mg/l)
0	32	0.99987	1.7921	4.58	14.6
4	39.2	1.00000			
5	41	0.99999	1.5188	6.54	12.8
10	50	0.99973	1.3077	9.21	11.3
15	59	0.99913	1.1404	12.8	10.2
20	68	0.99823	1.0050	17.5	9.2
25	77	0.99707	0.8937	23.8	8.4
30	86	0.99567	0.8007	31.8	7.6
35	95	0.99406	0.7225	42.2	7.1
40	104	0.99224	0.6560	55.3	6.6

6 Stable stratification is common in lakes and reservoirs where there is a specific gravity difference of about .001 or .002 between waters of the upper layer (epilimnion) and lower layer (hypolimnion). Such stratification inhibits vertical mixing and oxygen transfer to lower waters.

7 In stratified reservoirs, cool, incoming waters may travel almost directly to the dam outlet in a density current at a depth of compatible specific gravity. This reservoir characteristic is important in predetermining release temperatures and in selecting optimum discharge elevation.

C Water temperature affects velocity and sediment transport through changes in density and viscosity.

1 Stokes' law describes the velocity of settling particles in a non-turbulent medium according to the following equation.

$$V = \frac{d^2 g}{18} (\rho_s - \rho_w)$$

where V = settling velocity, cm/sec

ρ_s = density of settling particle, gm/cm^3

ρ_w = density of water, gm/cm^3

μ = viscosity of liquid, poises

d = diameter of particle, cm

g = acceleration of gravity = 980 cm/sec^2

As indicated, settling velocity is inversely proportional to the water viscosity and density.

2 Both properties contribute to increased settling rates at elevated temperatures. These increased settling rates may promote better water treatment plant operation, though probably to no measurable degree.

3 A difference in settling velocities can have a significant effect on the location and amount of sediment and sludge deposition in sluggish rivers, reservoirs and estuaries.

D Evaporation rate increases as water temperature rises and elevates water vapor pressure.

1 Evaporation is caused by the wind and the difference in water vapor pressure between the air and the water. Since vapor pressure is a driving force in evaporation, an increase in temperature will cause an increase in evaporation, assuming other factors to be constant.

2 Evaporation is one of the key mechanisms in cooling water bodies.

E Water temperature affects gas solubility and its resultant impact on reaeration.

1 Most living organisms depend on oxygen in one form or another to maintain their life and reproductive processes; thus an adequate supply of oxygen must be available for any healthy aquatic environment. Hence, the relation of water temperature to gas solubility is a very important aspect of thermal pollution.

2 Oxygen does not react chemically with water. Therefore, its solubility is directly proportional to its partial pressure at any given temperature under equilibrium conditions with the atmosphere. The effect of temperature on the solubility of oxygen in fresh water under one atmosphere of pressure is shown in Table 1.

3 Temperature changes cause complicated adjustments in the dynamic oxygen balance in waters and compound the difficulty of relating dissolved oxygen and other factors to oxygen demand, atmospheric reaeration, photosynthetic production, diffusion, mixing, etc. General temperature rises, which decrease the oxygen holding capacity, may limit oxygen quantities which are already less than optimum.

4 Atmospheric nitrogen, with a solubility about one-half that of oxygen, is usually not considered an important control parameter for water quality. However, recent evidence on the Columbia River indicates that fish may be seriously affected in waters which have become super-saturated with nitrogen through rapid warming or pressure reduction after dam discharge.

III CHEMICAL EFFECTS OF WATER TEMPERATURE

A Many factors affect chemical reactions, including the nature and concentration of reacting substances, catalytic influence and temperature. The last named is important because chemical changes speed up as the temperature rises. In general, the speed of a chemical change is approximately doubled for each 10° C (18° F) rise in temperature.

B In an irreversible reaction, higher temperatures will decrease the time required to produce the final products. In a reversible reaction, the process is complete when the reactants reach a point of dynamic stability, i.e., when the rate of forward reaction equals the rate of reverse reaction. In this case, temperature influences both the length of time required to reach equilibrium and the proportion of reactants and products at equilibrium conditions.

C Most of the chemical effects on water quality, which are influenced by temperature, center around microbial activity. Any chemical reaction or change that results from a life process is properly termed a biochemical reaction.

1 The majority of chemical reactions that organisms bring about occur through catalytic action at far lower temperatures than would be needed in the absence of catalysts. Such catalysts are known as enzymes, and are themselves temperature-sensitive.

2 The rate of microbial activity increases, to a point, with the rates of chemical reactions. The majority of organisms affecting chemical water quality are in the mesophylic classification and thrive in a temperature range of 10 to 40° C (18 to 104° F). For this group, activity usually reaches a maximum between 30 and 37° C (86 and 99° F), then falls off as enzymes become less active.

D Temperature affects not only the rate at which a reaction occurs, but the extent to which the reaction occurs, but the extent to which the reaction takes place.

1 When considering temperature changes in a receiving water, one must contemplate changes in ionic strength, conductivity, dissociation, solubility and corrosion.

2 With an increase in temperature, these changes might very well result in differing chemical requirements in the water treatment plant.

E Taste and odor problems induced by temperature-accelerated chemical or biochemical action are accentuated when oxygen is depleted.

1 Substances which may accumulate include hydrogen sulfide, sulfur dioxide, methane, partially oxidized organic matter, iron compounds, carbonates, sulfates, and phenols.

2 In addition to greater amounts of accumulating substances, tastes and odors are usually more noticeable in warmer water due to decreased solubility of gases.

F Biodegradable organic material entering water exerts a biochemical oxygen demand (BOD) which must be satisfied before assimilation of the material is completed.

1 When the temperature of a receiving water rises, the intensified action of microorganisms causes the BOD to be satisfied in a shorter distance from the discharge than would be accomplished at a lower temperature. Figure 1 depicts oxygen sag curves for a stream in which all conditions, i.e., streamflow, wasteflow, BOD of the waste, and initial percent DO saturation, were held constant, except temperature.

It is apparent from the curves that the deoxygenation effect caused by waste assimilation is exerted over a shorter stream distance at higher temperatures; also that oxygen depletion occurs to a greater extent, since the sag point is lower at elevated temperature. Hence, it is possible that the discharge of an organic waste that previously had not caused excessive oxygen depletion could pose problems at an elevated temperature.

G Chemical effects of slightly increased temperatures may have minor beneficial influences on water treatment.

1 Disinfectant action is generally more rapid at higher temperatures. For example, for a given dose of free chlorine, the period required to disinfect water at 46°F is more than nine times greater than at 104°F.

2 Reports on coagulant dosages are contradictory, although reports indicate a savings of 30 to 50¢ per million gallons per each 10°F rise in temperature.

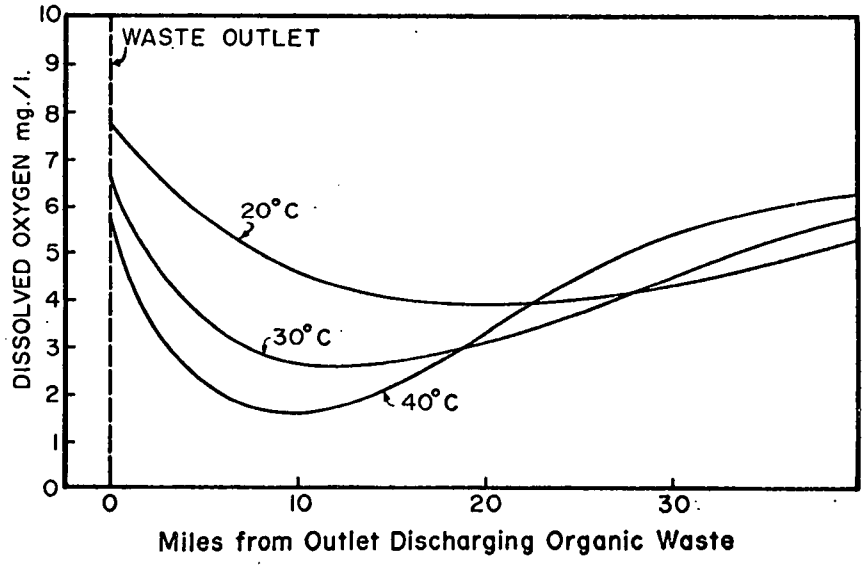
3 The potential beneficial effects must be weighed against the undesirable effects such as induced slime or algae growth, taste and odor problems, or unpalatable drinking water temperatures.

IV SUMMARY

A The physical and chemical effects of temperature change on water quality usually are not significant in themselves to water use but rather as they affect in secondary or tertiary sequence some other water property or phenomenon.

FIGURE 1

RELATION BETWEEN TEMPERATURE AND OXYGEN PROFILE
(After La Berge)



B The more important effects relate to:

1 Stratification and density currents

2 Sediment transport and deposition

3 Evaporation

4 Saturation with gases

5 Microbial activity

6 Taste and odor

7 Deoxygenation and reaeration

ACKNOWLEDGMENT:

Material for this outline was taken from "Thermal Pollution: Status of the Art," by Frank L. Parker and Peter A. Krenkel and "Industrial Waste Guide on Thermal Pollution," FWPCA, September 1968 (revised).

This outline was prepared by D. S. May, Former Microbiologist, Manpower and Training, PNWL, Corvallis, OR.

EFFECTS OF THERMAL POLLUTION ON FISH LIFE

I INTRODUCTION

A The physiology of fishes is directly affected by temperature.

1 Fishes are classed as Poikilothermic animals, i.e., their body temperatures follow changes in environmental temperatures rapidly and precisely.

2 In such animals, the factors favoring heat loss tend to equal the factors producing body heat, and thus the body approaches environmental temperatures.

3 In a majority of fishes, the body temperature differs by only 0.5 to 1.0°C (0.9 to 1.8°F) from that of the surrounding water.

4 A fundamental requirement of fishes is that the external temperature be well suited to internal tissue functionality.

B The single most important point in analyzing or predicting the effects of temperature change on a fishery is to look at the individual species important to the specific water body under study.

II GENERAL

A Metabolism--Rates of metabolism and activity increase with increasing temperature.

1 According to Van't Hoff's law, metabolic activity can double or even triple over a 10°C (18°F) rise in temperature.

2 This increase in metabolic rate and activity will occur over most of the tolerated temperature range and then often cease suddenly near the upper lethal temperature.

3 The rates of increased activity vary with different species, metabolic processes, and temperature ranges or levels.

4 The rates may also be modified by salinity and oxygen factors.

5 Changes in metabolic rates caused by temperature changes may be signaling factors for spawning or migration.

6 Chemical reactions within the fish's body cells may be accelerated by temperature increases.

7 Temperature induced changes in cell chemistry are associated with four possible death mechanisms.

a Enzyme inactivity caused by the acceleration of the enzyme reaction to such a state that the enzyme is no longer effective.

b The coagulation of cell proteins.

c The melting of cell fats.

d The reduction in the permeability of cell membranes.

8 Cells may also be killed by the toxic action of the products of metabolism.

B Reproduction - the temperature range within which many fishes reproduce is narrower than that required by the majority of functions.

1 Fishes generally spawn when a certain temperature level is reached. Of course, this level varies from species to species.

2 Some fish spawn on a drop in temperature, while others respond to a rise in temperature.

3 Even though the temperature requirements for breeding are narrow, fishes may populate a heated area by continued migration from the outside.

C Development - temperature changes affect fish development in several ways.

1 Abnormal temperatures can affect embryonic development.

2 Low temperatures may slow down development, but in some cases, fish attain a larger final size because of their slow, long continued growth rather than the rapid growth experienced at higher temperatures.

D Distribution - temperature is one of the more important factors governing the occurrence and behavior of fish life; it affects the general location of a given species and may also modify the species composition of a community or an ecosystem.

1 Tropical and subtropical fishes are more stenothermal than those found in fresh water.

2 Some cold water stenothermal forms may be eliminated by heated discharges, while the effect on some eurythermal (tolerant of a wide temperature range) species may be to increase the population.

3 In tropical areas, species live close to their upper thermal limits, thus the effect of a thermal discharge can be quite severe.

4 In northern areas, species may live in temperatures as much as 16°C (28.8°F) below their upper lethal temperature and will not be as severely affected.

5 Laboratory tests have shown that a slow rate of decrease in environmental temperature is more important for maintaining life than a slow rate of increase.

6 Lethal cold can be more important than lethal heat as a factor limiting the distribution of marine fish and as a hazard to some in their native habitats.

E Synergistic Action - synergism is defined as the simultaneous action of separate agents which together, have a greater total effect than the sum of their individual effects.

1 In reference to water temperatures, synergistic action refers to the fact that temperature rises increase the lethal effect of toxic substances to fish and may also increase the susceptibility of the fish to many diseases.

2 A 10°C (18°F) rise in temperature doubles the toxic effect of potassium cyanide, and an 8°C (14.4°F) rise triples the toxic effect of o-xylene.

3 The temperature effect on toxicity varies with each substance and with concentrations of any specific material; no hard and quick rule may be formulated to determine this temperature effect.

4 Since domestic and industrial wastes are numerous in our nation's waters, the synergistic action between temperature and toxicity is a relatively common occurrence.

a Fish kills have accompanied small temperature rises which might have been relatively harmless in an unpolluted stream free of toxic substances.

b The concentration of a substance may be harmless at one temperature but may contribute to fish mortalities when combined with the stress imposed by higher temperatures.

5 The virulence of fish pathogens may be increased by higher temperatures.

a The myxobacteria Chondrococcus columnaris, which can cause death through tissue destruction, becomes more virulent as temperature is increased.

F Dissolved Oxygen - two factors associated with rising water temperature are decreases in available oxygen and increases in metabolic rates.

1 These factors combine to render the aquatic environment less compatible to fish life at higher water temperatures.

2 At low water temperatures in the range of 0 to 4°C (32 to 39.2°F) a dissolved oxygen level of 1 to 2 mg/l is sufficient for survival of many freshwater fish species. When the temperature reaches 15 to 20°C (59 to 68°F), less than 3 mg/l of dissolved oxygen is often lethal.

3 At these temperatures, oxygen levels as high as 5 mg/l are sometimes required to support normal activity beyond that of merely staying alive.

G Acclimation - the temperature to which fish become adjusted over an extended period of time, i.e., the thermal history, is important because of its influence on lethal temperature levels.

1 The capacity to acclimate depends on the genetic background, environmental history, physiological conditions, and age of the organism involved.

a The resistance of animals to cold is much more variable than resistance to heat.

b The resistance to cold varies with size, smaller fish resisting best.

2 Acclimation to different temperatures may involve changes in orientation, migration, and other behavioral aspects such as territorialism and biological rhythms.

a Gradual temperature changes are tolerated much better than rapid changes.

b Brief or intermittent exposure to high temperature can result in markedly increased resistance to heat which is not readily lost on subsequent exposure to low temperature.

c It is the rapid onset of low temperatures that probably causes death, outstripping the ability of fish to acclimate and resulting in greater mortality.

d Deaths resulting from the inability of fish to rapidly acclimate to lowering temperatures have been reported.

3 Acclimation to low temperature usually tends to shift the lower thermal limit downward, and acclimation to high temperatures tends to shift the upper limits upward.

a The ability to acclimate affects the temperature range that a fish can tolerate.

b Fish acclimated to cold winter temperatures are often subjected to lethal temperatures in the spring as warmer water is encountered.

III FRESHWATER FISHES

A Maximum Temperatures - maximum temperatures have been determined for numerous species of freshwater fish.

1 These temperatures indicate the highest temperature at which a fish can survive, but they are often higher than the maximum temperature at which a species can survive for long periods.

2 Maintaining water temperature at these maximums does not insure the maintenance of a fish population.

3 Table 1 shows maximum and minimum temperatures for various species and acclimation temperatures.

a Values shown are LD_{50} temperatures, i.e. temperature survived by 50% of the test animals.

b These figures are based on specific test conditions, so care must be taken in interpreting the data.

TABLE 1

MINIMUM AND MAXIMUM TEMPERATURES FOR CERTAIN FRESHWATER FISHES

Fish	Acclimated To		Minimum Temperature*			Maximum Temperature*		
	°C	°F	°C	°F	Time, Hr.	°C	°F	Time, Hr.
Bass, largemouth	20.0	68.0	5.0	41.0	24	32.0	89.6	72
	30.0	86.0	11.0	51.8	24	34.0	93.2	72
Bluegill (Lepomis macrochirus purpurescens)	15.0	59.0	3.0	37.4	24	31.0	87.8	60
	30.0	86.0	11.0	51.8	24	34.0	93.2	60
Catfish, channel	15.0	59.0	0.0	32.0	24	30.0	86.0	24
	25.0	77.0	6.0	42.8	24	34.0	93.2	24
Perch, yellow	5.0	41.0	---	---	--	21.0	69.8	96
(winter)	25.0	77.0	4.0	39.2	24	30.0	86.0	96
(summer)	25.0	77.0	9.0	48.2	24	32.0	89.6	96
Shad, gizzard	25.0	77.0	11.0	51.8	24	34.0	93.2	48
	35.0	95.0	20.0	68.0	24	37.0	98.6	48
Shiner, common	5.0	41.0	---	---	--	27.0	80.6	133
(Notropis cornutus	25.0	77.0	4.0	39.2	24	31.0	87.8	133
frontalis)	30.0	86.0	8.0	46.4	24	31.0	87.8	133
Trout, brook	3.0	37.4	---	---	--	23.0	73.4	133
	20.0	68.0	---	---	--	25.0	77.0	133

*Values are LD_{50} temperature tolerance limits, i.e., water temperatures survived by 50 percent of the test fish.

c Temperature limits for a given species will vary slightly depending on the fish's rate of heating, size, and physiological condition.

4 A temperature need not kill a fish directly for it to be lethal.

a Brook trout were found to be comparatively slow in catching food minnows at 17.2°C (63°F) and virtually incapable of catching minnows at 21°C (70°F).

b Even though their lethal limit is 23 to 25°C (73.4 to 77°F) the fish could not survive in this temperature due to a lack of food (Table 1).

B Preferred Temperatures - most biologists agree that fish can live for short periods in waters of abnormally high temperatures, but at these high temperatures the fish cannot perpetuate their population.

1 Fish seek out the temperature that is best suited for their survival.

2 This "preferred temperature" is given in Table 2 for several species of yearling fish based upon laboratory experiments.

3 Table 3 shows the temperature at which fish in the natural environment seem to congregate, thus indicating their "preferred temperature."

TABLE 2

THE FINAL PREFERRED TEMPERATURE FOR VARIOUS SPECIES OF FISH AS DETERMINED BY LABORATORY EXPERIMENTS

Species	Final Preferred Temperature °C	°F	Authority
Bass, largemouth	30.0-32.0	86.0-89.6	Fry, 1950
Bass, smallmouth	28.0	82.4	Fry, 1950
Bluegill	32.3	90.1	Fry & Pearson, 1952
Carp	32.0	89.6	Pitt, Garside & Hepburn, 1956
Muskellunge	24.0	75.2	Jackson & Price, 1949
Perch, yellow	24.2	75.6	Ferguson, 1958
Perch, yellow	21.0	69.8	McCracken & Starkma, 1948
Trout, brook	14.0-16.0	57.2-60.8	Graham, 1948
Trout, brown	12.4-17.6	54.3-63.7	Tait, 1958
Trout, lake	12.0	53.6	McCauley & Tait, 1956
Trout, rainbow	13.6	56.5	Garside & Tait, 1958

4 The level of thermal acclimation influences the range of temperatures preferred.

In general, the difference between the acclimation temperature and the preferred temperature decreases as the acclimation temperature increases.

5 Competition between species is also important to distribution and survival since different species have different species have different preferred temperatures.

Temperatures higher than optimum may not kill trout, but they may produce environmental conditions favorable for the production of coarse fish and reduce the trout's food supply.

IV MARINE, ESTUARINE, AND ANADROMOUS FISHES

A Spawning - limits of temperature requirements for spawning are usually much more stringent than for adult fish survival.

1 The normal spawning temperature for sockeye salmon is between 7.2 and 12.8° C (45-55° F); lower and upper lethal limits are 0° C (32° F) and about 25° C (77° F), respectively.

2 Pink salmon spawn best near 10° C (50° F).

3 During migration salmon do not feed, so high water temperatures which increase their metabolic rate may result in fuel depletion before spawning can occur.

TABLE 3

PREFERRED TEMPERATURES FOR VARIOUS SPECIES OF FRESHWATER FISH
BASED ON FIELD OBSERVATIONS

Species	Preferred Temperature °C	°F	Water Body	Location	Authority
Alewife	4.4- 8.8	39.9-47.8	Cayuga Lake	New York	Galligan, 1951
Bass, largemouth	26.6-27.7	80.0-81.9	Norris Res.	Tennessee	Dendy, 1948
Bass, rock	14.7-21.3	58.5-70.3	Lakes	Wisconsin	Hile & Juday, 1941
" "	20.7	69.3	Streams	S. Ontario	Hallam, 1958
Bass, smallmouth	20.3-21.3	68.5-70.3	Nebish Lake	Wisconsin	Hile & Juday, 1941
" "	21.4	70.5	Streams	S. Ontario	Hallam, 1958
Bass, spotted	23.5-24.4	74.1-75.9	Norris Res.	Tennessee	Dendy
Perch, yellow (small)	12.2	54.0	Muskellunge Lake	Wisconsin	Hile & Juday, 1941
Perch, yellow (large)	20.2-21.0	68.4-69.8	Lakes	Wisconsin	Hile & Juday, 1941
Shad, gizzard	22.5-23.0	72.5-73.4	Norris Res.	Tennessee	Dendy
Trout, brook	14.2-20.3	57.6-68.5	Moosehead Lake	Maine	Cooper & Fuller
" "	15.7	60.3	Streams	S. Ontario	Hallam, 1958
" "	12.0-20.0	53.6-68.0	Redrock Lake	Ontario	Baldwin, 1948
Trout, lake	10.0-15.0	50.0-59.0	Cayuga Lake	New York	Galligan, 1951
" "	14.0	57.2	White Lake	Ontario	Kennedy, 1941
" "	11.0-11.5	51.8-52.7	Moosehead Lake	Maine	Cooper & Fuller, 1945
" "	8.0-10.0	46.4-50.0	Louisa & Redrock Lakes	Ontario	Martin, 1952
Walleye	20.6	69.1	Trout Lake	Wisconsin	Hile & Juday, 1941
"	22.7-23.2	72.9-73.8	Norris Res.	Tennessee	Dendy, 1948

4 Fish migration is hampered by unfavorable temperature conditions.

5 A thermal block of 21.1°C (70°F) at the mouth of the Okanogan River, Washington, prevented migration into the stream from the Columbia River.

6 Generally for salmon, upstream migration and reproduction occur best at temperatures between 7.2 and 15.6°C (45 and 60°F).

B Eggs - the incubation of eggs and development of fry generally have more critical temperature requirements than either fingerling or adult fish.

1 Table 4 shows the minimum and maximum temperatures reported for the successful hatching of various species of marine, estuarine, and anadromous fish eggs.

2 Care must be taken not to equate successful hatching with fry survival; Chinook salmon eggs incubated at 16.1°C (61°F) hatched successfully, but suffered severe mortality in the late fry stage.

C Young Fish - Table 5 shows the temperature limits for the survival of various species of young marine, estuarine, and anadromous fishes at several acclimation temperatures.

1 This information is based on laboratory tests which often produce data not directly transferable to the natural environment.

2 Laboratory tests on striped bass fingerlings showed an upper lethal temperature of 35°C (95°F), but studies in the Atlantic Ocean indicated striped bass fish kills occurring at temperatures of 25 to 27°C (77.0 to 80.6°F).

3 Fish in the estuarine environment are more susceptible to temperature changes than those in fresh water. However, wider ranges of tolerance between species exist in estuarine waters.

4 Decreases in temperature seem to have more of an effect on estuarine fishes than on freshwater fishes.

TABLE 4

TEMPERATURE RANGES FOR SUCCESSFUL EGG HATCHING OF VARIOUS MARINE, ESTUARINE, AND ANADROMOUS FISHES

Species	Lower Limit °C	Lower Limit °F	Upper Limit °C	Upper Limit °F	Authority
Bass, striped	12.8	55.0	23.9	75.0	Albercht, 1964
California killifish	16.6	61.9	28.5	83.1	Hubbs, 1965
California grunion	14.8	58.6	26.8	80.1	Hubbs, 1965
Salmon, Chinook	5.8	42.4	14.2	57.6	Combs & Burrows, 1957
	9.4	48.9	14.4	57.9	Seymour, 1956
	5.6	42.1	14.4	57.9	Leitritz, 1962
Salmon, sockeye	4.4-5.8	39.9-42.4	12.8-14.2	55.0-57.6	Combs, 1965
Sea lamprey	15.0	59.0	25.0	77.0	McCauley, 1963
	15.6	60.1	21.1	70.0	Piavis, 1961

TABLE 5
LETHAL TEMPERATURE RANGES FOR YOUNG MARINE, ESTUARINE, AND ANADROMOUS FISHES

Species	Acclimation Temperature °C	Acclimation Temperature °F	Lower Lethal Temperature °C	Lower Lethal Temperature °F	Upper Lethal Temperature °C	Upper Lethal Temperature °F	Authority
Greenfish	12.0-28.0	53.6-82.4	4.1-13.0	39.2-55.4	28.7-31.5	83.7-88.7	Doudoroff, 1942
Herring	7.5-15.5	45.5-59.9	-1.8 to -0.75	28.8-30.7	22.0-24.0	71.6-75.2	Blaxter, 1960
Salmon, Chinook	5	41	----	----	21.5	70.7	Brett, 1956
" "	10	50	0.8	33.4	24.1	75.7	" "
" "	15	59	2.5	36.5	25.0	77.0	" "
" "	20	68	4.5	40.1	25.1	77.2	" "
" "	23	73.4	7.4	45.3	----	----	Brett, 1952
" "	--	----	----	----	26.7	80.0	Kerr, 1953
Salmon, chum	5	41	----	----	21.8	71.2	Brett, 1956
" "	10	50	0.5	32.9	22.6	72.7	" "
" "	15	59	4.7	40.5	23.1	73.6	" "
" "	20	68	6.5	43.7	23.7	74.7	" "
" "	23	73.4	7.3	45.2	----	----	Brett, 1952
Salmon, pink	5	41	----	----	21.3	70.3	Brett. 1956
" "	10	50	----	----	22.5	72.5	" "
" "	15	59	----	----	23.1	73.6	" "
" "	20	68	----	----	23.9	75.0	" "
Salmon, silver	5	41	0.2	32.4	22.9	73.2	Brett, 1956
" "	10	50	1.8	35.1	23.7	74.7	" "
" "	15	59	3.5	38.3	24.1	75.7	" "
" "	20	68	4.5	40.1	25.0	77.0	" "
" "	23	73.4	6.4	43.5	----	----	Brett, 1952
Salmon, sockeye	5	41	0.0	32.0	22.2	72.0	Brett, 1956
" "	10	50	3.1	37.6	23.4	74.1	" "
" "	15	59	4.1	39.4	24.4	75.9	" "
" "	20	68	4.7	40.5	24.8	76.6	" "
" "	23	73.4	6.7	44.1	----	----	Brett, 1952
Topsmelt	20	68	10.1	50.2	31.8	89.2	Doudoroff, 1942

a In studies of young greenfish to determine the resistance and acclimation of marine fishes to temperature changes, Doudoroff found that heat resistance was gained rapidly and lost slowly.

b Acclimation to decreasing temperatures was slower than acclimation to increasing temperatures.

c Transposed to the practical case, this fact implies that the shutdown of a power generating plant may be more detrimental than its normal discharge of heat.

5 Anadromous fingerlings have maximum growth in the temperature range of 10 to 15.6° C (50 to 60° F).

6 Research on the effects of temperature on swimming speed indicates that for young sockeye salmon optimum cruising speed occurred at 15° C (59° F), and for young silver salmon at 20° C (68° F); thus, the fish's mobility for protection and feeding is affected by temperature changes.

D Adult Fish - Table 6 shows the lethal temperature limits for several species of adult marine, estuarine, and anadromous fishes.

1 Adult fish are usually able to select their preferred temperatures, unless trapped in shallow water or forced to migrate through thermal blocks.

TABLE 6

LETHAL TEMPERATURE LIMITS FOR ADULT MARINE, ESTUARINE, AND ANADROMOUS FISHES

Species	Acclimation Temperature °C	Acclimation Temperature °F	Lower Lethal Temperature °C	Lower Lethal Temperature °F	Upper Lethal Temperature °C	Upper Lethal Temperature °F	Authority
Alewife	---	---	---	---	26.7-32.2	80.0-90.0	Trembley, 1960
Bass, striped	---	---	6.0- 7.5	42.8-45.5	25.0-27.0	77.0-80.0	Talbot, 1966
California killifish	14.0-28.0	57.2-82.4	---	---	32.3-36.5	90.1-97.7	Doudoroff, 1942
Common silverside	7.0-28.0	44.6-82.4	1.5- 8.7	34.8-47.8	22.5-32.5	73.3-90.3	Hoff & Westman, 1966
Flounder, winter	21.0-28.0	69.8-82.4	1.0- 5.4	33.8-41.6	---	---	" " "
" "	7.0-28.0	44.6-82.4	---	---	22.0-29.0	71.6-84.2	" " "
Herring	---	---	-1.0	30.2	19.5-21.2	67.1-70.1	Brawn, 1960
Northern swellfish	14.0-28.0	57.2-82.4	8.4-13.0	47.1-55.4	---	---	Hoff & Westman, 1966
" "	10.0-28.0	50.0-82.4	---	---	28.2-33.0	82.9-90.4	" " "
Perch, white	4.4	40.0	---	---	27.8	82.0	Trembley, 1960
Salmon (general)	---	---	0.0	32.0	26.7	80.0	Columbia Basin Interagency Comm., 1966

ACKNOWLEDGMENTS:

Material for this outline was taken from the "Industrial Waste Guide on Thermal Pollution," Alden G. Christianson and Bruce A. Tichenor, principal authors.

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EFFECTS OF POLLUTION ON AQUATIC LIFE

I INTRODUCTION

A The effluent from any given industrial plant may be combined with municipal sewage, and/or wastes from other industries. This may occur in the sewerage system or in a natural body of water.

1 Toxic wastes may inhibit biota of treatment plant as well as life in receiving stream.

2 Organic wastes may simply increase sewage-type load on plant and stream.

3 The above effects may be reinforced or neutralized by a complex of industrial wastes.

B The general overall character of a body of water may be subtly changed over a period of time.

II The principle of limiting factors (see Figure 1) deals with the response of organisms to various factors in the environment.

A Liebig's Law of the Minimum (Figure 1) states that the distribution of a species may be limited by one or more <u>essential</u> environmental factors which occur in minimal quantities.

B Shelford on the other hand pointed out in his Law of Tolerance (Figure 1) that there are also maximum values of most environmental factors which can be tolerated. In between these two extremes there are ranges which may be called "optimum" for factors useful to the organism. Purely deleterious factors on the other hand have a maximum tolerable value, but no optimum. The range between the maximum concentration (greater than zero) which kills no organism and the minimum concentration which kills all organisms is known as the "critical range."

C These principles apply to all aquatic life whether in a stream, lake, estuary, or treatment plant. They are the basis for the control or regulation of biological conditions.

III INDIRECT TOXICITY: MODIFICATIONS OF THE ENVIRONMENT WHICH AFFECT AQUATIC LIFE

A Deposition of inert precipitates and silt tends to smother bottom organisms. Contributing materials include silt or sand from erosion due to poor agricultural practices, rock flour or tailings from mining or quarry operations, mica, coal washings, sawdust and debris from lumbering, insoluble precipitates or complexes from chemical industries.

1 Vulnerable organisms include important fish foods such as insect larvae and snails; also fish eggs, bottom-living algae such as diatoms, and many others.

2 Physical injury to delicate membranes of eyes, and gills may also result.

3 Inert suspended materials and dyes reduce light penetration, suppress photosynthesis and hence biological productivity. They also prevent game fish and other predators from seeing their prey, thereby reducing the efficiency of food utilization.

The word "stream" should be interpreted in most cases to mean "river," "lake," "estuary," etc., as applicable.

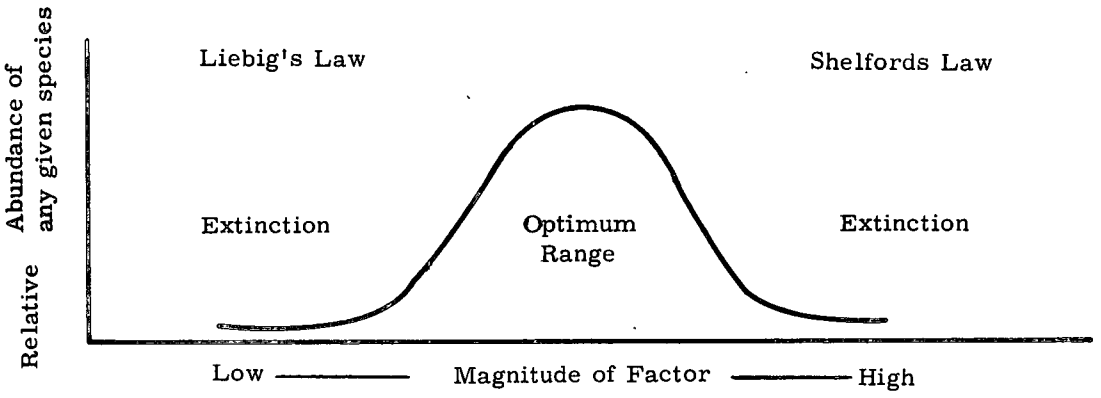

Figure 1. EFFECTS OF ENVIRONMENTAL FACTORS

B Wastes of significant heat content may change the "climate" of a body of water. Temperature may be higher or lower than normal.

1 Abnormally low summer temperatures may prevent the reproduction of some of the typical inhabitants, on the other hand colder water forms such as trout may be enabled to survive.

2 Abnormally high winter temperatures may encourage a rapid development of some species, thus for example, causing an early emergence of some insect followed by its death from normal winter temperatures. Southern forms may also invade more northerly waters, sometimes leading to a year-round nuisance from flying swarms of adults such as caddis flies.

3 Artificially produced high temperatures, often lack dependability. It is discouraging for organisms to spend six days in summer temperatures in January, only to freeze to death over the weekend because no one warned them that the plant would shut down!

4 Excessively high summer temperatures, even for a few hours once a year, probably represent the greatest temperature danger. Some species of fish can adjust to temperatures approaching 100° F, if the change takes place slowly. Each species however, has some maximum temperature above which it cannot survive (Figure 1).

a Quick temperature changes are fatal at much lower values.

b Lack of oxygen due to low solubility at high temperatures or from an increase in the rate of the BOD, also contributes greatly to high temperature mortalities.

C Oxygen-consuming wastes kill by depleting the free dissolved oxygen resources.

1 Amount present, rather than percentage of saturation, is usually more significant.

2 Minimum amounts rather than averages are most critical.

a Any species can survive something less than the optimum concentration of DO for a limited period of time. There is, however, some concentration for any given temperature, which will eventually result in the death of that species. Let us call this the "critical" DO.

b As the DO falls below the critical concentration, survival time eventually drops to zero.

c The absolute values of these thresholds vary with the species and other factors. Five mg O_2 per liter is often listed as a minimum permissible value to maintain a well-rounded healthy population of fishes on a year-round basis.

3 Low oxygen tensions may also increase the toxicity of certain chemicals.

D pH

1 "pH" is a logarithmic expression of the hydrogen ion concentration in a solution. Hydrogen ions (H^+) in certain concentrations are toxic to aquatic life (as are also hydroxyl ions: OH^-). Aquatic life in relative abundance and variety can be found in waters ranging from approximately pH 5 to 9. Thriving communities including algae, insects, and fish have been studied in waters with a pH of at least 11.

2 Many species of aquatic organisms can adjust to pH values over a wide range. Sudden change of any kind however can be fatal.

3 Most metals and other toxic substances in dilute solution tend to become less toxic at high pH values. A notable exception is ammonia.

IV POLLUTION WHICH RENDERS FISH OR SHELLFISH UNUSABLE OR INTERFERES WITH THEIR CAPTURE

A Radioactivity at levels currently found in our waters has not been observed to adversely affect aquatic life itself. It may however, be taken up with food materials and render fish or fishery products unusable.

1 Radioactive nuclides (forms of chemicals) are taken up by the plants (predominantly algae) in the processes of photosynthesis and other types of protoplasmic synthesis. There is no selection between nuclides on the basis of radioactivity.

2 As the chemicals originally assimilated by the algae are "eaten up the food chain" (from algae to invertebrates to small fish to large fish to man and other predators) their radioactivity moves along with them.

3 Thus radioactivity is acquired by fishes essentially through food, and scarcely at all by direct assimilation or absorption.

4 Plankton-feeding organisms such as herrings, oysters, and clams acquire radioactivity directly from the algae on which they feed. Since they concentrate this food from large volumes of water, they may be much "hotter" than the surrounding water itself.

B Fish may be repelled or driven out of an area by obnoxious chemicals. This may simply result in their scarcity or absence from a given locale, or it may prevent their swimming up a river to spawn. In this case the species would soon disappear and be lost to the community.

C Color, odor, oil, floating scum, bacterial slimes, and other such materials tend to discourage sport fishing and interfere with gear used by commercial fisheries.

D Sublethal concentrations of chemicals such as phenol, benzene,oil, 2-4-D, etc., may impart an unpleasant taste to fish flesh, even when present in very dilute concentrations. This is nearly as detrimental to the fisheries as a complete kill, and of course applies to shellfish as well as fin fish.

E Minamata disease was first described from Minamata, Japan, as a disorder resulting from eating various seafoods taken from Minamata Bay, Kyushu, Japan. The disease results from industrial toxicity, in this case an organic mercury compound, transmitted to a wide variety of local marine seafood species. These organisms are not known to be affected, but acting as "transvectors,"

pass the toxin along to predators or human consumers. Over 30% mortality occurred in Minamata among people eating local seafood.

1 It may be important to note that a fish kill was recently reported from a TVA lake in this country resulting from mercury leaching from corroded 50 gallon drums used as floats by marinas.

2 Bird and fish kills have recently occurred in Swedish lakes resulting from mercury compounds from pulp mills. Levels in pike exceed the WHO standards for human consumption and the local population has been advised not to eat pike more than once a week! Cases of high mercury levels are increasing.

V DIRECT TOXICITY: AFFECTS THE ORGANISM ITSELF

Fish kills are often the result of direct toxicity. If this is sufficiently potent to kill at once, or within a few days, it is called acute, and is often observed as a "fish kill."

Action that may require weeks or months to be effective may be referred to as low-level, cumulative, or chronic toxicity, and is more often observed as simply a reduction of productivity: "Fishin' ain't what it used to be." Examples of chemicals often believed to be involved include: acids, alkalines, ammonia, chlorine, cyanides, metals, phenols, solvents, sulfides, synthetic organic chemicals, oil field brines, pesticides, herbicides, detergents and others.

A Acute toxicity may be so broadly effective that many forms of life are affected at one time, or it may be highly selective. It may result from a low concentration of a highly toxic material or a high concentration of a relatively less toxic material.

1 It is frequently encountered as a "slug" resulting from a dump or spill, followed by normal, relatively non-toxic conditions as the mass of water containing the poison flows on downstream, or is deflected by tidal movements.

2 Acute toxicity can be evaluated by means of the toxicity bioassay technique and various modifications (Figure 2).

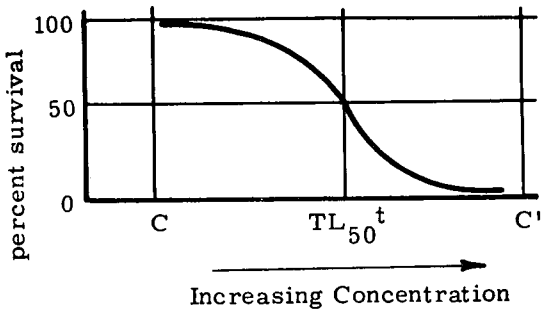

Figure 2 - Critical Range

C: maximum concentration at which no fish die, C': minimum concentration at which all die. TL_{50}^{t}, 50% tolerance limit (concentration tolerable to 50% of the population) for time t.

B Chronic or low-level toxicity may change the entire population balance.

1 Susceptible species of either fish or fish food organisms may die off, thereby permitting tolerant species to flourish for lack of competition.

2 If algae and/or invertebrate food organisms are killed off fish may die or move out of the area.

3 Weakened individuals are more susceptible to attack by parasites and disease, such as the aquatic fungus Saprolegnia.

4 Reproductive potential may be altered. Eggs or fry may or may not be more susceptible to toxic substances than adults.

5 Host fish for mussel (unionidae) life cycle may not survive.

6 The result may be a slow and subtle alteration of the characteristics of a stream over an extended period of time.

C The specific physiological mechanisms involved are infinite in variety and but little known. Included are such processes as enzyme inhibition as in the case with some of the pesticides, and over stimulation of mucous membranes of the gills, leading to death by suffocation.

D There are a number of excellent diagnostic techniques for the examination of dying fish, these include pathogenic bacteria, parasites, some metals, and certain pesticides. None are routine but require specific handling and preservation techniques .

E A recently developed procedure for protecting aquatic life from deleterious substances is biomonitoring. This is the continuous monitoring or surveillance of an effluent for toxicity by means of a system for exposing living organisms (such as fish or invertebrates) to a continuously flowing stream in a dilution just below the known danger point. Should the toxicity of the substance increase the test organisms respond in some recognizable manner, thus giving warning that corrective measures need to be initiated.

VI MECHANISMS OF POLLUTION TOLERANCE AND SENSITIVITY

The fact that some organisms are more resistant to pollution than others needs no emphasis. The matter of "why?" and "how?" on the other hand, is quite another question. In some cases the answer is obvious, in others not. In general we can say that the adaptations of certain species enable them to resist certain types of natural conditions such as organic deposits or sand bars. When man artificially creates conditions such as sludge banks, or sand bars, organisms which can tolerate such conditions move in, survive, and often thrive. Other forms are eliminated.

A Organic pollution is essentially non-toxic. Its typical result as noted above is oxygen depletion, physical turbidity, and smothering blankets of sediment or sludge.

B Devices and mechanisms for living in oxygen-poor or oxygen-free water include the following:

1 Obtaining oxygen from the air by means of periodic trips or access to the surface.

a The snorkel tube of the rat-tailed maggot.

b Periodic trips of the mosquito larvae and Corixidae or water boatmen. The mosquito takes air directly into its respiratory system, the water boatman into a trap or space beneath the wing covers, as well as into a layer of air held by fine hairs or "pile" all over its body.

c Behavior of the air breathing snails such as Physa which have an internal lung cavity.

d Insects which tap into air tubes in aquatic plants.

e Fishes which gulp air at surface or breathe surface water.

2 Special devices and behavior for respiration of water

a Hind intestine respiratory structures of dragonfly larvae permits respiration in silt-laden water.

b Movement of gill covers and similar structures in isopods and certain insect groups maintains a current of water over respiratory organs.

c Body movements of chironomid larvae create water current in tibe. Sludge worms

and other annelids also create water movement by means of sinuous body movements.

3 Physiological and behavioral adaptations to endure low oxygen tensions.

a Forms possessing accessory respiratory pigments such as hemoglobin might be expected to be able to be able to extract the last vestige of dissolved oxygen from the water. Two groups famous for resisting low DO do have hemoglobin: the larvae of certain Chironomid midge flies, and small annelid worms such as sludge worms. (it should be noted however, that the hemoglobin in each case is simply dissolved in the blood plasma, rather than being concentrated in special corpuscles as is the case in the more efficient vertebrate system.)

b The mere possession of hemoglobin however, does not seem to assure tolerance of low DO (Walshe '47). Larvae of the midge Tanytarsus spp, have hemoglobin, but will not tolerate oxygen-poor waters. Hemoglobin-bearing Chironomus bathopilus is moderately tolerant, and Chironomus plumosus is highly tolerant, however.

c During periods of low DO, Chironomus plumosus apparently respires carbohydrates as usual, but excretes excess lactic acid instead of accumulating it.

d Various species of Daphnia (microcrustacea) have been shown to accumulate hemoglobin in oxygen-poor waters but not in oxygen-rich waters (Fox '47). No clear adaptive significance has yet been proven however.

C Advantageous Feeding Habits

All highly organic pollution tolerant organisms are scavengers, and hence find an abundance of food. Most are relatively defenseless and hence have normally high reproductive rate. The result in a polluted situation is thus usually an extreme abundance.

D The reverse problem is why are intolerant species intolerant?

1 A physiological requirement for higher oxygen levels is probably most basic.

2 Turbidity would hamper any organisms employing sight in any way.

3 Absence of light would suppress the growth of green algae, and hence also restrict the growth of algae feeders.

E Inert silts by themselves have many damaging effects such as abrasive or smothering action.

Biological mechanisms for enduring inert silt or sand pollution are not numerous, and consequently such locations are usually known as biological deserts. Since some life exists even in deserts however, a few forms may occasionally be found. In general they are typical sand or mud dwellers. Since the available food in such a substrate is at best of a very low order, inhabitants of these situations must either seek buried or trapped food particles or capture food from the passing waters.

1 If there is no BOD involved, and water and oxygen circulate down into the deposit, burrowing forms such as certain mayflies, annelid worms, ammocetes lamprey larvae, microcrustaceans, and others may burrow down to depths of two feet or more. Fish eggs normally deposited in gravel and newly hatched larvae are also dependent on circulating water. Such a population can be killed overnight by a layer of fine sediment or sludge which seals the surface to water circulation.

2 Water or plankton feeders include clams and mussels which can move about freely in a soft, shifting bottom, thus keeping on top of silt or sand as

it accumulates. If deposition is actively taking place, however, there will probably be so much turbidity in the water that plankton (food) organisms are unable to live. Under such circumstances certain clams and snails have the ability to close the shell so tightly by means of valves or an operculum that all contact is lost with the environment for extended periods, during which CO_2 tends to lower the rate of body metabolism. Organisms of this type have been reported to be dug up with sand and gravel and incorporated into concrete products while still alive. Emergence of a population of asiatic clams (Corbicula) for example, just as a big block of concrete is setting is said to be rough on contractors!

3 An interesting situation occasionally develops in estuaries where mud of moderate organic content is slowly deposited over oyster beds. The oysters are unable to move, but as they grow, their shells tend to bend upward above the accumulating silt, and may grow to several inches in length while growing very little in width. Crowding brings about a similar reaction in the effort to avoid being buried.

F Few generalizations can be offered relative to toxic pollution except that toxicity is relative, and all forms do not respond equally to a given toxicant.

1 Few mechanisms of toleration can be listed, beyond the natural resistance that certain forms may have for a given condition. For example, some marine species may survive a salt concentration that is toxic to freshwater species. Over a period of several generations, some species may develop a genetic resistance to some toxicant such as insecticides in the same way that DDT-resistant strains of houseflies have developed. Copper sulfate, and chlorine-resistant strains of algae such as Cosmarium for example, may develop in treated water supply reservoirs.

2 Some bottom in-fauna organisms such as annelid worms may retreat down into burrows until a slug of undesirable water passes.

3 Molluscs may close shells tightly for the same purpose. The metabolic rate is known to diminish with the increase of CO_2 inside the closed shell, thereby enabling them to remain tightly sealed for extended periods of time.

VII EFFECTS OF LIFE HISTORY STAGES

A In order to survive in a polluted area, each life history stage of an indigenous organism must be able to survive in turn.

B If some given life history stage cannot tolerate conditions, and the species is present:

1 Fortuitous changes may occur at the proper time(s) to permit survival of the more susceptible stages(s) or:

2 Recruitment from less polluted areas may occur.

C Some examples of reproductive stages or procedures which might affect pollution sensitivity:

1 Egg or egg-like stages are often enclosed in protective membranes, jelly masses, or cases. May remain dormant until favorable conditions develop.

2 Eggs may be deposited in locations where they are less exposed to polluted water as:

buried in the gravel,
on the surface film,
on rocks over the water moistened by spray,
on mud surface near water,
or in locations where maximum water circulation is encountered as at lip of waterfall.

3 Eggs may require minimal DO due to low metabolic rate.

4 Eggs deposited on or in bottom may be susceptible to smothering.

5 Newly hatched larvae often continue to live on stored yolk material for a time. On beginning to take natural food, they may be killed by toxic content thereof, such as organochlorines.

6 Some forms such as certain sludge worms commonly reproduce by (vegetative) fragmentation, hence avoiding egg and larva stages.

VIII NATURAL SELECTION AND ACCLIMATIZATION TO POLLUTION

A Known biological mechanisms for selective breeding of pollution resistant strains operate in nature among fishes as among other organisms.

1 Studies of population genetics indicate that after some finite number of generations of population stress (e.g., exposure to a given pollutant), permanent heritable resistance may be expected to develop.

2 If the environmental stress (or pollutant) is removed prior to the time that permanent resistance is developed in the population, reversion to the non-resistant condition may occur within a relatively few generations.

3 Habitats harboring populations under stress in this manner are often marked with the dead bodies of the unsuccessful individuals.

B Individual organisms on the other hand can over a period of time (less than one life cycle) develop a limited ability to tolerate different conditions, e.g., pollutants:

1 With reference to all categories of pollutants both relatively facultative and obligate species are encountered (e.g., euryhaline vs stenohaline, eurythermal vs stenothermal).

2 This temporary somatic acclimatization is not heritable.

C A given single-species collection or sample of living fishes may therefore represent one or more types of pollution resistance:

1 A sample of an original population which has been acclimated to a given stress in toto.

2 A sample of the surviving portion of an originalpopulation, which has been "selected" by the ability to endure the stress. The dead fish in a partial fish kill are that portion of the original population unable to endure the stress.

3 A sample of a sub-population of the original species in question which has in toto over a period of several generations developed a heritable stress resistance.

D Any given multi-species field collection will normally contain species illustrative of one or more of the conditions outlined above.

ACKNOWLEDGMENTS:

Certain portions of this outline contain material from a prior outline by Croswell Henderson and revisions by R. M. Sinclair.

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II SURVEY PLANNING

	Outline Number
Industrial Waste Surveys	6
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Statistical Considerations in Survey Planning	8

INDUSTRIAL WASTE SURVEYS

I INTRODUCTION

A The industrial waste survey is the project by which data is collected and the water pollution control problems generated by a specific plant. It includes a study of production processes, the wastes they generate, the quantities of such wastes and their effect on the waters which receive them.

B The survey should be a cooperative venture of the industrial plant(s) involved and the public agency having a clean water responsibility. This cooperative approach can yield a better mutual understanding of the problems and responsibilities of both industry and agency.

C Every survey will follow a definite, basic plan. Modifications to this plan are made to conform with specific local requirements and modifying factors of geography, weather, plant product, receiving water use and the like.

II OBJECTIVES

A The industrial waste survey is designed to determine the total pollution load from an industry and to indicate the source, quantity, concentration and characteristics of each major individual waste. Constituent balances are computed when feasible.

B The industry is afforded an opportunity to review their waste creating processes. Process modification or revision to eliminate or reduce pollution may result.

C Industry can be made more aware of the problems their wastes create in receiving waters. Officials in the health and regulatory agencies are exposed to the problems the industry faces in water pollution control.

D Defining the problem together, industry and the control agency can plan for abatement methods and procedures that are mutually acceptable.

E Industry is given another tool for use in future planning. This will reduce future pollution loads.

F The magnitude and complexity of a problem being defined, the regulatory agency is furnished data on which to base a reasonable pollution abatement action, should this step become necessary.

III ORGANIZATION OF PROJECT

A Outline program in detail in a letter from regulatory agency to the company. The letter should contain the following points:

1 Conduct survey at a time when plant operations are normal, insofar as this is possible.

2 Agency to assign professional from its staff to work with industry technical staff in organization and conduct of survey.

3 Analytical work will be performed in agency laboratory.

4 Industry to install necessary flow measuring devices.

5 Industry will provide personnel for collecting samples.

6 Information and data obtained during the surveys are held confidential.

7 Suggest date for the survey allowing ample time to organize the work.

8 Request conference at plant office for discussion of the survey.

B Conference with Management

1 Industry and agency should each designate one man to be their contact in organizing the program.

2 Knowledge of the plant and process is a prime requisite for industry's representative.

3 Industry's representative should be acquainted in the company and be delegated sufficient authority to expedite the survey.

4 Examination of an up-to-date Plant Sewer Plan is invaluable and should be included at this conference.

5 Plant inspection and location of sampling stations should be made after this conference.

6 Decide on types of flow measuring equipment to be installed and preferred locations.

7 Prepare an over-all estimate of cost of project to the company, itemized statement, and report back to management for approval and authority to proceed.

C Henceforth, survey activities proceed under the supervision of the agency engineer acting through the company representative.

IV TECHNICAL STAFF

This is a multiprofessional group requiring the services of an engineer, a chemist, and a biologist. Each professional interest is an important and integral part of the unit. Competence is essential in the fields of sanitary, chemical, and hydraulic engineering. The chemist must be versed in sanitary chemistry with an aptitude for research. The role of the biologist required specialized training in the fields of biology relating to stream sanitation. The possible role of each team member may be outlined as follows:

A Engineer

The engineer is responsible for the overall organization of the work and the specific duties he may be assigned are:

1 Study of the industrial processes that have the wastes produced as their byproducts.

2 Establishment of the hydraulics of the production system and most particularly the waste conveying system.

3 Working in conjunction with the chemist and the biologist establish the sampling program.

4 Take overall responsibility working in conjunction with other team members to analyze data and prepare reports.

B Chemist

The chemist is responsible for the chemical analytical work and gives counsel on all matters pertaining to this phase of the program. Specific duties include:

1 Collaboration in developing sampling schedule.

2 Instructions for preservation of samples.

3 Selection of appropriate analytical procedures.

4 Determination of significance of interfering substances.

5 Development of new or modified analytical procedures when necessary.

6 Check all data and confirm or reject questionable results.

7 Aid in analysis of data.

C Biologist

The aquatic biologist evaluates pollutional materials by determining their effect on aquatic life. His duties include:

1 Bioassays to:

a Evaluate toxicity of wastes

b Determine required dilution for toxic substances to render them innocuous

c Test efficacy of treatment processes

2 Determines present and potential future "health" of receiving water and aid in establishing degree of necessary pollution reduction to achieve or maintain proper water quality.

3 Determines whether or not such pollutants as excess nutrients, heat, silt and other industrial wastes of a non-toxic nature may be detrimental to the receiving water and its aquatic life.

V PROCESS STUDY

A Sufficient information must be made available on process and plant operation, to make possible correct interpretation of the analytical data obtained from the survey. Recognition must be given of the fact that each manufacturing plant may employ special operation procedures, developed by that organization, which may be termed secret processes. Some of these developments may be patented whereas others may be of value without resorting to protection through patent procedures.

B The agency personnel should be familiar with various manufacturing processes in order that the major waste sources will be recognized. The Stream Control Agency representative should hold in strict confidence any process or operating information obtained during the survey when so requested by the industry.

VI HYDRAULIC STUDIES

It is necessary that the volume corresponding to each sample be determined. Various methods can be used for measuring flow, the more common ones being:

A Weirs may be installed in sewer manholes, at sewer outlets, in channels, and in special weir boxes. (Estimate flow for design basis and investigate possible damage resulting from computed water level rise).

1 Sharp crested, rectangular weirs

$$Q = 3.34\, L_H^{1.47}\left(1 + 0.56\frac{H^2}{d^2}\right)$$

where: Q = discharge c.f.s.

H = measured head in feet

d = depth of water upstream from weir in feet

a Correction for end contractions:

$$L = L^1 - 0.1\, NH$$

where L = effective length of weir

L^1 = measured length of weir

N = number of end contractions

2 Right-angled, V-notch

$$Q = 2.52\, H^{2.47}$$

B Discharge Computed from Size of Sewer, Slope, and Depth of Flow

1 Measure sewer size

2 Determine slope by use of level

3 Investigate material and condition

C Compute Discharge from Cross Section Area and Velocity Measurements Made by:

1 Pitot tube

2 Timing of floats

D Critical Depth - Rectangular Section

$$\frac{Q^2}{g} = b^2 \times d_c^3$$

where Q = c.f.s.

g = 32.16 ft./sec./sec.

b = width of channel

d_c = critical depth

1 Reference Engineering News-Record Volume 85, page 1034 (November 25, 1920) "The Hydraulic Jump and Critical Depth in the Design of Hydraulic Structures" by Julian Hinds.

E Check total measured discharge against metered water consumption.

F Miscellaneous considerations in making such measurements

1 Hazards of working in sewers, and establishment of safety program.

2 Install flow measuring equipment and accumulate some data during week preceding survey.

3 Work up all data daily.

4 Sedimentation back of weirs may clog sewers and fill weir box with solids.

VII SAMPLING PROGRAM

A Collect representative composite samples over each 24 hour period.

B Sample major individual wastes and check against outfall.

C Period of sampling may vary between 5 and 14 days. (Obtain sufficient data for purposes of averaging).

D Interval between sample portions should be governed by variations in quantity and quality of discharge but will normally be not greater than one hour.

E When to weigh samples (proportional to flow).

F Prepare table for weighing samples rather than curve.

G Employ one sampler per shift.

1 Instruct all samplers at one time; demonstrate, then observe

H Carry laboratory technique into the sampling work.

1 Use of graduates is good psychology.

I Ice samples during compositing.

J Deliver adequate quantities of daily samples to laboratory promptly.

K Record unusual occurrences.

VIII PARAMETERS OF POLLUTION

A The general sanitary criteria frequently are not well adapted to characterizing an industrial waste. Pollution parameters must be worked out for the waste(s) and the stream involved.

B Decision as to those determinations to be made should be based on knowledge of the wastes and uses of the stream below the point of discharge.

C The determinations should be jointly agreed on by the industrial representative, the agency engineer, the chemist who will perform the analytical work, and the aquatic biologist doing the receiving water studies.

D The industry will frequently suggest special tests and may have proven analytical procedures.

IX ANALYTICAL WORK

A In the interest of comparing techniques, it may prove advantageous to split samples with the industrial laboratory.

B Samples should be saved until results have been checked. In case of doubt regarding a value, the determination should be rerun.

X REVIEW OF DATA

A All data, particularly hydraulics data, should be worked up and reviewed daily. Computation should be made as rapidly as laboratory results are available.

B Following completion of the field work and data analysis, results should be reviewed with representatives of the industry. This joint review of the results of the investigation is advisable even though agency personnel and plant representatives work closely throughout the investigation.

XI PERIOD OF STUDY

A The length of time required to conduct an industrial waste survey depends on the magnitude and complexity of the problem, the wastes produced, the size of the plant, the present treatment if any, and the receiving water used for final disposal.

B In the larger plants, it is desirable to make a separate study of each major department. The survey in each department should extend through a minimum of ten operating days. The time period required must yield sufficient, accurate data for averaging.

C Irregularities, such as clean-up periods, should be the object of special study. Investigational research must pin-point all significant waste sources.

XII REPORT

A The final report should include the following information: describe the plant, process, and survey project in sufficient detail to make the work a useful permanent record.

B Tie-in waste data with production.

C Discuss and record the data fully. A full record of the project must be created for future use and reference.

D Record and explain unusual occurrences.

E The report should not be considered an official record until it has been reviewed and approved by the industry. This is a courtesy to industry and an invaluable check on the finished work.

XIII MISCELLANEOUS CONSIDERATIONS

A Such investigational research may be expected to serve as basis for development of an industrial waste control program.

B Knowledge of the complex nature of the problem will aid the control agency in justifying the time required for necessary research.

C Agency representatives should be briefed on hazards by the Safety Department the same as new employees.

D Restricted areas should be clearly defined prior to initiating the projects.

E Concerted effort should be made to produce results which will be of maximum value to both the industry and the agency.

XIV SOURCES OF INFORMATION

A Technical Journals covering the field of Sanitary Engineering

B Trade Journals

C Publications of Industrial Associations

D University Engineering Experiment Station Bulletins

E U.S. Public Health Service, Industrial Waste Guides

F FWPCA Publications

ACKNOWLEDGMENT

This outline contains certain portions of a previous outline by Hayse H. Black.

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INDUSTRIAL LIQUID WASTE SURVEYS

I INTRODUCTION

The purpose of industrial liquid waste surveys is to define the problem and propose definite alternative solutions to the problem.

A Inspect or consider carefully liquid processes.

B Determine the liquid waste sources, quantities and characteristics by measurement.

C Review liquid waste data and interpret requirements.

II ORGANIZATION

A Industry

B Consultants or consulting engineers

C Municipalities

D State agencies

E Federal Water Pollution Control Administration

III DEFINITION OF THE PROBLEM

The in-plant liquid waste discharges and their relation to the total combined effluent, municipal sewer and/or stream

A Process Study

1 Literature review of process information

2 Information on industry in general and the plant operations specifically; i.e., number of production units, operating day, seasonal variations, employees

3 Physical layout of the plant

4 Raw materials, intermediates and final product list

5 Schematic flow sheet of actual plant operation

6 Alternative processes used by the industry

7 By-product or salvage operations and in-plant housekeeping procedures

8 Liquid flow diagram (from source of supply to final effluent discharge)

B Parameters of Pollution - Effluent Criteria

1 Literature review of water quality criteria

2 Regulatory agencies - Federal and State

3 Municipal sewer ordinances

4 Independent studies

C Plant and Stream Hydraulic Studies

1 Literature review of applicable hydraulics

2 Definition by means of a hydraulic flow diagram

3 Actual measurement of flows

D Analytical Work - Chemist and Biologist

1 Literature review of pertinent methods

2 Determining analytical requirements

3 Planning the analytical schedule

E Sampling Program

1 Literature review of sampling methods, handling procedures, and preservation

2 Collection considerations

a Manual sampling

1) Volume required for analysis

2) Grabs

3) Composites, interval

4) Sampling proportional to flow (weighted)

5) Sample at point of homogeneity

6) Precautions with wastes containing settleable solids, oil, or volatile materials

7) Equipment and its care

8) Recording observations

b Automatic sampling

1) Commercial units

a) Types and description

b) Installation and calibration

c) Maintenance

d) Limitations

e) Advantages and disadvantages

f) Cost

2) Improvised units

3) Instrumentation

c Handling of samples

1) Identification tags

2) Protection in the field

3) Multiple bottles dictated by analytical requirements

4) Shipment and containers

5) Storage limitations

6) Bottle recommendations

d Sample preservation

1) Refrigeration

2) Chemical treatment

e Miscellaneous sampling problems and pitfalls

1) Industrial plants

a) Submerged outfalls

b) Deep manholes

c) Steam-filled sewers

d) Coated sewers and sedimentation

e) Toxic or explosive liquids or vapors

f) Solvents

2) Stream or estuary

a) Floating material

b) Access to ideal cross section

F Review of Data - Waste Water Characteristics

The in-plant, effluent and stream balance

1 Statistical design of the program

a Anticipated uses of data

b Minimum period for survey

c Minimum number of samples

d Minimum number of determinations

2 Correlation of effluent data with plant operations

a Raw materials

b Finished products

c Intermediate products

d By-products or salvaged materials

e Production, yield

f Processes employed

g Water use, reuse and recycle

3 Evaluation of Data

a Flow balance - usually pounds

b Material balance - also in pounds

c Statistical analysis

1) Distribution

2) Levels of significance

3) Errors

4) Frequency

5) Confidence limits

6) Means

7) Deviation

8) Probability

IV EXPLORING THE SOLUTIONS TO THE PROBLEM

A Research

1 Literature review of treatment methods

2 In-plant or effluent treatability studies

a Effect of variations in flow rates on treatment plant hydraulics and process performance

b Effect of variation in liquid waste quality on process performance

c Need for equalization capacity for either flow or quality reasons

d Possibility for waste water segregation and separate treatment systems

e In-plant controls, treatment or process change versus terminal treatment

B Process Engineering

1 Sizing facilities

2 Cost estimating

V REPORT

A Preliminary Engineers Report

B Summary Report

FIGURE 1. SIMPLIFIED FLOW DIAGRAM-CUCUMBER PICKLING

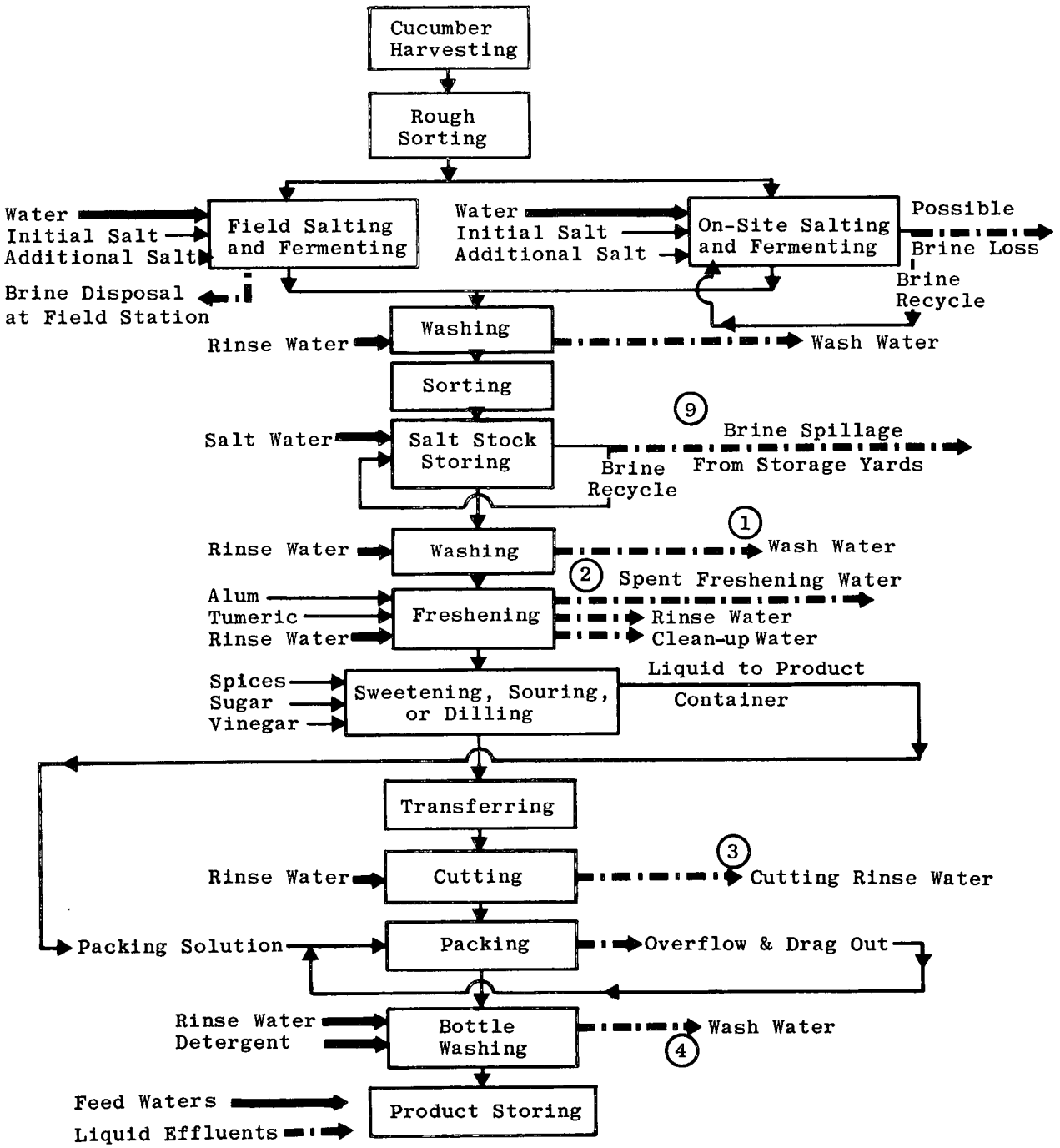
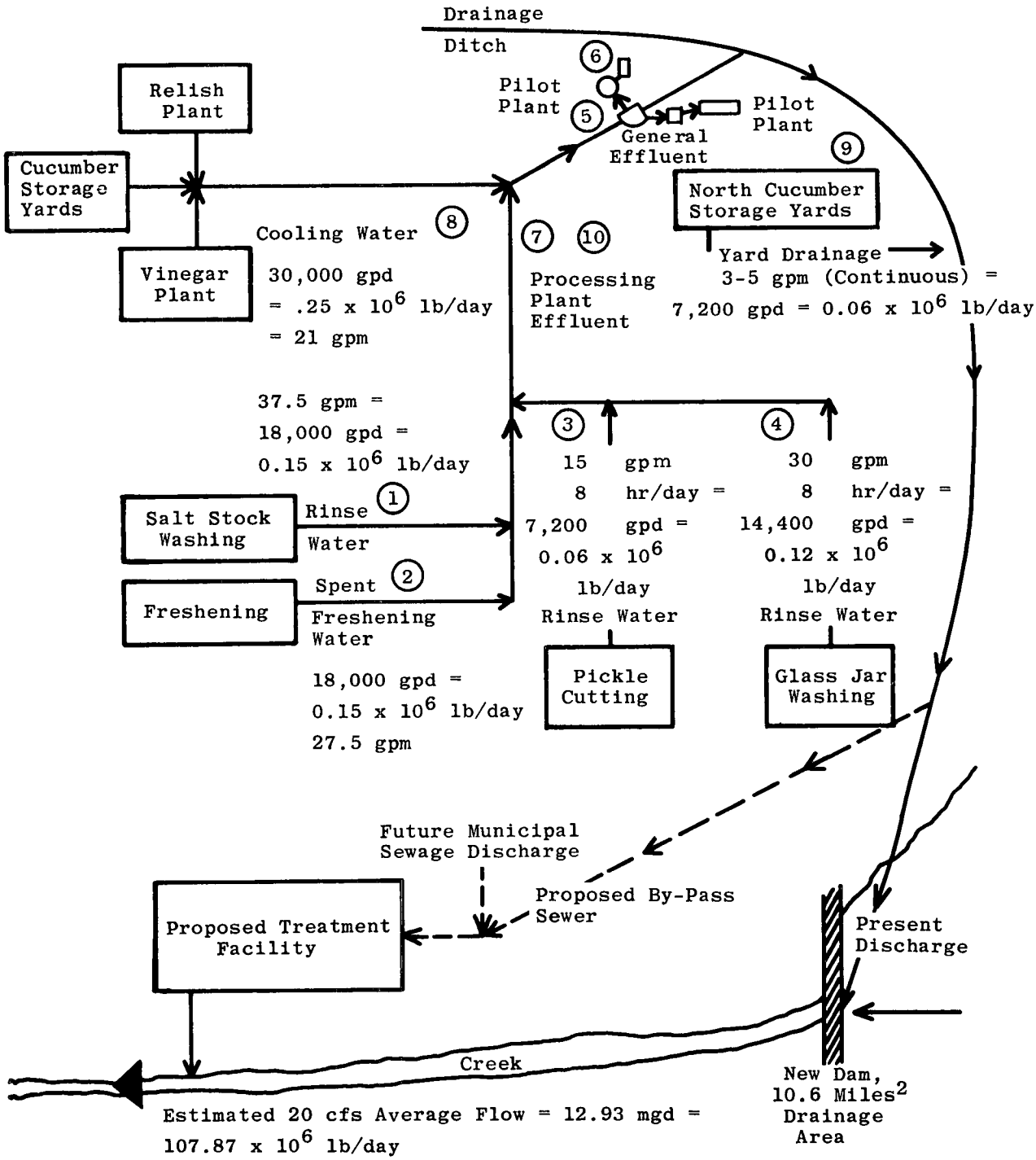


FIGURE 2. SCHEMATIC DISCHARGE DIAGRAM



Procedures for Determining Pollutional Characteristics of Foundry Wastes
Precision of Recorded Results

Characteristic	Result Reported to Nearest -	Significant Figures (Not more Than)	Example of Reported Result
Flow	—	—	—
Temperature °C	one	two	22
Dissolved oxygen	tenth	two	6.9
pH	tenth	two	9.1
Alkalinity	one	three	117
Acidity	one	three	76
Turbidity	one	two	270
Total solid	one	three	173
Total volatile solids	one	three	122
Color	five	two	45
Total suspended solids	one	three	110
Volatile suspended solids	one	three	101
Sulfate	one	three	21
Total oil and grease	one	two	72
Soluble oil	one	two	22
5-day biochemical oxygen demand	one	two	280
Chemical oxygen demand	one	three	324
Chemical oxygen demand	one	three	324
Ammonia nitrogen	tenth	two	0.6
Nitrate nitrogen	tenth	two	0.7
Organic nitrogen	tenth	two	1.3
Total phosphate	hundredth	two	0.84
Phenol	hundredth	two	0.16
Cyanide			
Copper	hundredth	two	0.21
Lead	hundredth	two	0.58
Cadmium	hundredth	two	0.74
Zinc	hundredth	two	0.62
Nickel	hundredth	two	0.79
Chromium	hundredth	two	0.52
Manganese	hundredth	two	0.71
Soluble iron	hundredth	two	0.41
Aluminum	tenth	two	1.1
Boron	hundredth	two	.18
Magnesium	one	two	2
Lithium	tenth	two	1.2

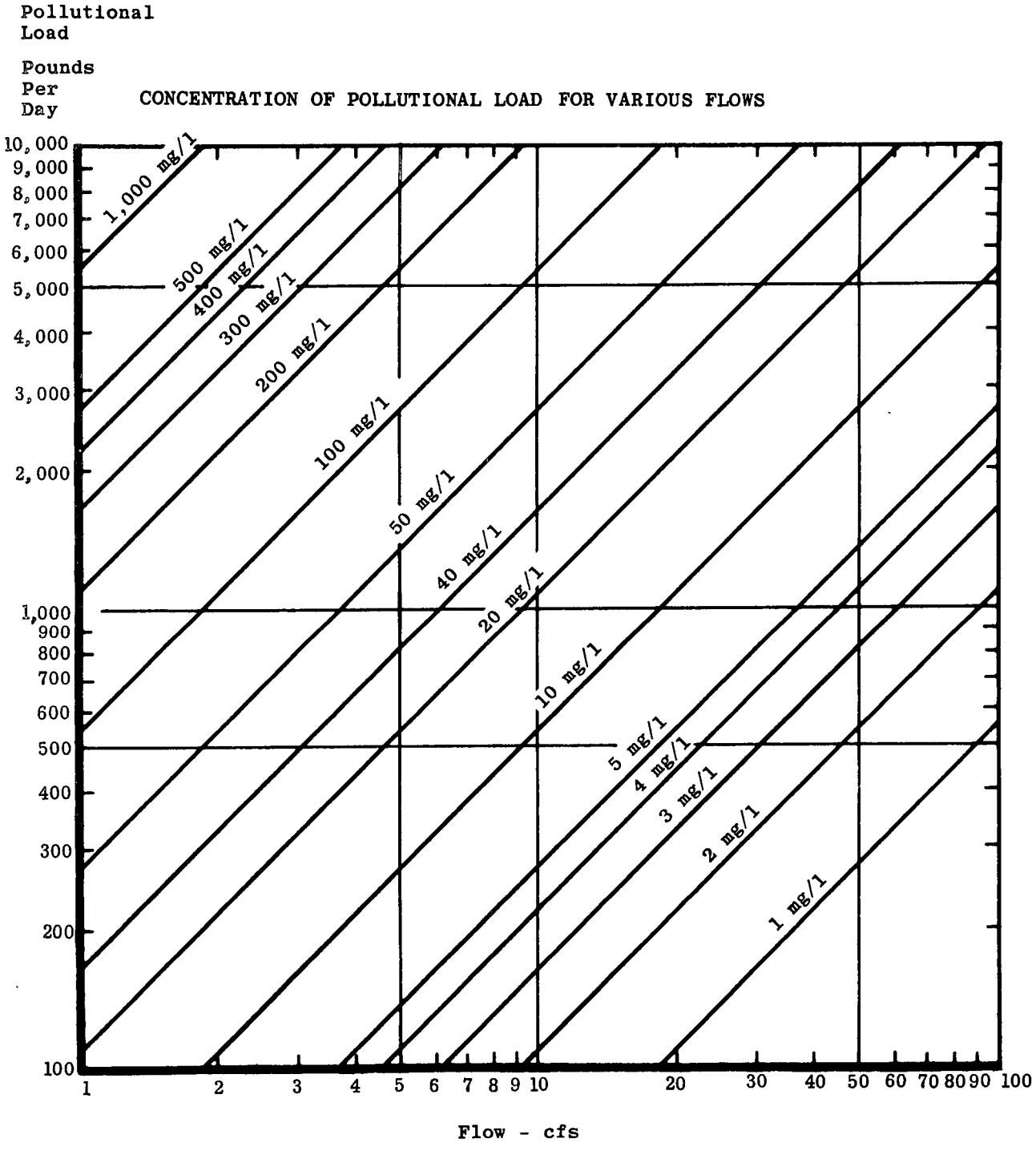
Table 6

Procedures for Determining Pollutional Characteristics of Foundry Wastes

Characteristic	Sample Container Number	Type of Sampling Container	Sample Volume Rec'd Min.	Sample Preservation	Sample Storage Limitation	Reference*	Notes
Flow							Four steps for the preservation of all sampling containers:
Temperature °C						I pg 311	
Dissolved oxygen						IV pg 504	
pH	1	Plastic	1 gallon	None	Within 8 hrs.	I pg 225	1. Dichromate acid rinse.
Alkalinity	1	↓	↓	↓	↓	IV pg 438	2. Tap water rinse.
Acidity	1	↓	↓	↓	↓	IV pg 438	3. Distilled water rinse.
Turbidity	1	↓	↓	↓	↓	I pg 312	4. Allowed to dry.
Total solids	1	↓	↓	↓	↓	III pg 423	
Total volatile solids	1	↓	↓	↓	↓	III pg 423	
Color	1	↓	↓	↓	Within 48 hrs.	IV pg 443	Sample containers for metals should be finally rinsed in 1:1 HNO_3.
Total suspended solids	1	↓	↓	↓	↓	III pg 424	
Volatile suspended solids	1	↓	↓	↓	↓	III pg 425	
Sulfate	1	↓	↓	↓	↓	I pg 287	
Total oil and grease	2	Widemouthed glass-stoppered bottle	1 guart	Acidified and stored in refrigerator	Within 24 hrs.	III pg 383	Flow, temperature, and dissolved oxygen measured during time of collection.
Soluble oil	3	Widemouthed glass-stoppered bottle	1 guart	Acidified and stored in refrigerator	Within 24 hrs.	API**733-58	
5-day biochemical oxygen demand	4	Plastic	1 gallon	Immediate storage on ice	Within 4 hrs.	III pg 415	Explanation of arrows:
Chemical oxygen demand	4	↓	↓	↓	↓	IV pg 510	The quantity of sample designated is sufficient to do all tests as grouped and covered by pointing arrow.
Chemical oxygen demand	4A	↓	↓	Acid preserved; 3.5 ml conc. H_2SO_4 per gallon of sample	Within 5 days	IV pg 510	
Ammonia nitrogen	5	Plastic	1 gallon	Acid preserved; 3.5 ml conc. H_2SO_4 per gallon of sample	Within 14 days	III pg 389	
Nitrate nitrogen	5	↓	↓	↓	↓	III pg 393	The analytical parameters suggested are for guidance purposes only and the intent is not to say that all of these measurements must be made. In many instances certain of these parameters will not apply and thus the determination may be eliminated. The waste engineer must use his own judgment in this respect and plan his survey accordingly.
Organic nitrogen	5	↓	↓	↓	↓	III pg 402	
Total phosphate	5	↓	↓	↓	↓	I pg 230	
Phenol	6	Plastic	1 gallon	Acid preserved; adjust pH to 4 with H_3PO_4; add 3.8 gms. $CuSO_4$ per gal.	Within 24 hrs.	IV pg 514	
Cyanide	7	Plastic	1 gallon	NaOH to pH 11 store in cool place	Within 14 days	IV pg 448	
Copper	8	Plastic	1 gallon	Acid preserved with 19 ml conc. HNO_3 per gallon of sample	Within 30 days	IV pg 479	
Lead	8	↓	↓	↓	↓	IV pg 485	
Cadmium	8	↓	↓	↓	↓	IV pg 470	
Zinc	8	↓	↓	↓	↓	IV pg 494	
Nickel	8	↓	↓	↓	↓	IV pg 492	
Chromium	8	↓	↓	↓	↓	IV pg 474	
Manganese	8	↓	↓	↓	↓	IV pg 489	
Soluble iron	8A	Glass - screw cap	50 to 100 ml	Fixed with 1,10 phenanthroline	Within 5 days	IV pg 482	
Aluminum	9	Plastic	1 gallon	None	Within 7 days	I pg 57	
Boron	9	↓	↓	↓	↓	I pg 60	
Magnesium	9	↓	↓	↓	↓	I pg 168	
Lithium	9	↓	↓	↓	↓	I pg 166	

*Standard Methods for the Examination of Water and Waste Water, 12th edition, 1965.
**American Petroleum Institute, 1957.

Courtesy of James L. Holdaway
Chemist, TA & I Activities, FWPCA


Pollutional Load
Pounds Per Day
CONCENTRATION OF POLLUTIONAL LOAD FOR VARIOUS FLOWS
10,000
9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
900
800
700
600
500
400
300
200
100
1,000 mg/1
500 mg/1
400 mg/1
300 mg/1
200 mg/1
100 mg/1
50 mg/1
40 mg/1
20 mg/1
10 mg/1
5 mg/1
4 mg/1
3 mg/1
2 mg/1
1 mg/1
1
2
3
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9
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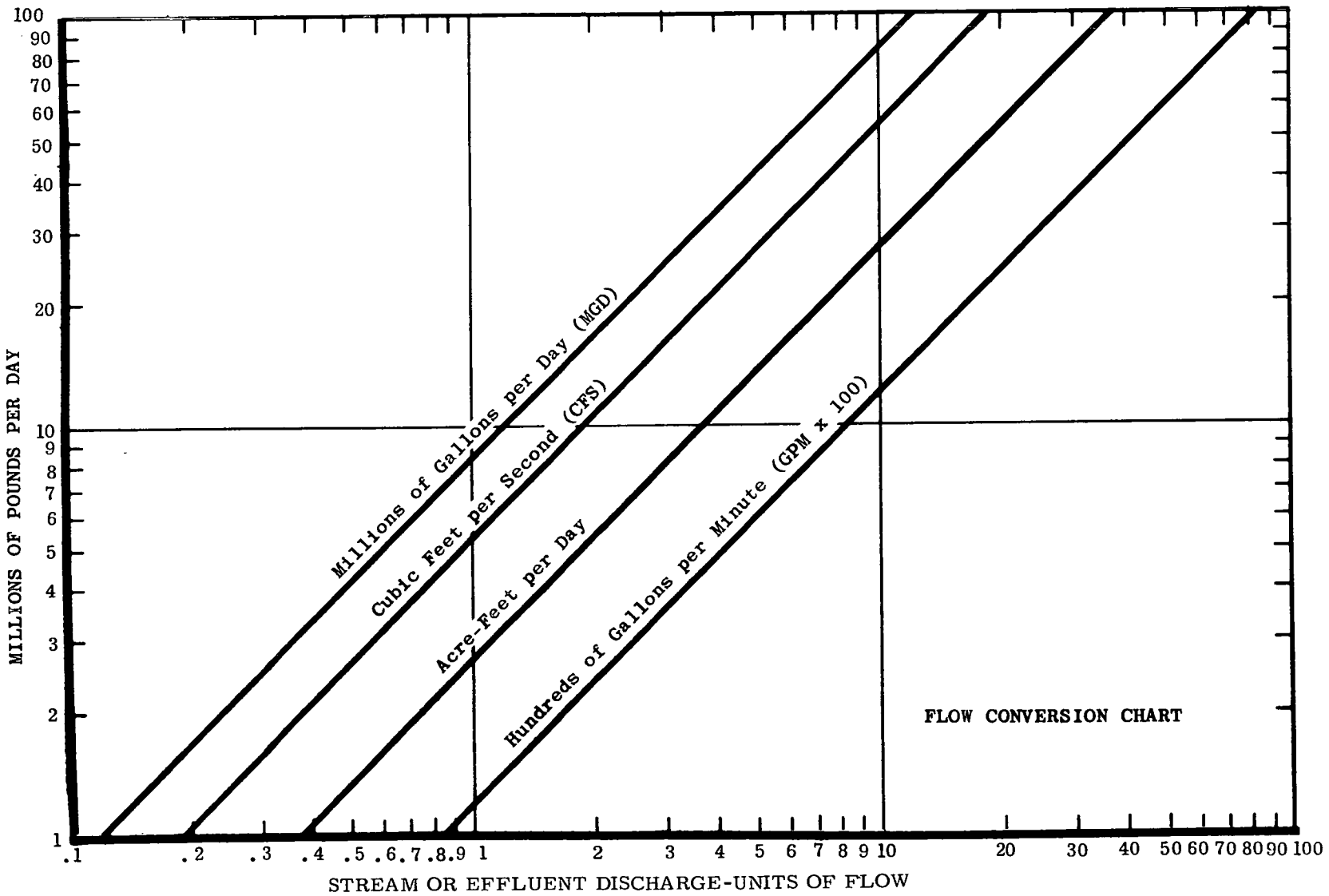
30
40
50
60
70
80
90
100
Flow - cfs


FLOW CONVERSION CHART
Millions of Gallons per Day (MGD)
Cubic Feet per Second (CFS)
Acre-Feet per Day
Hundreds of Gallons per Minute (GPM x 100)
MILLIONS OF POUNDS PER DAY
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
90
100
STREAM OR EFFLUENT DISCHARGE-UNITS OF FLOW

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This outline was prepared by Thomas J. Powers, Director, Water Quality Standard Branch, Federal Building, Cincinnati, OH 45202.

STATISTICAL CONSIDERATIONS IN SURVEY PLANNING

I NEED FOR ADVANCE PLANNING

A Sample must be representative of the population from which it was drawn.

B The size of the sample should not be larger than is necessary to give statistically valid results. It is uneconomical otherwise.

C The user of the sample must specify in advance the confidence level and the confidence interval that will be acceptable to him.

D Types of Samples

1 Census (100% sample). Obviously not applicable here. One cannot analyze all the water in a stream, lake, or bay.

2 Random Sample. All the drops of water in the population have the same chance of being drawn in the sample. You can divide the surface area of the body of water into equal sub-areas, number each one, and then draw numbers randomly (out of a hat, or by reference to a table of random numbers). This is a good method if the water is homogeneous in regard to the characteristic in which we are interested.

3 Stratified Sample. If our body of water is known to be heterogeneous (coliform count varies with depth, for instance), the population can be divided into strata, or layers, and random samples drawn from each stratum. This method cannot be used unless some information about the body of water and its strata is available. Clearly, the strata must be related to the characteristic being studied, and there should be homogeneity within each stratum. For a non-homogeneous population, a properly stratified sample may be expected to yield more reliable results than a random sample of the same size. Of course, a stratified sample taken from a homogeneous body of water is no more reliable than a random sample of equal size.

4 There are other types of samples, but random and stratified samples are the ones most commonly used in water studies.

II METHOD OF DETERMINING SAMPLE SIZE

A Assume that the confidence coefficient is set at 95 percent and the confidence interval ± 1 unit.

B A sample taken from a body of water is usually so small compared to the total amount of water present that we may regard the reciprocal of the population size as practically zero.

C Some indication of the standard deviation of the population must be obtained, either from past experience or from a pilot study.

III COMPUTATIONS

A Sample size for finite populations can be calculated by the formula:

$$n = \frac{\sigma_x^2}{\frac{h^2}{Z^2} + \frac{\sigma_x^2}{N}}$$

where n_2 = sample size

σ_x = the population variance

Z = standard normal deviate

h = half-width of the confidence interval

N = size of population

B Assume we have estimated σ_x to be about 3.2. We have set h at ± 1, N is so large that σ_x is practically zero, and Z (from a table of areas under a normal curve) is found to be 1.96 for a 95% confidence coefficient.

C Substituting these values in our formula, we find

$$n = \frac{(3.2)^2}{\frac{(\pm 1)^2}{(1.96)^2} + \frac{(3.2)^2}{N}}$$

(where $\frac{(3.2)^2}{N}$ is taken as zero)

Sample size is 40.

IV EVALUATION OF PRECISION OBTAINED

A Suppose that a simple random sample of 40 was selected and the following results obtained:

Mean of the sample $\overline{X} = 17.10$
Standard deviation $s_x = 3.60$

B The standard deviation of the sample mean,

$$s_{\overline{x}} = \frac{s_x}{\sqrt{n}} = \frac{3.6}{\sqrt{40}} = 0.57$$

C Then, the confidence interval will be $\overline{X} \pm Z\, s_{\overline{x}}$ or $17.10 \pm 1.96\,(.57)$ which is 17.10 ± 1.12 or between 15.98 and 18.22 at the 95% confidence level.

V COMMENTS

A Our confidence interval is a bit larger than was specified in advance. This is due to the fact that we underestimated the variance of the population.

B If we made a larger estimate of the variance, our confidence interval would have been narrower but the sample would have been larger.

C Specifying a higher coefficient of confidence will also increase the required sample size, other things being equal.

D The result of underestimating the population variance will be that the confidence interval will be wider than the desired one. It will not, however, affect the validity of the confidence interval for evaluating the precision of the estimate actually obtained.

This outline was prepared by Henry P. Shotwell, North Atlantic Water Quality Management Center, EPA, OWP, Edison, NJ.

III ANALYTICAL PROCEDURES

	Outline Number
Acidity, Alkalinity, pH and Buffers	9
Laboratory Procedure for Total Alkalinity	10
Laboratory Procedure for Total Acidity	11
The Specific Conductance Measurement	12
Specific Conductivity Laboratory	13
Chemical Oxygen Demand and COD/BOD Relationships	14
Solids Relations in Polluted Water	15
Determination of Suspended Solids	16
Laboratory Procedure for Total Solids	17
Laboratory Procedure for Non Filterable (Suspended) Solids	18
Laboratory Procedure for Filterable (Dissolved) Solids	19
Laboratory Procedure for Volatile Solids	20
Bioassay and Biomonitoring	21
Special Applications and Procedures for Bioassay	22
The Use of Bio-Assays: Case Histories	23

ACIDITY, ALKALINITY, pH AND BUFFERS

I DEFINITIONS OF ACIDS AND BASES

A Arrhenius Theory of Acids and Bases (Developed about 1887)

1 Acid: A substance which produces, in aqueous solution, a hydrogen ion (proton), H^+.

2 Base: A substance which produces, in aqueous solution, a hydroxide ion, OH^-.

3 The Arrhenius theory was confined to the use of water as a solvent.

B Bronsted and Lowry Theory of Acids and Bases (Developed about 1923)

1 Acid: A substance which donates, in chemical reaction, a hydrogen ion (proton).

2 Base: A substance which accepts, in chemical reaction, a hydrogen ion (proton).

3 Bronsted and Lowry had expanded the acid-base concept into non-aqueous media; i.e., the solvent could, but did not have to be, water.

C Further development of acid-base theory dealing with electron pair donation or acceptance is unimportant.

II DEFINITIONS OF ACIDITY, ALKALINITY AND NEUTRALITY

A Acidity

A condition in which there is a preponderance of acid materials present in the water.

B Alkalinity

A condition in which there is a preponderance of alkaline (or basic) materials present in the water.

C Neutrality

1 It is possible to have present in the water chemically equivalent amounts of acids and bases. The water would then be described as being neutral; i.e., there is a preponderance of neither acid nor basic materials. The occurrence of such a condition would be rare.

2 The term "neutralization" refers to the combining of chemically equivalent amounts of acids and bases. The two products of neutralization are a salt and water.

$$HCl + NaOH = NaCl + H_2O$$

Hydrochloric acid	Sodium Hydroxide	Sodium Chloride (a salt)

D The key word in the above definitions is "preponderance." It is possible to have a condition of acidity while there are basic materials present in the water, as well as conversely.

III HOW ARE DEGREES OF ACIDITY AND ALKALINITY EXPRESSED?

The pH scale is used to express various degrees of acidity and alkalinity. Values can range from 0 to 14. These two extremes are of theoretical interest and would never be encountered in a natural water or in a waste water. pH readings from 0 to just under 7 indicate an acidic condition; from just over 7 to 14, an alkaline condition. Neutrality exists if the pH value is exactly 7. pH paper, or a pH meter, provides the most convenient method of obtaining pH readings. Some common liquids and their pH values are listed in Table 1.

TABLE 1. pH Values of Common Liquids	
Household lye	13.7
Bleach	12.7
Ammonia	11.3
Milk of magnesia	10.2
Borax	9.2
Baking soda	8.3
Sea water	8.0
Blood	7.3
Distilled water	7.0
Milk	6.8
Corn	6.2
Boric acid	5.0
Orange juice	4.2
Vinegar	2.8
Lemon juice	2.2
Battery acid	0.2

5.9 - 8.4 is the common pH range for most natural waters.

IV HARD AND SOFT WATERS

In addition to being acidic or basic, water can also be described as being hard or soft.

A Hard water contains large amounts of calcium, magnesium, strontium, manganese and iron ions, relative to the amount of sodium and potassium ions present. Hard water is objectionable because it forms insoluble compounds with ordinary soap.

B Soft water contains small amounts of calcium, magnesium, strontium, manganese and iron ions, relative to the amount of sodium and potassium ions present. Soft water does not form insoluble compounds with ordinary soap.

V TITRATIONS

A The conversion of pH readings into such quantities as milligrams (mg) of acidity, alkalinity, or hardness, is not easily carried out. These values are more easily obtained by means of a titration.

B In a titration, an accurately measured volume of sample (of unknown strength) is combined with an accurately measured volume of standard solution (of known strength) in the presence of a suitable indicator.

C The strength (called normality) of the sample is then found using the following expression:

milliliters (ml) of sample × normality (N) of sample = ml of standard solution × N of standard solution.

Three of the four quantities are known, and

N of sample = ml of standard solution × N of standard solution/ml of sample.

D In modified form, and a more specific application of the above equation, alkalinity is calculated in the following manner (12th ed. Standard Methods).

mg of alkalinity as mg $CaCO_3$/liter (l) = ml of standard H_2SO_4 × N of standard H_2SO_4 × 50 × 1000/ml sample.

VI INDICATORS

The term "suitable indicator" was used above. At the end of a titration, the pH of the solution will not necessarily be 7. It may be above or below 7. A suitable indicator, therefore, is one which undergoes its characteristic color change at the appropriate pH. Below are a few examples of indicators and the pH range in which they undergo their characteristic color changes. In some cases, mixed indicators may be used in order to obtain a sharper and more definite color change.

Indicator	Operational pH Range
Methyl Yellow	2.8 - 4.0
Methyl Orange	3.1 - 4.4
Methyl Red	4.4 - 6.2
Cresol Purple	7.4 - 9.0
Phenolphthalein	8.0 - 9.6
Alizarine Yellow	10.0 - 12.0

TABLE 2. pH Range of Indicators

VII BUFFERS

A A buffer is a combination of substances which, when dissolved in water, resists a pH change in the water, as might be caused by the addition of acid or alkali. Listed below are a few chemicals which, when combined in the proper proportions, will tend to maintain the pH in the indicated range.

Chemicals	pH Range
Acetic Acid + Sodium Acetate	3.7 - 5.6
Sodium Dihydrogen Phosphate + Disodium Hydrogen Phosphate	5.8 - 8.0
Boric Acid + Borax	6.8 - 9.2
Borax + Sodium Hydroxide	9.2 - 11.0

TABLE 3. pH Range of Buffers

B A buffer functions by supplying ions which will react with hydrogen ions (acid "spill"), or with hydroxide ions (alkali "spill").

C In many instances, the buffer is composed of a weak acid and a salt of the weak acid; e.g., acetic acid and sodium acetate.

1 In water, acetic acid ionizes or "breaks down" into hydrogen ions and acetate ions.

$$HC_2H_3O_2 = H^+ + C_2H_3O_2^-$$

(acetic acid) (hydrogen ion) (proton) (acetate ion)

This ionization occurs to only a slight extent, however, most of the acetic acid remains in the form of $HC_2H_3O_2$; only a small amount of hydrogen and acetate ions is formed.

2 Thus, acetic acid is said to be a weak acid.

3 In the case of other acids, ionization into the component ions occurs to a large degree, and the term strong acid is applied; e.g., hydrochloric acid.

$$HCl = H^+ + Cl^-$$

(hydrochloric acid) (hydrogen ion) (proton) (chloride ion)

4 The terms "strong" and "weak" are also applied to bases. In water solutions, those which break down into their component ions to a large extent are termed "strong", and those which do not are "weak". Sodium hydroxide is a relatively strong base, while ammonium hydroxide is realtively weak.

5 Sodium acetate (a salt of acetic acid) dissociates or "breaks down" into sodium ions and acetate ions when placed in water.

$$NaC_2H_3O_2 = Na^+ + C_2H_3O_2^-$$

(sodium acetate) (sodium ion) (acetate ion)

This dissociation occurs to a large extent, and practically all of the sodium acetate is in the form of sodium ions and acetate ions.

D It would be difficult and expensive to prepare large quantities of buffers for use in a treatment plant. However, certain naturally occurring buffers may be available (carbon dioxide is an example). It dissolves in water to form the species indicated below.

$$CO_2 + H_2O = H_2CO_3$$

(carbon dioxide) (Water) (carbonic acid)

$$H_2CO_3 = H^+ + HCO_3^-$$

(hydrogen ion) (proton) (hydrogen carbonate ion) (bicarbonate)

The hydrogen ions react with hydroxide ions which might appear in the water as the result of an alkali "spill".

$$H^+ + OH^- = H_2O$$

(in the buffer) (hydroxide ion "spilled")

The hydrogen carbonate ions react with hydrogen ions which might appear in the water as the result of an acid "spill".

$$H^+ + HCO_3^- = H_2CO_3$$

(hydrogen ion) (proton) "spilled" (in the buffer)

This buffering action will be in effect as long as there is carbonic acid present.

E Buffering action is not identical with a process in which acid wastes are "neutralized" with alkali wastes, or conversely. The desired effect is achieved in both cases, however (i.e., the pH is maintained within a desired range.)

This outline was prepared by C. R. Feldmann, Chemist, National Training Center, MDS, WPO, EPA, Cincinnati, OH 45268

LABORATORY PROCEDURE FOR TOTAL ALKALINITY

I METHOD SUMMARY

A In the current methods manual[1] of the Environmental Protection Agency, the following method is specified for use in Office of Water Programs laboratories. The sample is titrated with 0.02N hydrochloric or sulfuric acid to a final pH of 4.5, the end point being determined electrometrically.

1 The sample must not be filtered, diluted, concentrated or altered in any way.

2 Results are reported as mg$CaCO_3$/liter.

3 The procedure can be found in Standard Methods[2] and ASTM Book of Standards.[3]

B The procedure as given in the above references has been adapted for this laboratory session to accommodate group participation and to accomplish instructional objectives.

II DISCUSSION

In this manual, outline 8 considers the relationships among the 3 forms of alkalinity commonly found in water. Refer to the graphs in outline 8 for the following:

For Case 1, $(OH)^-$ alkalinity only, pH values change very gradually until the approach of pH 9. Then an abrupt change occurs and the addition of a few ml of titrant causes the value to change rapidly to about pH 4.

For Case 2, $(CO_3)^=$ alkalinity only, there is a gradual change of pH values as the acid titrant is added. Around pH 9 there is an abrupt change of the scale reading. Around pH 6, the change is again gradual. Around pH 5, another rapid change occurs until pH 3 is reached.

A pH of 8.3 represents the average pH when $(OH)^-$ has been totally neutralized and $(CO_3)^=$ has been half neutralized to $(HCO_3)^-$. A pH of 4.5 represents the average pH occurring when $(HCO_3)^-$ has been neutralized to CO_2 and H_2O. (See Case 3).

In order to obtain standardized data, the EPA method specifies stopping alkalinity titrations at pH 4.5. At this pH, any $(OH)^-$, $(CO_3)^=$ and $(HCO_3)^-$ in the sample will be neutralized. Since all three of these alkalinity forms may be present, the results are expressed as <u>total</u> alkalinity.

It is useful to express total alkalinity as mg $CaCO_3$/liter.

III INSTRUCTIONAL OBJECTIVES

A You will use the adapted EPA method to determine total alkalinity by titrating 3 solutions of known alkalinities and one unknown to an end point of pH 4.5. You will then use the data to calculate the total alkalinity for each as mg $CaCO_3$/liter.

1 By slowly adding the HCl titrant to solutions of $(OH)^-$, of $(CO_3)^=$ and of $(HCO_3)^-$ and observing the pH scale, the characterizing response of each alkalinity at different pH values can be observed.

2 Recording the volume of HCl used to reach pH 8.3 and then pH 4.5 will also illustrate the pH characteristics of the three forms of alkalinity.

3 Calculating the total alkalinity of these three solutions will familiarize you with the calculations for the determination.

B You will also do titrations on the same solutions using color indicators --- phenolphthalein (colorless at pH 8) and methyl orange (amber-orange at pH 4.6) --- in order to contrast values obtained by the pH determination.

C Using experience gained in the lab session, you will estimate the types of alkalinity present in the unknown sample.

IV REAGENTS

A Carbon Dioxide-Free Distilled Water

B Anhydrous Sodium Carbonate (primary standard)

C Hydrochloric Acid Titrant (0.02N)

D Phenolphthalein

E Methyl Orange

V STANDARDIZATION of the HYDROCHLORIC ACID TITRANT

A Set the temperature reading on the pH meter dial to match the temperature of the buffer and sample solutions.

B Standardize the pH meter against a reference buffer solution.

C Weigh accurately 0.088 ± 0.001 g of the dried sodium carbonate and transfer it to a 500 ml conical flask.

D Add 50 ml of water and swirl to dissolve the carbonate.

E While stirring the solution, add the hydrochloric acid titrant from a 100 ml buret until a pH of 4.5 is attained.

F Calculate the normality of the hydrochloric acid solution as follows:

$$A = \frac{B}{0.053 \times C}$$

A = normality of the hydrochloric acid

B = g of sodium carbonate used

C = ml of hydrochloric acid consumed

0.053 = millequivalent weight of Na_2CO_3

VI TITRATIONS to pH END POINTS

For each of the solutions marked Case 1 $(OH)^-$, Case 2 $(CO_3)^=$ and Case 3 $(HCO_3)^-$ and for the assigned unknown, A or B, the following procedure is to be followed. All data and the calculation results should be recorded on the Data Table provided.

A Calibrating the pH meter

1 Pour about 50 ml of the buffer solution into a small beaker.

2 Set the temperature reading on the pH meter dial to match the temperature of the reference buffer.

3 Immerse the electrode(s) into the buffer solution.

4 Turn the meter to "ON"(or "Read" or "pH").

5 Using the "Balance" (or "Asymm") knob, set the scale reading to 6.84.

6 Turn the meter to "Off" (or "Hold" or "Standby").

7 Remove electrode(s) from buffer and save this solution for possible later use.

8 Rinse electrode(s) with distilled water, then immerse them in a small beaker of distilled water until time to use.

B Prepare the buret by rinsing 3 times using about 15 ml HCl each time. Then fill the buret with HCl and adjust the volume so that the top of the liquid column is positioned for a reading.

C Titration Procedure:

1 Each titration will require up to 25 ml 0.02N HCl titrant. Refill the buret as needed before beginning each titration.

2 Pipet 50.0 ml of the solution to be used into a beaker.

3 Remove the pH electrode(s) from the beaker of distilled water and immerse electrode(s) in the solution to be titrated. The sample solution should cover the glass bulb(s).

4 Turn pH meter to "ON" (or "Read" or "pH").

5 On the Data Table, record the ml of HCl in the buret at the start of the titration.

6 Record the initial pH of the sample on the Data Table.

7 While gently swirling either the electrode or the sample in the beaker, slowly add the HCl titrant, observing the scale on the pH meter. Stop adding titrant when pH is about 8.3 and record the buret reading. (This step is not part of the EPA procedure. It is included here for instructional purposes).

8 Again gently swirling either the electrode or the beaker, continue slow addition of the HCl titrant, observing the meter scale. Be very cautious when the scale approaches ph 5.0. Stop titrating at pH 4.5. If a lower pH is inadvertently reached, note this on the Data Table.

9 On the Data Table, record the ml HCl remaining in the buret.

10 Set pH meter to "OFF" (or "Hold" or "Standby").

11 Rinse the pH electrode(s) with distilled water and immerse in the beaker of distilled water.

12 Empty the sample solution and rinse the beaker with distilled water.

13 Using the next solution, repeat this procedure (C, steps 1 through 12) until data has been recorded for the 3 knowns and the 1 unknown sample. Then proceed to part VII.

DATA TABLE
TITRATIONS TO pH END POINTS

	CASE 1 (OH^-)	CASE 2 ($CO_3^=$)	CASE 3 (HCO_3^-)	SAMPLE ____
Initial pH				
ml@pH 4.5				
ml@pH 8.3				
ml@Start	____	____	____	____
TOTAL ml. HCl				
TOTAL ALKALINITY (mg $CaCO_3$ /liter)				

VII TITRATIONS to COLOR END POINTS

If time permits, the following procedure should be used to titrate the 3 solutions of known constituents and the assigned unknown, A or B. At least, do one of the known solutions and the unknown used for the pH titration. All data and the calculation results should be recorded on the Data Table provided.

A Indicators Used

1 Phenolphthalein indicator is a deep pink around pH 10 and becomes colorless at pH 8. In the Data Table, this colorless end point is designated as P. End Pt.

2 Methyl orange indicator gives a yellow color to a colorless solution. At pH 4.6 (referred to as M.O. End Pt. on Data Table) it becomes amber-orange. This end point color requires practice to detect. If the solution acquires a pinkish cast, you are past the desired end point.

B Titration Procedure

1 Each titration will require up to 25 ml 0.02N HCl titrant. (If pH determinations have been done, refer to these results for approximations of HCL titrant to be used). Refill the buret as needed before beginning each titration.

2 Pipet 50.0 ml of the solution to be used into a beaker.

3 Place a piece of white paper under the beaker.

4 Add 3 drops phenolphthalein indicator to the sample and swirl to mix.

5 On the Data Table record the ml of HCl in the buret at the start of the titration.

6 Using the known relationship of the color of phenolphthalein to different pH values, record your estimate of the initial pH of the sample on the Data Table.

7 If the solution remains colorless, record 0.0 for P. End Pt. and continue with step 9.

If there is pink color in the solution, slowly add HCl titrant while stirring the sample.

As the end point is approached, a lingering colorless region where the titrant first contacts the sample will be observed. Add the titrant very cautiously at this time, stirring the sample solution and allowing time for total mixing and contact before adding more HCl titrant.

The end point occurs when the entire solution is colorless. Stop adding the HCl titrant.

8 Record the ml of HCl in the buret for the P. End Pt. on the Data Table.

9 Add 3 drops of methyl orange indicator to the same sample solution.

10 If the sample solution becomes amber-orange, record 0.0 for M.O. End Pt. and continue at step 12.

If the solution becomes yellow, slowly add HCl titrant while stirring the sample.

As the end point is approached, a lingering amber-orange region where the titrant first contacts the sample will be observed. Add the titrant very cautiously at this time, stirring the sample solution and allowing time for total mixing and contact before adding more HCl titrant.

The end point occurs when the entire solution is amber orange. Stop adding the HCl titrant. (If the solution develops a pinkish cast, you are past the desired end point and should note this on the Data Table).

11 Record the ml of HCl in the buret for the M.O. End Pt. on the Data Table.

12 Empty the sample solution and rinse the beaker with distilled water.

13 Choose the next solution according to time available and repeat this procedure (B, steps 1 thru 12).

DATA TABLE

TITRATIONS TO COLOR END POINTS

	CASE 1 $(OH)^-$	CASE 2 $(CO_3)^=$	CASE 3 $(HCO_3)^-$	SAMPLE ____
initial pH (Estimate)				
ml. @ M.O. End Pt.				
ml. @ P. End Pt.				
ml. @ Start	____	____	____	____
TOTAL ml. HCl				
TOTAL ALKALINITY (mg $CaCO_3$ /liter)				

VIII CALCULATIONS:

A Calculate Total Alkalinity for each solution titrated, using the following:

$$\text{mg } CaCO_3/1 = \frac{A \times N \times 50,000}{\text{ml. of sample}}$$

A = total ml of standard acid required for titration to pH 4.5 end point

N = normality of standard acid

50 = equivalent weight of $CaCO_3$

1000 converts ml to liters

B Record calculation results on the Data Tables.

REFERENCES

1 Methods for Chemical Analysis of Water and Wastes, EPA-AQCL, Cincinnati, OH 45268, (1971)

2 Standard Methods for the Examination of Water and Wastewater, 13th edition, APHA-AWWA-WPCF, Method 102 (1971)

3 ASTM Book of Standards, Part 23, p. 154 (1970)

This outline was prepared by A. Donahue, Chemist, National Training Center, DTTB, MDS, WPO, EPA, Cincinnati, OH 45268.

LABORATORY PROCEDURE FOR TOTAL ACIDITY

I REAGENTS

For detailed discussion of reagent preparation, consult reference 2.

A Carbon Dioxide - Free Distilled Water

B Potassium Hydrogen Phthalate (primary standard)

C Sodium Hydroxide Titrant (0.02 N)

II STANDARDIZATION OF THE SODIUM HYDROXIDE TITRANT

A Set the temperature reading on the pH meter dial to match the temperature of the buffer and sample solutions.

B Standardize the pH meter against a reference buffer solution.

C Weigh accurately 0.19 ± 0.005 g of the dried potassium hydrogen phthalate and transfer it to a 500 ml conical flask.

D Add 100 ml of reagent water and swirl gently to dissolve the phthalate.

E While stirring the solution(magnetic bar and stirrer), add the sodium hydroxide from a 100 ml buret until a pH of 8.3 is attained.

F Calculate the normality of the sodium hydroxide solution as follows:

$$A = \frac{B}{0.20423XC}$$

A = normality of the sodium hydroxide

B = g of potassium hydrogen phthalate

C = ml of sodium hydroxide solution

0.20423 = milliequivalent weight of potassium hydrogen phthalate ($KHC_8H_4O_4$)

III PROCEDURE

A Pipet 100 ml of the sample into a 400 ml beaker.

B Titrate with the sodium hydroxide to pH 8.3

C Calculation

Total acidity as mg of $CaCO_3$/l =

$$\frac{A \times N \times 50000}{\text{ml of sample}}$$

A = ml of standard NaOH titrant

N = N of standard NaOH titrant

50 = equivalent weight of $CaCO_3$

1000 - converts ml to liters

REFERENCES

1 Methods for Chemical Analysis of Water & Wastes, EPA-AQCL, 1971, Cincinnati, OH 45268.

2 A.S.T.M. Book of Standards, Part 23, D 1067-70, pp. 155-158.

This outline was prepared by Charles R. Feldmann, Chemist, National Training Center, WPO, MDS, DTTB, EPA, Cincinnati, OH 45268.

THE SPECIFIC CONDUCTANCE MEASUREMENT

I INTRODUCTION

An electrical conductivity measurement of a solution determines the ability of the solution to conduct an electrical current. Very concentrated solutions have a large population of ions and transmit current easily or with small resistance. Since resistance is inversely related to conductivity $K = \frac{1}{R}$, a very concentrated solution has a very high electrical conductivity.

Electrical conductivity is determined by transmitting an electrical current through a given solution, using two electrodes. The resistance measured is dependent principally upon the ionic concentration, ionic charge, and temperature of the solution although electrode characteristics (surface area and spacing of electrodes) is also critical. Early experiments in standardizing the measurement led to construction of a "standard cell" in which the electrodes were spaced exactly 1 cm and each had a surface area of 1 cm^2. Using this cell, electrical conductivity is expressed as "Specific Conductance". Modern specific conductance cells do not have the same electrode dimensions as the early standard cell but have a characteristic electrode spacing/area ratio known as the "cell constant".

$$K_{sp} = \frac{1}{R} \times \frac{\text{distance (cm)}}{\text{area (cm}^2)}, \quad K_{sp} = \frac{1}{R} \times k$$

$$k = \text{cell constant}$$

Specific conductance units are Mhos/cm or reciprocal ohms/cm. Most natural, fresh waters in the United States have specific conductances ranging from 10 to 1,000 micromhos/cm. (1 micromho = 10^{-6} mho).

II CONDUCTIVITY INSTRUMENTS

Nearly all of the commercial specific conductance instruments are of a bridge circuit design, similar to a Wheatstone Bridge. Null or balance is detected either by meter movement, electron "ray eye" tubes, or headphones. Since resistance is directly related to temperature, some instruments have automatic temperature compensators, although inexpensive models generally have manual temperature compensation.

Conductivity instruments offer direct specific conductance readout when used with a cell "matched" to that particular instrument.

Electrodes within the cell may become damaged or dirty and accuracy may be affected; therefore, it is advisable to frequently check the instrument readings with a standard KCl solution having a known specific conductance.

III CONDUCTIVITY CELLS

Several types of conductivity cells are available, each having general applications. Dip cells are generally used for field measurement, flow cells for measurement within a closed system, and pipet cells for laboratory use. Many modifications of the above types are available for specialized laboratory applications; the Jones cells and inductive capacitance cells are perhaps the most common.

Examples of various cell ranges for the RB3 - Industrial Instruments model (0-50 micromhos/cm scale range) are in Table 1.

Cell Number	Relative Conductivity Value	Maximum range micromhos/cm	Most accurate range micromhos/cm
Cell VSO2	1	0 - 50	2 - 30
Cell VS2	10	0 - 500	20 - 300
Cell VS20	100	0 - 5000	200 - 3000

Table 1

IV Computation of Calibration Constant

A calibration constant is a factor to which scale readings must be multiplied to compute specific conductance.

$K_{sp} = cM$

where K_{sp} = actual specific conductance

c = calibration constant

M = meter reading

For example, a 0.001 N KCl solution (147 micromhos/cm standard) may show a scale reading of 147.

$$147 = c\ 147,\ c = \frac{147}{147} = 1.00$$

In this case the cell is perfectly "matched" to the instrument, the calibration constant is 1.00, and the scale reading represents actual specific conductance. A variety of cells, each covering a specific range, may be used with any one instrument. However, a calibration constant for each cell must be computed before solutions of unknown specific conductance can be determined.

V RELATIONSHIP OF SPECIFIC CONDUCTANCE TO IONIC CONCENTRATION

Natural water consists of many chemical constituents, each of which may differ widely in ionic size, mobility, and solubility. Also, total constituent concentration and proportions of certain ions in various natural waters range considerably. However, it is surprising that for most natural waters having less than 2,000 mg/l. dissolved solids, specific conductance values are closely related to dissolved solids values, ranging in a ratio of .62 to .70. Of course this does not hold true for certain waters having considerable amounts of nonionized soluble materials, such as organic compounds and nonionized, colloidal inorganics.

Properties of some inorganic ions in regard to electrical conductivity are shown below:

Ion	Micromhos/cm per meq/l conc.
Calcium	52.0
Magnesium	46.6
Sodium	48.9
Potassium	72.0
Bicarbonate	43.6
Carbonate	84.6
Chloride	75.9

VI ESTIMATION OF CONSTITUENT CONCENTRATIONS

Generally speaking, for waters having a dissolved solids concentration of less than 1,000 mg/l, calcium and magnesium (total hardness), sodium, bicarbonate and carbonate (total alkalinity), and sulfate are the principal or most abundant ions, representing perhaps 90-99% of the total ionic concentration of the water. Specific conductance, total hardness and total alkalinity are all simple and expedient measurements which can be performed in the field. Therefore, the remaining principal ions are sodium and sulfate, and concentrations of these can be estimated by empirical methods. For example, we find that a certain water has:

K_{sp} = 500 micromhos/cm
Total Hardness = 160 mg/l or 3.20 meq/l
Total Alkalinity = 200 mg/l or 3.28 meq/l, as bicarbonate.

Next we multiply the specific conductance by *0.011 (500 × 0.011 = 5.50) to estimate the total ionic concentration in meq/l.

* This factor may vary slightly for different waters

Cations (meq/l)		Anions (meq/l)
Calcium	3.20	Carbonate 0.00
Magnesium		Bicarbonate 3.28
Sodium 5.50-3.20 = 2.30		Sulfate 5.50-3.28 = 2.22
Total Cations 5.50		Total Anions 5.50

Realizing that several variables are involved in empirical analysis, application rests entirely upon testing the formula with previous complete laboratory analyses for that particular water. If correlation is within acceptable limits, analytical costs may be substantially reduced. Empirical analysis can also be used in determination of proper aliquots (dilution factor) necessary for laboratory analysis.

Records of laboratory chemical analysis may indicate that a particular stream or lake shows a characteristic response to various streamflow rates or lake water levels. If the water's environment has not been altered and water composition responds solely to natural causes, a specific conductivity measurement may be occasionally used in substitution for laboratory analyses to determine water quality. Concentration of individual constituents can thus be estimated from a specific conductance value.

VII APPLICATIONS FOR SPECIFIC CONDUCTANCE MEASUREMENTS

A Laboratory Operations[2]

1 Checking purity of distilled and de-ionized water

2 Estimation of dilution factors for samples

3 Quality control check on analytical accuracy

4 An electrical indicator

B Agriculture

1 Evaluating salinity

2 Estimating Sodium Adsorption Ratio

C Industry[3]

1 Estimating corrosiveness of water in steam boilers

2 Efficiency check of boiler operation

D Geology

1 Stratigraphic identification and characterization

a geological mapping
b oil explorations

E Oceanography

1 Mapping ocean currents

2 Estuary studies

F Hydrology

1 Locating new water supplies

a buried stream channels (See Fig. 1)
b springs in lakes and streams (See Fig. 2)

2 Detection and regulation of sea water encroachment on shore wells

G Water Quality Studies

1 Estimation of dissolved solids (See Section V, also reference 2)

2 Empirical analysis of constituent concentrations (See Section VI, also reference 2)

3 Quality control check for salt water conversion studies

4 Determination of mixing efficiency of streams (See Fig. 3)

5 Determination of flow pattern of polluted currents (See Fig. 3)

6 Identification of significant fluctuations in industrial wastewater effluents

7 Signal of significant changes in the composition of influents to waste treatment plants

FIGURE 1

DETECTION OF BURIED STREAM CHANNELS

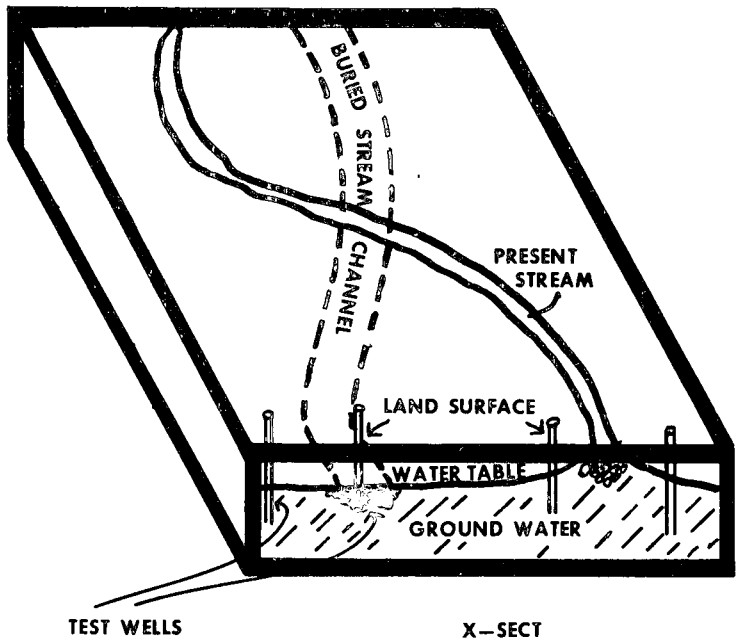


FIGURE 2

DETECTION OF SPRINGS IN LAKES AND STREAMS

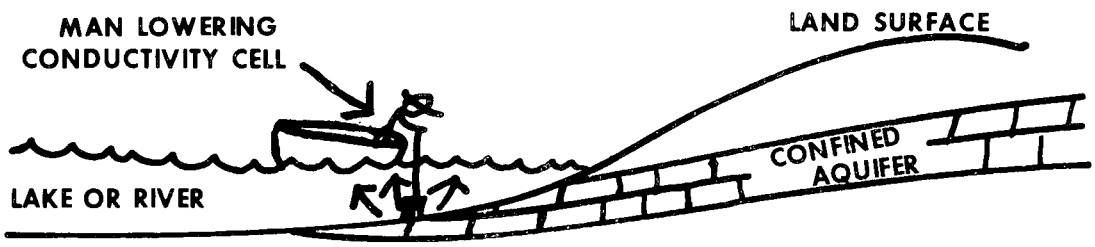
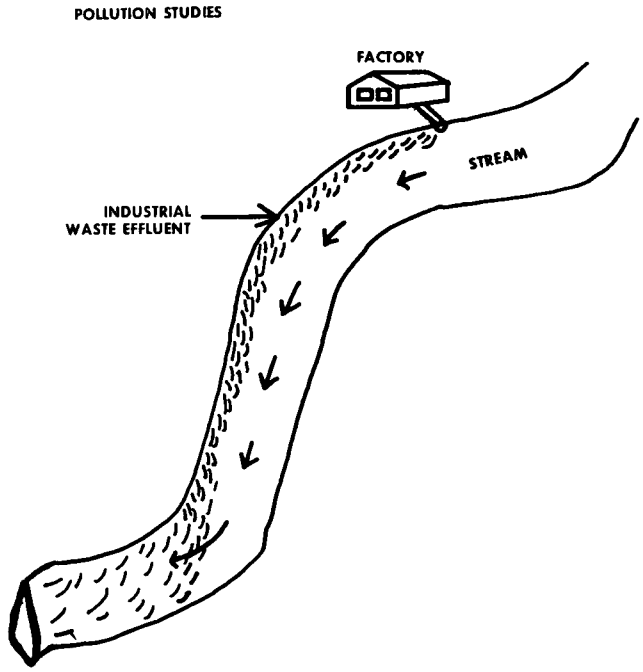


FIGURE 3



VIII EPA METHODOLOGY

A The current EPA Methods Manual[1] specifies that specific conductance be measured with a self-contained conductivity meter, Wheatstone bridge-type or equivalent.

Samples should preferably be analyzed at 25°C. If not, temperature corrections should be made and results reported at 25°C.

1 The instrument should be standardized using KCl solutions

2 It is essential to keep the conductivity cell clean

B The EPA manual specifies using the procedure as described in Standard Methods[2] or in ASTM Standards[3].

C Precision and Accuracy[1]

Forty-one analysts in 17 laboratories analyzed 6 synthetic water samples containing the following K_{sp} increments of inorganic salts: 100, 106, 808, 848, 1640 and 1710 micromhos/cm.

The standard deviation of the reported values was 7.55, 8.14, 66.1, 79.6, 106 and 119μ mhos/cm respectively.

The accuracy of the reported values was -2.0, -0.8, -29.3, -38.5, -87.9 and -86.9μ mhos/cm bias respectively.

REFERENCES

1 Methods for Chemical Analysis of Water and Wastes, EPA-AQCL, Cincinnati, OH 45268. 1971.

2 Standard Methods for the Examination of Water and Wastewater, APHA-AWWA-WPCF, 13th edition, 1971.

3 ASTM Standards, Part 23, 1970.

This outline was prepared by John R. Tilstra, Chemist, National Eutrophication Research Program, Corvallis, Oregon with additions by Audrey E. Donahue, Chemist, DTTB, MDS, OWP, EPA, Cincinnati, OH 45268.

SPECIFIC CONDUCTIVITY LABORATORY

I EQUIPMENT AND REAGENTS

A Equipment

1 Solu Bridge conductivity meters

2 Probes

a Cell VSO2

b Cell VS2

c Cell VS2O

3 Thermometers

4 400 ml beakers

B Reagents

1 Standard KC1 solutions

Normality of KC1 Solution	Specific Conductance micromhos/cm.
0.0001	14.9
0.001	147.0
0.01	1413.0
0.1	12900.0

2 Distilled water

II CHECKING THE INSTRUMENT

A The measurement of specific conductivity as presented in sections II and III is written for one type of conductivity meter and probe.

B A battery check is made by depressing the Battery Check switch, and at the same time pressing the on-off button. The meter needle should deflect to the right (positive) and come to rest in the green zone.

C Place a 10, 000 ohm resistor in the holes of the electrical contacts on the meter. Turn the temperature knob to read room temperature. Depress the on-off button and bring the meter needle to a reading of 0 by turning the specific conductance switch. The specific conductance reading should be approximately 200 micromhos/cm.

III DETERMINATION OF THE CALIBRATION CONSTANT

A Move the temperature switch so that its reading is the same as the temperature of the standard KCl and sample solutions.

B Connect probe Cell VS02 to the conductivity meter.

C Rinse the probe in the beaker of distilled water, wipe the excess water with a kimwipe and place probe in the first beaker of KCl solution (0.0001 N).

D Make certain the cell is submerged to a point at least 1/2 inch above the air hole and that no entrapped air remains. The cell should also be at least 1/2 inch from the inside walls of the flask.

E Press and hold down the ON-OFF button, simultaneously rotating the main scale knob until the meter reads zero. Release the button. (If the meter needle remains off scale or cannot be nulled, discontinue testing in that solution.)

F Record the scale reading in Table 1 and proceed to KC1 solutions 0.001N, 0.01N, 0.1 N.

G Repeat steps C through F using the VS2 and VS20 probes.

H Compute the cell calibration constant-a factor by which scale readings must be multiplied to compute specific conductance:

$K_{sp} = cM$

where K_{sp} = actual specific conductance,
c = calibration constant
M= meter reading

(continued next page)

TABLE 1 DATA FOR CALIBRATION CONSTANTS

Probe	Cell VSO2				Cell VS2				Cell VS20			
KCl Solutions	0.0001N	0.001N	0.01N	0.1N	0.0001N	0.001N	0.01N	0.1N	0.0001N	0.001N	0.01N	0.1N
Test # 1												
2												
3												
Cell Constant												

See I B Reagents for the actual specific conductance values of the KC1 solutions used for the probes.

Record the computed cell constants on Table 1.

IV DETERMINATION OF THE SPECIFIC CONDUCTANCES OF THE SAMPLES

Determine the K_{sp} values of samples A, B and C using the procedure as described in Section III, steps C through F. Record data in Table 2.

V EPA METHODOLOGY

The current EPA Manual[1] specifies using the procedures found in References 2 and 3. These procedures have been adapted for this laboratory session.

ACKNOWLEDGMENT

This outline contains certain portions of previous outlines by Messrs. J. W. Mandia, and J. R. Tilstra.

REFERENCES

1 Methods for Chemical Analysis of Water and Wastes, EPA-AQCL, Cincinnati, OH 45268, 1971.

2 Standard Methods for the Examination of Water and Wastewater, 13th Edition. 1971.

3 Book of ASTM Standards, Part 23, 1970.

This outline was prepared by C. R. Feldmann, Chemist, National Training Center, and revised by Audrey E. Donahue, Chemist, National Training Center, DTTB, MDS, OWP, EPA, Cincinnati, OH 45268.

TABLE 2. SPECIFIC CONDUCTIVITY TESTS

Sample	A			B			C		
Probe	Cell VSO2	Cell VS2	Cell VS2O	Cell VSO2	Cell VS2	Cell VS2O	Cell VSO2	Cell VS2	Cell VS2O
1									
2									
3									
Cell Constant									
Sp. Cond. μmhos/cm									

CHEMICAL OXYGEN DEMAND AND COD/BOD RELATIONSHIPS

I DEFINITION

A The Chemical Oxygen Demand (COD) is an estimate of the proportion of the sample matter susceptible to oxidation by a strong chemical oxidant. The current edition of Standard Methods,[2] specifies organic material which is generally the situation but not necessarily applicable.

B A variety of terms have been and are used for the test described here as COD:

1 Oxygen absorbed (OA) primarily in British practice.

2 Oxygen consumed (OC) preferred by some, but unpopular.

3 Chemical oxygen demand (COD) current preference.

4 Complete oxygen demand (COD) misnomer.

5 Dichromate oxygen demand (DOC) earlier distinction of the current preference for COD by dichromate or a specified analysis such as Standard Methods.

6 Others have been and are being used. Since 1960, terms have been generally agreed upon within most professional groups as indicated in I-A and B-3 and the explanation in B-5.

C The concept of the COD is almost as old as the BOD. Many oxidants and variations in procedure have been proposed, but none have been completely satisfactory.

1 Ceric sulfate has been investigated, but in general it is not a strong oxidant.

2 Potassium permanganate was one of the earliest oxidants proposed and until recently appeared in Standard Methods (9th ed.) as a standard procedure. It is currently used in British practice as a 4-hr. test at room temperature.

a The results obtained with permanganate were dependent upon concentration of reagent, time of oxidation, temperature, etc., so that results were not reproducible.

3 Potassium iodate or iodic acid is an excellent oxidant but methods employing this reaction are time-consuming and require a very close control.

4 A number of investigators have used potassium dichromate under a variety of conditions. The method proposed by Moore at SEC is the basis of the standard procedure.[1, 2] Statistical comparisons with other methods are described.[3]

5 Effective determination of elemental carbon in wastewater was sought by Buswell as a water quality criteria.

a Van Slyke[4] described a carbon determination based on anhydrous samples and mixed oxidizing agents including sulfuric, chromic, iodic and phosphoric acids to obtain a yield comparable to the theoretical on a wide spectrum of components.

b Van Hall, et al.,[5] used a heated combustion tube with infrared detection to determine carbon quickly and effectively by wet sample injection.

6 Current development shows a trend to instrumental methods automating

conventional procedures or to seek elemental or more specific group determination.

II RELATIONSHIP OF THE COD TEST WITH OTHER OXIDATION CRITERIA IS INDICATED IN TABLE 1.

A Table 1

Test	Test Temp. °C	Reaction time	Oxidation system	Variables
BOD	20	days	Biol. prod. Enz. Oxidn.	Compound, environment, biota, time, numbers. Metabolic acceptability, etc.
COD	145	2 hrs.	50% H_2SO_4 $K_2Cr_2O_7$ May be catalyzed	Susceptibility of the test sample to the specified oxidation
IDOD	20	15'	Diss. oxyg.	Includes materials rapidly oxidized by direct action, Fe^{+2}, SH.
Van Slyke Carbon detn.	400+	1 hr.	H_3PO_4 HIO_3 H_2SO_4 $K_2Cr_2O_7$ Anhydrous	Excellent approach to theoretical oxidation for most compounds (N-nil)
Carbon by combustion +IR	950	minutes	Oxygen atm. catalyzed	Comparable to theoretical for carbon only.
Chlorine Demand	20	20 min.	HOCl soln.	Good NH_3 oxidn. Variable for other compounds.

B From Table 1 it is apparent that oxidation is the only common item of this series of separate tests.

1 Any relationships among COD & BOD or any other tests are fortuitous because the conditions of test tend to give results indicating the susceptibility of a given sample to oxidation under specified conditions that are different for each test.

2 If the sample is primarily composed of compounds that are oxidized by both procedures (BOD and COD) a relationship may be established.

a The COD procedure may be substituted (with proper qualifications) for BOD or the COD may be used as an indication of the dilution required for setting up BOD analysis.

b If the sample is characterized by a predominance of material that can be chemically, but not biochemically oxidized, the COD will be greater than the BOD. Textile wastes, paper mill wastes, and other wastes containing high concentrations of cellulose have a high COD, low BOD.

c If the situation in item b is reversed the BOD will be higher than the COD. Distillery wastes or refinery wastes may have a high BOD, low COD, unless catalyzed by silver sulfate.

d Any relationship established as in 2a will change in response to sample history and environment. The BOD tends to decrease more rapidly than the COD. Biological cell mass or detritus produced by biological action has a low BOD but a relatively high COD. The COD/BOD ratio tends to increase with time, treatment, or conditions favoring stabilization.

II ADVANTAGES AND LIMITATIONS OF THE COD TEST[2] AS RELATED TO BOD

A Advantages

1 Time, manipulation, and equipment costs are lower for the COD test.

2 COD oxidation conditions are effective for a wider spectrum of chemical compounds.

3 COD test conditions can be standardized more readily to give more precise results.

4 COD results are available while the waste is in the plant, not several days later, hence, plant control is facilitated.

5 COD results are useful to indicate downstream damage potential in the form of sludge deposition.

6 The COD result plus the oxygen equivalent for ammonia and organic nitrogen is a good estimate of the ultimate BOD for many municipal wastewaters.

B Limitations

1 Results are not applicable for estimating BOD except as a result of experimental evidence by both methods on a given sample type.

2 Certain compounds are not susceptible to oxidation under COD conditions or are too volatile to remain in the oxidation flask long enough to be oxidized.

Ammonia, aromatic hydrocarbons, saturated hydrocarbons, pyridine, and toluene are examples of materials with a low analytical response in the COD test.

3 Dichromate in hot 50% sulfuric acid requires close control to maintain safety during manipulation.

4 Oxidation of chloride to chlorine is not closely related to BOD but may affect COD results.

5 It is not advisable to expect precise COD results on saline water.

IV BACKGROUND OF THE STANDARD METHODS COD PROCEDURE

A The COD procedure[1] considered dichromate oxidation in 33 and 50 percent sulfuric acid. Results indicated preference of the 50 percent acid concentration for oxidation of sample components. This is the basis for the present standard procedure.

B Muers[6] suggested addition of silver sulfate to catalyze oxidation of certain low molecular weight aliphatic acids and alcohols. The catalyst also improves oxidation of most other organic components to some extent but does not make the COD test universally applicable for all chemical pollutants.

C The unmodified COD test result (A) includes oxidation of chloride to chlorine. Each mg of chloride will have a COD equivalent of 0.23 mg. Chlorides must be determined in the sample and the COD result corrected accordingly.

1 For example, if a sample shows 300 mg of COD per liter and 200 mg Cl^- per liter the corrected COD result will be 300 -(200 x 0.23) or 300 - 46 = 254 mg COD/l on a chloride corrected basis.

2 Silver sulfate addition as a catalyst tends to cause partial precipitation of silver chloride even in the hot acid solution. Chloride corrections are questionable unless the chloride is oxidized before addition of silver sulfate, i.e., reflux for 15 minutes for chloride oxidation, add Ag_2SO_4, and continue the reflux or use of $HgSO_4$ (D).

D Dobbs and Williams[7] proposed prior complexation of chlorides with $HgSO_4$ to prevent chloride oxidation during the test. A ratio of about 10 of Hg^{++} to 1 of Cl^- (wt. basis) appears essential. The Cl^- must be complexed in acid solution before addition of dichromate and silver sulfate.

1 For unexplained reasons the $HgSO_4$ complexation does not completely prevent chloride oxidation in the presence of high chloride concentrations.

2 Factors have been developed to provide some estimate of error in the result due to incomplete control of chloride behavior. These tend to vary with the sample and technique employed.

E It is not likely that COD results will be precise for samples containing high chlorides. Sea water contains 18000 to 21000 mgCl^-/l normally. Equivalent chloride correction for COD exceeds 4000 mg/l. The error in chloride determination may give negative COD results upon application of the correction.

Incomplete control of chloride oxidation with $HgSO_4$ may give equally confusing results.

$HgSO_4$ appears to give precise results for COD when chlorides do not exceed about 2000 mg/l. Interference increases with increasing chlorides at higher levels.

F The 12th edition of Standard Methods reduced the amount of sample and reagents to 40% of amounts utilized in previous editions. There has been no change in the relative proportions in the test. This step was taken to reduce the cost of providing expensive mercury and silver sulfates required. Results are comparable as long as the proportions are identical. Smaller aliquots of sample and reagents require more care during manipulation to promote precision.

G The EPA Methods for COD

1 For routine level COD (samples having an organic carbon concentration greater than 15 mg/liter and a chloride concentration less than 2000 mg/liter), the EPA specifies the procedures found in Standard Methods [2] and in ASTM[8].

2 For low level COD (samples with less than 15 mg/liter organic carbon and chloride concentration less than 2000 mg/liter), EPA provides an analytical procedure [9]. The difference from the routine procedure primarily involves a greater sample volume and more dilute solutions of dichromate and ferrous ammonium sulfate.

3 For saline samples (chloride level exceeds 1000 mg/liter and COD is greater than 250 mg/liter), EPA provides an analytical procedure[9] involving preparation of a standard curve of COD versus mg/liter chloride to correct the calculations. Volumes and concentrations for the sample and reagents are adjusted for this type of determination.

V The precision of the unmodified COD result shows a standard deviation of ± 4% of the mean [3] on low chloride samples. Silver sulfate modified COD results are likely to show a standard deviation about twice that without catalysis, due to questionable chloride behavior. The determination of chloride frequently shows a coefficient of variation ($s/\bar{x}$) of 10 to 15%, hence high chloride samples result in COD precision controlled more by chloride behavior than organic oxidation.

VI REMARKS PERTINENT TO EFFECTIVE COD DETERMINATIONS INCLUDE:

A Sample size and COD limits for 0.25 N reagents are approximately as given. For 0.025 N reagents multiply COD by 0.1. Use the weak reagents for COD's in the range of 5-50 mg/l, (low level).

Sample Size	mg COD/l
20 ml	2000
10 ml	4000
5 ml	8000

B Most organic materials oxidize relatively rapidly under COD test conditions. A significant fraction of oxidation occurs during the heating upon addition of acid. The color change of dichromate after acid addition indicates the approximate fraction of dichromate remaining. If the mixed sample color changes from yellow to green after acid addition the sample was too large. Discard without reflux and repeat with a smaller aliquot until the color after mixing does not go beyond a brownish hue. The dichromate color change is less rapid with sample components that are slowly oxidized under COD reaction conditions.

C Chloride concentrations should be known for all test samples and results interpreted accordingly.

D Special precautions advisable for the regular COD procedure and essential when using 0.025 N reagents include:

1 Keep the apparatus assembled when not in use.

2 Plug the condenser breather tube with glass wool to minimize dust entrance.

3 Wipe the upper part of the flask and lower part of the condenser with a wet towel before disassembly to minimize sample contamination.

4 Steam out the condenser after use for high concentration samples and periodically for regular samples. Use the regular blank reagent mix and heat, without use of condenser water, to clean the apparatus of residual oxidizable components.

5 Distilled water and sulfuric acid must be of very high quality to maintain low blanks on the refluxed samples for the 0.025 N oxidant.

ACKNOWLEDGEMENT:

Certain portions of this outline contain training material from prior outlines by R. C. Kroner, R. J. Lishka, and J. W. Mandia.

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See Next Page.

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SOLIDS RELATIONS IN POLLUTED WATER

I MPN, oxygen demand, and solids have been major water pollution control criteria for many years. This discussion is concerned primarily with solids and their interrelations with oxygen demand.

A Engineered treatment or surface water self-purification depends upon:

1 The conversion of soluble or colloidal contaminants into agglomerated masses that may be separated from the water.

2 Oxidation of putrescible components into stable degradation products.

3 Item 1 is the major concern in most treatment systems because item 2 requires a greater investment in time, manpower and capital costs.

B Stress on oxygen demand removal frequently results in an unduely small amount of attention to the contribution of solids in the oxygen demand picture.

1 Oxygen demand formulations generally are specified to be applicable in the absence of significant deposition.

2 Increasing impoundment, tidal estuaries, and incomplete solids removal, generally ensure that solids deposition will be significant.

3 The BOD test stresses the fraction of oxygen demand that is exerted relatively rapidly. It includes only the fraction of unstable material that is exerted under test conditions - usually short term.

4 Contributions of a bed load of solids to oxygen demand frequently are incompletely recognized because they have a more local effect, are difficult to measure, tend to move, and are incompletely understood.

II A given wastewater may have several forms of solids in changeable proportions with time and conditions.

A Solids may be classified among the charted forms according to biological, chemical or physical properties. It is not possible to precisely classify a given material into any one form because they usually are mixtures that may include or be converted into other forms.

B Interrelationships are indicated by diagram in Figure 1. Some changes occur more readily than others.

1 Settleable solids generally consist of a mixture of organic, inorganic, entrained dissolved or colloidal solids with living and dead organisms.

a They may be hydrolyzed into smaller molecules to acquire colloidal or dissolved characteristics.

b They may be converted into a larger fraction of living material or vice versa.

2 Colloidal solids also are likely to be a mixture of organic and inorganic materials, living or dead containing associated dissolved materials.

a They are likely to agglomerate to form settleable masses with time or changing conditions.

b Chemical reactions may solubilize the colloidal masses for recombination into other forms.

3 Dissolved solids are most readily available of all forms for biological, chemical or physical conversion.

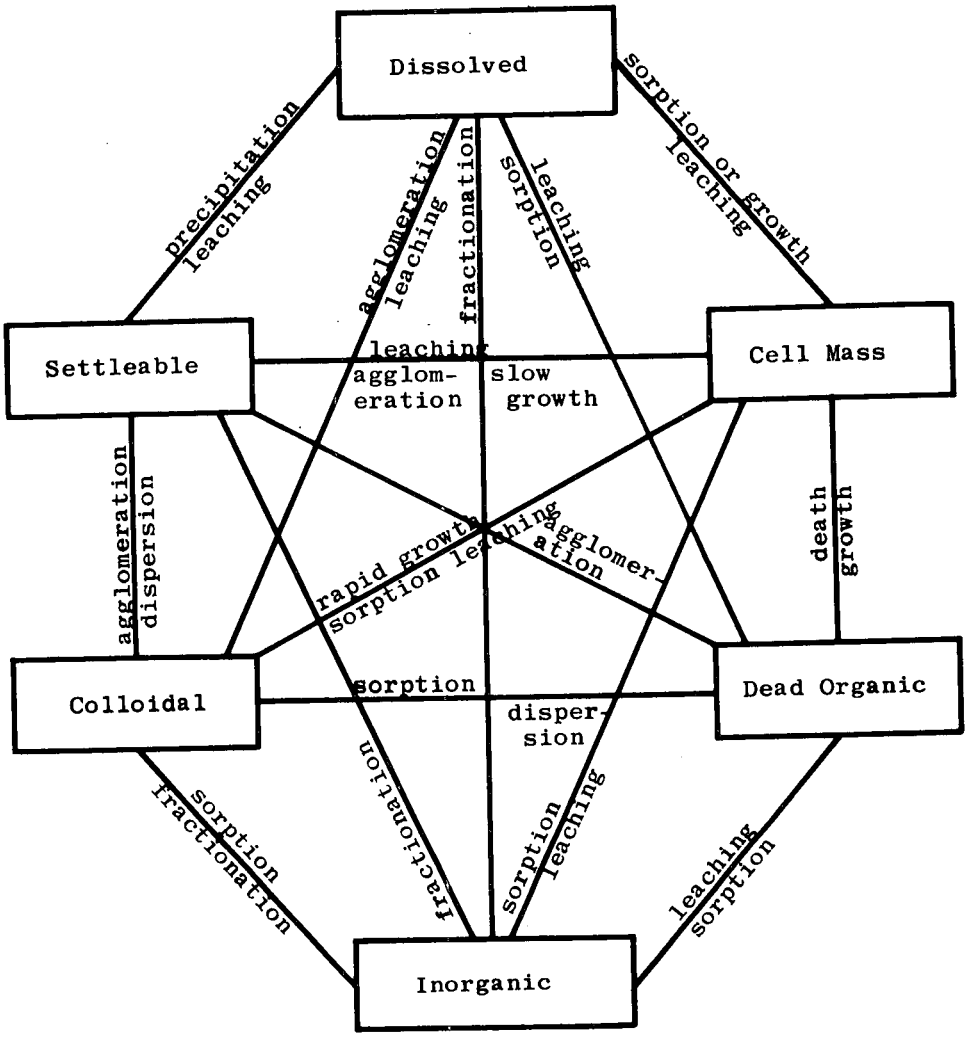

Figure 1. SOLIDS INTERRELATIONSHIPS IN WATER

a They may be assimilated into cell mass to become colloidal during a state of rapid growth or form settleable masses during slow growth. Surface phenomena are likely to encourage inclusion of other forms of solids with cell mass.

C Stabilization occurs with each conversion because energy is expended with each change.

1 Biological changes involve oxidation to obtain enough energy to synthesize cells.

a Products consist of cell mass and degradation products.

b Oxidation tends toward production of CO_2, H_2O, NO_3^-, SO_4^{-2}etc. CO_2 has limited water solubility and partially leaves the aqueous environment. More soluble constituents tend to remain with it for recycle.

c Biological residues tend to recycle. Eventually the mass consists of relatively inert and largely insoluble residues. These make up the

bed load that may decompose at a rate of less than 1% per day, but accumulates in mass until it becomes dominant in water pollution control activities.

III Treatment is an engineered operation designed to utilize events in surface water self-purification in a smaller package in terms of space and time. Effective treatment presupposes oxidation either in the plant or in facilities to minimize feedback of solids components to the aqueous environment.

A Primary treatment consists of a separation of floatable or settleable solids and removal from the used water.

1 Prompt removal is essential to minimize return of solubilized or leached materials from the sludge mass.

2 Sludge and scum are highly putrescible and difficult to drain.

3 Subsequent treatment prior to disposal serves to enhance drainability, reduce solids or volume for burial or burning.

B Secondary treatment generally involves some form of aerobic biological activity to oxidize part of the colloidal and dissolved contaminants and convert most of the remainder into a settleable sludge.

1 Aerobic systems favor assimilation of nutrients into cell mass at the expense of part of the available energy represented by oxidation to products such as CO_2 and water.

2 Cell mass and intermediate degradation products are only partially stabilized and tend to recycle with death and decay.

3 Rapid growth of cells tends to produce sludges that are highly hydrated and thin.

4 A compromise must be reached to produce a favorable balance among separation of solids and feedback of lysed materials.

a Cell growth continues as long as essential nutrients are available.

b Under limiting nutrient conditions the population may show a relatively low rate overall dieoff but variety is changing.

c Species most favored by the new conditions tend to grow while others die, lyse and release part of their stored nutrients for subsequent use.

C Anaerobic digestion of solids separated during treatment is one process used to increase solids stability and drainability while reducing total volume or mass for disposal.

1 Growth of cell mass is relatively slow under anaerobic conditions while hydrolytic cleavage is relatively large in comparison to that during aerobic metabolism.

a Feedback to the aqueous environment represents a significant fraction of the input in the form of ammonia, colloidal solids, low molecular weight acids, and other products.

b Mass of the sludge is reduced by the fraction of methane, carbon dioxide, and other gases produced in process.

c Remaining solids tend to be more concentrated, are lower in putrescibility and give up their water more readily.

2 The liquid fraction of the products remaining after anaerobic digestion contain nutrients, oxygen demand, solids, and malodorous constituents that are objectionable in surface waters if released without further aerobic stabilization.

3 Digester liquids are much more concentrated than raw sewage and nutritionally unfavorable, hence they are difficult to treat and tend to shock aerobic treatment processes.

D Suitable disposal of solids resulting from treatment operations takes various forms of which the most desirable is to oxidize it completely to gaseous products of oxidation or inert ash. The objective is to limit feedback into the aqueous environment and delay the charted interchanges.

1 Deposition of sludge as a cover on crop land is effective providing surface drainage is properly designed to limit washoff.

2 Burial in areas above the flood plain provides a suitable disposal.

3 Incineration under controlled conditions to produce complete burning of organics is preferable.

a Incineration of digested sludge implies substantial feedback in process.

b Incineration of freshly formed sludge is difficult because of drainability and concentration problems. It is preferable from the standpoint of maximum destruction of organic pollutants and minimum feedback in process. Current investigations are directed toward improving feasibility of this means of disposal of solids.

IV ANALYTICAL PROCEDURES

A The Analytical Quality Control Laboratory, Office of Water Programs, Environmental Protection Agency has published a manual titled, Methods for Chemical Analysis of Water and Wastes, 1971.

B In this manual solids are classified into four groups:

1 Total solids
2 Non-filterable (suspended) solids
3 Filterable (dissolved) solids
4 Volatile solids

C The procedure for the determination of 1, 2, and 3 above is given in the Analytical Quality Control Laboratory Manual.

Standard Methods for the Examination of Water and Wastewater, 13th Ed., page 538, Method 224D (1971) is the reference cited by the Analytical Quality Control Laboratory Manual.

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DETERMINATION OF SUSPENDED SOLIDS

I Wastewater stabilization includes the conversion of solid, liquid, or gaseous pollutants to (a) materials at a higher oxidation state or (b) to a more removable form. Both are interrelated, but (b) is favored during conventional treatment.

A Economics of treatment are more favorable when pollutants can be removed and treated in more concentrated form.

B Pollutant characteristics guide selection of operations applicable for contaminant conversion to suspended solids.

C Control of suspended solids removal is a major factor in treatment efficiency. Incomplete removal leads to feedback of nutrients from the unstable solids during later stages of stabilization.

II Characterization of the various forms of solids that may exist or be formed during stabilization of polluting materials necessarily depends upon operational factors. These are usually conditional, but their appreciation is essential.

A Dissolved solids include solid, liquid, or gaseous materials that are dispersed in the aqueous system in molecular or ionic form. The "solution" may be colored but it is likely to be clear unless the concentration of some items in the mixture approaches their solubility limits.

B Colloidal solids include a stage or condition of suspension where the solubility limit has been reached and the ionic or molecular dispersion tends to agglomerate to form "clumps" of insoluble materials or particulates. These particulates are large enough to scatter light and form cloudy or turbid suspensions but are not large enough to subside without further agglomeration.

C Suspended solids include the colloidally dispersed solids and the suspended solids that have agglomerated to form particulates that will subside or settle under quiescent conditions to form a solids concentrate or sludge. Size is a major criterion but density, shape, and interface characteristics among the liquid and solid are important factors.

D Total solids include A, B and C that may be present in the whole sample.

E Solids interrelationships are discussed in a prior outline. Determination of suspended solids is the object of this one.

III Sources of suspended solids include both Natural and man-made operations.

A Rainfall washes particulate material from the air and from the surfaces of forest, farmland, undeveloped land and urban or industrial centers.

B Municipal water supplies are controlled to maintain negligible suspended solids. Some may be formed in distribution systems.

C Groundwaters may contain dissolved solids that form suspended solids upon exposure to air or oxidation.

D Wastewaters are likely to contain varied suspended solids or components that may be converted to suspended solids by biological, chemical or physical transformations. Their nature varies with the origin such as household, commercial, industrial process, mining, washing, or other operations.

E Breaks below the groundwater level in partially filled sewers allow infiltration of suspended materials characteristic of the surrounding soils and water movement in them.

F Combined sewer systems, either intentional or otherwise, permit surface drainage from roofs, streets, parking lots, lawns, etc. to enter sanitary sewers.

IV The determination of suspended solids relate to operational factors determining the particular result obtained.

A A fence of wire or bars of appropriate sized openings may serve as a barrier to passage of horses and cattle but fail to stop cats or dogs.

B Smaller sized particles are commonly separated by filtration, centrifugation, subsidence, or other hydraulic gradation.

1 Roots, branches, rags, etc., usually are separated by bar racks or screens with relatively large openings.

2 Grit, sand and small, but heavy, particles generally are separated hydraulically in chambers allowing 1 to 3 minutes detention time.

3 Filtration is the most commonly applied technique for determination of the relatively low density particulates that tend to remain in aqueous suspension largely as a result of turbulence. Since pore sizes of filters differ, it is essential to specify the media used to interpret results.

V Standard Methods[1] refers to residues from whole sample evaporation as total residue, suspended solids as the non-filterable residue retained on or in the filter and dissolved residue as that appearing in the filtrate.

A Many factors influence the results obtained during suspended solids determinations such as

1 Chemical and physical nature of the solids

2 Sampling techniques

3 Pore size of the filter

A membrane filter of 0.5μ pore size may retain particulates that are not retained on paper.

4 Area, condition, and consistency of filter media.

5 Technique and manipulative care in drying, weighing, storage, transfer, and temperature.

B Standard Methods includes three methods for non-filterable residue or suspended solids.

1 Gooch crucible

2 Membrane filter[2, 3]

3 Buechner funnel-aluminum dish (aerator or sludge suspended solids).

C A spectrophotometric method was described by Krawczyk and Gonglewski[4]. The importance of homogenization to improve sampling uniformity was stressed.

D Chanin, et. al.[5] described the use of glass fiber media for the determination of suspended solids.

VI Precision, sensitivity, and applicability of various methods for determination of suspended solids are indicated in the cited references.

A Table I indicates data from several references on precision of the Gooch crucible, asbestos fiber mat determination.

B Table 2 presents data published on the precision of the Gooch crucible, glass fiber determination.

C Smith and Greenberg[7] compared results of 5 replicates each of eight samples (influents, primary effluents, final effluents and industrial waste samples) by five different methods of determination including:

1 Gooch crucible, asbestos mat

2 Gooch crucible, glass fiber mat

3 Buechner funnel, wire cloth, glass fiber mat

TABLE 1

GOOCH CRUCIBLE
ASBESTOS MAT

Range of Values mg/l	Ref.	Number of Replicates	Mean mg/l	Standard Deviation mg/l + or -	Sample Size Filtered ml
170-308	6	10	224	47	25
218-288	6	10	242	24	25
- -	7	5	360	13	50
- -	7	5	80	25	100
- -	7	5	104	8	100
- -	7	5	152	6	100
- -	7	5	1,023	79	25
- -	7	5	95	7	100
- -	7	5	297	27	50
- -	7	5	96	2	200
14-26	a	10	17	4	100
190-213	(d) 4	10	203	7	100
100-132	(d) 4	10	122	9	100
52-66	(d) 4	10	59	4	100

a Private communication, Lake Huron Program Office Methods Manual

TABLE 2

GOOCH CRUCIBLE
FIBER FILTER

Range of Values mg/l	Ref.	Number of Replicates	Mean mg/l	Standard Deviation mg/l + or -	Sample Size Filtered ml
13-22	a	9	18	3	100
20-24	a	9	22	1	100
60-72	a	10	67	4	100
- -	6	5	1086	14	25
- -	6	5	361	47	50
- -	6	5	306	15	50
- -	6	5	146	3	100
- -	6	5	104	1	100
- -	6	5	100	1	100
- -	6	5	84	3	100
- -	6	5	79	5	100
104-436	5	12	296	119	25
60-196	5	14	111	38	25
8-152	5	11	100	54	25
56-100	5	9	76	17	50

4 Membrane filter 0.4 to 0.5 μ pore size

5 Gooch crucible, glass fiber mat, celite filter aid

a Their conclusions based upon carefully controlled technique indicated that yield and precision were not statistically different among the five tested methods.

b Determining factors other than in (a) included: manipulation time, required skills, speed of filtration, consistence of mat quality, equipment cost and availability.

c Methods 2 and 3 more frequently gave a lower coefficient of variation among those tested and were more favorable with respect to (b).

VII Section VI indicates that good results are possible among any of the tested methods but it was easier to obtain precise results with certain methods. The Gooch Crucible-asbestos mat requires a high degree of skill and manipulative time to provide consistent filtration. The membrane filter tends toward slow filtration, sampling or manipulative difficulties, and is more expensive.

A Certain precautions essential to consistent results with Gooch crucible-asbestos mats include:

1 A thin suspension of asbestos in distilled water is essential. A walnut-sized wad of fiber/1 is desirable.

2 Shake the suspension vigorously; allow it to settle 10-20 seconds. Pour the suspension into another container and discard asbestos slivers.

3 A more uniform suspension of asbestos is achieved after 10-30 seconds treatment in a Waring blendor or equivalent.

4 Allow to stand overnight or for a sufficient time to form an asbestos fiber concentrate on the bottom. Discard any milky fines in suspension and rewash, if necessary until a reasonably clear supernatant is obtained.

5 Insert the clean gooch crucible (30 ml or other selected size and diameter) into a Walters crucible adapter fitted to an 0.5 or 1 1 suction flask.

6 Shake the asbestos suspension vigorously, add the mixed suspension to the crucible until it is 1/2 to 2/3 full.

7 Allow the fiber to "mat" for 1/2 to 2 minutes, then apply vacuum slowly. If a hole forms in the mat the vacuum was applied too soon and too rapidly.

8 Add additional suspension (vacuum off) and apply vacuum to withdraw water and form a mat of 2-3 mm. Waiting period before vacuum application is not essential once a mat has formed. Water penetration rate is an effective means to judge mat quality. Good filtering is obtained if the exit stream from the Walters adapter is continuous but slow enough to be slightly off axis.

9 Wash the mat with successive portions of distilled water (200-250 ml) to clear the mat of fines.

10 Remove the crucible, wipe the outside with clean tissue or cloth and dry and weigh.

B Precautions and aids for glass fiber mat usage:

1 Gooch crucibles employing glass fiber mats of 2.4 cm diameter may encourage slow filtration; different shaped units such as the asphalt filtration crucible are designed to use larger diameter mats which may be desirable for aerator or sludge solids tests.

2 It is advisable to insert glass fiber mats with the smooth side up. A second mat may be required if the prewetting rinse

suggests unusually rapid water passage. Careful placement of the mat is essential.

C Membrane filter precautions include:

1 The filters are fragile and must be carefully handled to prevent damage during use.

2 Prewashing in distilled water for 24 hours helps to remove glycerol or other softening agent that is likely to be eluted by the sample.

3 Filters tend to curl on drying. An individual desiccator is described[3] that helps to control drying at ambient temperature and curling in process.

D Beuchner funnel suspended solids determinations include the (a) aluminum dish-paper, (b) wire cloth-glass fiber and (c) paper filtration. The aluminum dish is designed to support the paper and prevent losses during drying. The wire cloth promotes more rapid filtration and support. When neither supports are used, the paper or glass fiber may be folded once with the solids inside during drying.

1 Buechner funnel filtrations always present the problem of solids adherence to funnel sidewalls instead of the filter media. Solids losses due to incomplete transfer to the filter may be minimized but not eliminated. A square ended spatula aids transfer. It is advisable to adjust sample size to yield > 100 mg of non-filterable residue to reduce percentage error for Buechner funnel tests.

E General precautions applicable for precise results on suspended solids include:

1 Filters or crucibles must be clearly identified, dried, generally at 103° C, and stored in a desiccator until weighed and used.

2 The balance should contain a desiccant to control atmospheric moisture during weighing. This should be changed regularly and the doors opened only as necessary.

3 Filters may be dried in a desiccator (preferably 24 hours).

4 For rapid, control work with Buechner funnel-paper filtering, the papers may be oven dried and equilibrated with room moisture for 10 minutes to reduce changes due to rapid moisture pickup after oven drying.

5 Manufactured filters must be handled carefully with forceps, polished if necessary to prevent puncture or damage to the filter surface.

6 Place the filter media carefully in the crucible covering all openings in the support.

a Special care must be used for membrane filter holders to clamp the filter in place firmly without rupture or displacement.

7 Wet the filter media with distilled water preferably directed at the center of the mat first. Allow the mat to become thoroughly wet before applying vacuum then prewash the filter with about 100 ml of distilled water.

8 With the vacuum on, add the selected aliquot of sample.

a The sample volume should be large enough to minimize percentage errors during weighing. Less precise technique requires more weight difference between the pre and post filtration weights. Three to five mg weight difference is adequate for Gooch crucible technique, > 100 mg required for Buechner funnel tests. Homogenize the sample if sampling uniformity is questionable.

9 Rinse the non-filterable residue with distilled water to wash sidewall solids down onto the filter mat and to minimize occluded solubles in the solids and filter mat.

10 Dry and weigh under the same conditions as used for preweighing.

11 Final weight - Initial weight (mg)

$$\times \frac{1000}{\text{ml sample aliquot}} =$$

suspended solids in mg/l
Results are usually expressed in mg/l (g × 1000).

12 It is not feasible to dry suspended solids to a constant weight because of the interchange of moisture, volatiles or changes due to oxidation in process. Weight must be defined in terms of a routine that minimizes weight change errors.

13 It is not advisable to pre-ignite glass fiber mats for the determination of sample volatile solids as recommended for asbestos fiber mats. Glass fiber generally will soften at about 400° C but is likely to tolerate ignition at 550 to 600° C without fusion. It is advisable to check a given supply of fiber glass circles by igniting 5 or 6 under carefully controlled ignition temperatures and time sequence. If the glass fiber mats are uniform in weight and composition their weight loss on ignition will be comparable. This amount of ignition loss may be subtracted from the ignition loss for samples to obtain a corrected value for sample volatile suspended solids (VSS) if the loss is acceptably consistent.

14 The aluminum dish may be fabricated from an aluminum milk dish (listed in apparatus supply catalogues) by punching or drilling 1/16 inch holes in the bottom comparable to those of the Buechner funnel into which it is inserted. The aluminum dish and filter may be weighed before and after sample filtration and drying. An O ring of silicone M rubber slightly smaller than the dish may be used to provide a vacuum seal with the Buechner funnel. Sample contents must not overfill the dish during manipulation to avoid loss of solids by adherence to the funnel surfaces.

VIII The FWPCA "Methods for Chemical Analysis of Water and Wastes", method for non-filterable solids (Storet number 00530) prescribes filtration through glass fiber media with drying at 105° C. (1969, in press)

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This outline was prepared by D. F. Krawczyk, Acting Chief Consultant, Laboratory Services, Pacific Northwest Water Laboratory, Corvallis, Oregon and F. J. Ludzack, Chemist, National Training Center, Environmental Protection Agency, WPO, Cincinnati, OH 45268

LABORATORY PROCEDURE FOR TOTAL SOLIDS

I INTRODUCTION

A This procedure was excerpted from methods for Chemical Analysis of Water and Wastes, 1971, Environmental Protection Agency, Office of Water Programs, Analytical Quality Control Laboratory.

B The procedure is applicable to surface and saline waters, domestic and industrial wastes.

C The practical range of the determination is 10-30000 mg/l.

D Nonhomogenous materials (large floating particles or submerged agglomerates) should be excluded from the sample. Floating grease and oil should be included in the sample and dispersed in a blender before measuring the aliquot.

E Samples should be analyzed as soon as possible.

II EQUIPMENT

A Porcelain, Vycor, or platinum evaporating dishes, 100 ml capacity; smaller sizes may be used as required.

B Muffle furnace, $550 \pm 50^{\circ}C$

C Drying oven, $103 - 105^{\circ}C$

D Desiccator

E Analytical balance

F Steam bath

III PROCEDURE

A Heat the clean evaporating dish in a muffle furnace at $550 \pm 50^{\circ}C$ for 1 hour.

B Cool the dish in a desiccator.

C Weigh the dish on an analytical balance.

D Store the dish in the desiccator and weigh just before use.

E Shake the sample container vigorously.

F Measure 100 ml of the well mixed sample in a graduated cylinder. (At least 25 mg of residue should be obtained; less volume of sample may be used if the sample appears to be high in solids content. If it is low in solids content, more sample may be added to the dish after drying).

G Rapidly, but without spilling, pour the sample into the evaporating dish.

H Dry the sample on a steam bath, or at $98^{\circ}C$ (to prevent boiling and splattering) in the oven.

I Dry the evaporated sample in the oven at $103 - 105^{\circ}C$ for at least one hour.

J Cool the dish in the desiccator and then weigh it.

K Repeat the heating at $103 - 105^{\circ}C$, cooling and weighing until the weight loss is less than 4% of the previous weight, or 0.5 mg, whichever is less.

IV CALCULATIONS

$$\text{mg total solids/l} = \frac{(\text{wt dish + residue})^* - (\text{wt dish})^* \times 1000 \times 1000}{\text{ml of sample}}$$

* in grams

This outline was prepared by C. R. Feldmann, Chemist, National Training Center, WPO, EPA, Cincinnati, OH 45268.

LABORATORY PROCEDURE FOR NONFILTERABLE (SUSPENDED) SOLIDS

I INTRODUCTION

A This procedure was excerpted from Methods for Chemical Analysis of Water and Wastes, 1971, Environmental Protection Agency, Office of Water Programs, Analytical Quality Control Laboratory.

B The procedure is applicable to surface and saline waters, domestic and industrial wastes.

C The practical range of the determination is 20 - 20000 mg/l.

D All nonhomogeneous particulates (such as leaves, sticks, fish and lumps of fecal matter) should be excluded from the sample.

E Sample preservation is not practical; the analysis should be done as soon as possible.

II EQUIPMENT

A Glass fiber filter discs, 4.7 cm or 2.2cm, without organic binder. Reeve Angel type 984H, 934H, Gelman type A, or equivalent.

B Membrane filter funnel (for use with the 4.7 cm disc), or

C 25 ml Gooch crucible (for use with the 2.2 cm disc).

D Gooch crucible adapter.

E 500 ml suction flask

F Drying oven, 103 - 105°C

G Desiccator

H Analytical balance, 200 g capacity, capability of weighing to 0.1 mg.

III PROCEDURE

A Assemble the filtering apparatus and suction flask (either the 2.2 cm disc, Gooch crucible and adapter, or the 4.7 cm disc and membrane filter funnel).

B Apply suction to the flask and wash the disc with three successive 20 ml portions of distilled water.

C Continue the suction until all water has passed through the disc.

D Remove the Gooch crucible plus 2.2 cm disc and dry in the oven at 103 - 105°C for one hour, or,

E Remove the 4.7 cm disc from the membrane filter funnel and dry in the oven at 103 - 105°C for one hour. In D or E, if the disc is not to be used immediately, store it in the desiccator.

F Weigh the 4.7 cm disc or 2.2 cm disc plus Gooch crucible just before use.

G Assemble the filtering apparatus.

H Apply suction to the flask.

I Shake the sample container vigorously.

J Measure 100 ml of the well mixed sample in a 100 ml graduated cylinder. (If the sample appears to be low in solids, a larger volume may be used).

K Rapidly, but without spilling, pour the sample into the funnel or crucible.

L Continue the suction until all of the water has passed through the disc.

M Remove the 4.7 cm disc from the funnel and dry in the oven at 103 - 105°C to constant weight, or

N Remove the Gooch crucible plus 2.2 cm disc and dry in the oven at 103 - 105°C to constant weight.

Note: Drying to constant weight refers to the process of:

1) drying the disc (or disc plus crucible) at 103 - 105°C, 2) cooling in the desiccator, 3) weighing, 4) repeating steps 1), 2), and 3). If there is no difference in the two

final weights, the disc (or disc plus crucible) has been dried to constant weight. In practice, the initial drying period is sometimes extended to several hours. A second heating step is then generally not carried out.

IV CALCULATIONS

mg nonfilterable (suspended) solids/1 =

$$\frac{(\text{wt of 4.7 cm disc + residue})^* - (\text{wt of 4.7 cm disc})^* \times 1000 \times 1000}{\text{ml of sample filtered}}$$

or

$$\frac{(\text{wt of 2.2 cm disc + Gooch crucible + residue})^* - (\text{wt of 2.2 cm disc + Gooch crucible})^* \times 1000 \times 1000}{\text{ml of sample filtered}}$$

*in grams

This outline was prepared by C. R. Feldmann, Chemist, National Training Center, WPO, EPA, Cincinnati, OH 45268.

LABORATORY PROCEDURE FOR FILTERABLE (DISSOLVED) SOLIDS

I INTRODUCTION

A This procedure was excerpted from Methods for Chemical Analysis of Water and Wastes, 1971, Environmental Protection Agency, Office of Water Programs, Analytical Quality Control Laboratory.

B The procedure is applicable to surface and saline waters domestic and industrial wastes.

C The practical range of the determination is 10-20000 mg/l.

D Samples high in calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying and desiccation, and quick weighing.

E To insure complete conversion of bicarbonate to carbonate, samples high in bicarbonate content will require careful and possibly prolonged drying at 180°C.

F Excessive residue in the evaporating dish will crust over and entrap water that will not be driven off during drying.

G Samples should be analyzed as soon as possible.

II EQUIPMENT

A Glass fiber filter discs, 4.7 cm or 2.2 cm, without organic binder. Reeve Angel type 984H, Gelman type A, or equivalent.

B Membrane filter funnel (for use with the 4.7 cm disc), or

C 25 ml Gooch crucible (for use with the 2.2 cm disc).

D Gooch crucible adapter

E 500 ml suction flask

F Drying oven, 180 ± 2°C

G Muffle furnace, 550°C

H Drying oven, 180 ± 2°C

I Desiccator

J Porcelain, Vycor, or platinum evaporating dish, 100 ml capacity.

K Steam bath

L Analytical balance, 200 g capacity, capability of weighing to 0.1 mg.

III PROCEDURE

A Assemble the filtering apparatus and suction flask (either the 2.2 cm disc, Gooch crucible and adapter, or the 4.7 cm disc and membrane filter funnel).

B Apply suction to the flask and wash the disc with three successive 20 ml portions of distilled water.

C Continue the suction until all water has passed through the disc.

D Remove the Gooch crucible plus 2.2 cm disc and dry in the oven at 103 - 105°C for 1 hour, or,

E Remove the 4.7 cm disc from the membrane filter funnel and dry in the oven at 103 - 105°C for 1 hour. In D or E, if the disc is not to be used immediately, store it in the desiccator

F Weigh the 4.7 cm disc or 2.2 cm disc plus Gooch crucible just before use.

G Heat the clean evaporating dish in the muffle furnace at 500°C for 1 hour.

H Store the dish in the desiccator and weigh just before use.

I Assemble the filtering apparatus.

J Apply suction to the flask.

K Shake the sample container vigorously.

L Measure 100 ml of the well mixed sample in a 100 ml graduated cylinder. (A larger or smaller volume may be used if the dissolved solids content is thought to be low or high).

M Rapidly, but without spilling, pour the sample into the funnel or crucible.

N Continue the suction for at least three minutes to assure water removal from the disc.

O Using a 100 ml graduated cylinder, transfer 100 ml fo the filtrate to the evaporating dish.

P Evaporate the filtrate to dryness on the steam bath.

Q Dry the evaporated sample for at least 1 hour at 180 $\pm$ 2 ^{o}C.

R Cool the dish in the desiccator.

S Weigh the dish.

T Repeat the drying, cooling, and weighing steps until two successive weighings are the same, or the weight loss is less than 0.5 mg.

Note: The filtrate from the Non-Filterable (Suspended) Solids determination may be used in this procedure.

IV CALCULATIONS

mg filterable (dissolved) solids/l =

$$\frac{(\text{wt dish + residue})^* - (\text{wt dish})^* \times 1000 \times 1000}{\text{ml of sample}}$$

*in grams

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LABORATORY PROCEDURE FOR VOLATILE SOLIDS

I INTRODUCTION

A In the manual, Methods for Chemical Analysis of Water and Wastes, 1971, Environmental Protection Agency, Office of Water Programs, Analytical Quality Control Laboratory, the reference given for the determination of volatile solids is Standard Methods for the Examination of Water and Wastewater, 13th ed., p 538, Method 224D, 1971.

B The Analytical Quality Control Laboratory manual states that the test is subject to many errors due to:

1 Loss of water of crystallization.

2 Loss of volatile organic material prior to combustion.

3 Incomplete oxidation of certain complex organics.

4 Decomposition of mineral salts during combustion.

The principal source of error is said to be failure to obtain a representative sample.

C The procedure in the 13th ed of Standard Methods involves ignition of the filter disc from the determination of non-filterable (suspended) solids at 550°C for 15 minutes, cooling the disc in a desiccator and weighing.

D The equipment and procedure paragraphs below are therefore those from the Analytical Quality Control Laboratory manual.

II EQUIPMENT

A Glass fiber filter discs, 4.7 cm or 2.2 cm, without organic binder Reeve Angel type 984H, Gelman type A, or equivalent.

B Membrane filter funnel (for use with the 4.7 cm disc), or

C 25 ml Gooch crucible (for use with the 2.2 cm disc).

D Gooch crucible adapter.

E 500 ml suction flask.

F Desiccator.

G Analytical balance, 200 g capacity, capability of weighing to 0.1 mg.

H Muffle furnace, 550°C.

III PROCEDURE

A Assemble the filtering apparatus and suction flask (either the 2.2 cm disc, Gooch crucible and adapter, or the 4.7 cm disc and membrane filter funnel).

B Apply suction to the flask and wash the disc with three successive 20 ml portions of distilled water.

C Continue the suction until all water has passed through the disc.

D Remove the Gooch crucible plus 2.2 cm disc and dry in the oven at 103 - 105°C for 1 hour, or,

E Remove the 4.7 cm disc from the membrane filter funnel and dry in the oven at 103 - 105°C for 1 hour. In D or E, if the disc is not to be used immediately, store it in the desiccator.

F Weigh the 4.7 cm disc or 2.2 cm disc plus Gooch crucible just before use.

G Assemble the filtering apparatus.

H Apply suction to the flask.

I Shake the sample container vigorously.

J Measure 100 ml of the well mixed sample in a 100 ml graduated cylinder. (If the sample appears to be low in solids, a larger volume may be used).

K Rapidly, but without spilling, pour the sample into the funnel or crucible.

L Continue the suction until all of the water has passed through the disc.

M Remove the 4.7 cm disc from the funnel and ignite in the muffle furnace at 550°C for 1 hour, or,

N Remove the Gooch crucible and 2.2 cm disc and ignite in the muffle furnace at 550°C for 1 hour.

O Cool the 4.7 cm disc or 2.2 cm disc plus Gooch crucible in the desiccator.

P Weigh the 4.7 cm disc or 2.2 cm disc plus Gooch crucible.

IV CALCULATIONS

mg volatile solids/l =

$$\frac{(\text{wt of 4.7 cm disc + residue})^* - (\text{wt of 4.7 cm disc})^* \times 1000 \times 1000}{\text{ml of sample filtered}}$$

or

$$\frac{(\text{wt of 2.2 cm disc + Gooch crucible + residue})^* - (\text{wt of 2.2 cm disc + Gooch crucible})^* \times 1000 \times 1000}{\text{ml of sample filtered}}$$

*in grams

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BIOASSAY AND BIOMONITORING

I INTRODUCTION

A An assay is an evaluation.

B A bioassay is an evaluation in which living organisms provide the scale.

1 The scale or degree of response may be the rate of growth or decrease of a population, colony, or individual; a behaviorial, physiological, or reproductive response, or simply a live or no-live response.

2 All types of bioassays may have a role to play in water quality evaluation at one time or another.

3 The particular group of bioassays discussed below are those which contribute to the evaluation of the effects of liquid wastes on aquatic environments in which experimental organisms such as fish are subjected to a series of concentrations of a known or suspected toxicant under adequately controlled conditions for a stipulated period of time.

C Historical Highlights

1 Prior to 1940, there was little or no uniformity in performing or reporting bioassays of water pollutants.

2 By mid-forties, the need for a standardized technique was becoming painfully obvious.

a The Atlantic Refining Company privately published the first statement of what is today, basically, our standard method (Hart, Doudoroff, and Greenbank, 1945).

b This was refined and accorded wide (but not universal) industrial, academic, and governmental acceptance in 1951 (Doudoroff, et al, 1951).

3 This method was first developed for the use of fishes, but has been found adaptable to a wide variety of organisms.

D Other Types or Plans of Bioassay

1 Many other designs for the expression of toxicity have been devised such as those based on time-concentration curves. Each has its advantages and proponents, but the basic Standard Method design remains the most widely used.

a In situ exposure of experimental organisms in cages or live cars, at selected sites above and below a suspected point or pollution is an obvious and time tested procedure, but lacks the precision of laboratory tests. It has the advantages of popular appeal, and of expressing actual environmental conditions.

b The familiar BOD test is a bioassay of the organic content of water subject to biodegradation.

E Biomonitoring

Water quality surveillance or monitoring by means of observing biota can be considered from two aspects: field and laboratory. It differs from bioassay primarily in the objective: a bioassay is an attempt to determine a specific defined value or threshold, whereas a biomonitoring operation is an attempt to use living organisms to ascertain whether or not aquatic life is endangered.

1 Periodic biological field surveys, samples, or other observation may demonstrate recent excessive pollution for example.

2 Organisms in a series of flow-through tanks in a laboratory may demonstrate the occurrence of an unacceptable

increase in the toxicity of an effluent, without measuring "how much" or "what."

II THE STANDARD METHOD BIOASSAY

A Introduction

1 This procedure is intended for use by industrial and other laboratories.

2 Its objective is to evaluate the toxicity of wastes and other water pollutants to fish or other aquatic organisms.

3 Potential applications are numerous.

a Dilution and/or treatment necessary to avoid acute toxic effects can be estimated.

b The efficacy of an existing treatment can be tested.

c The potential usefulness of a proposed treatment can be estimated.

4 The design of the test need not involve a chemical knowledge of the toxicant.

a Synergism, antagonism, and other interactions of chemical components cannot always be anticipated, but are automatically included in the result.

b All chemical and physical information available is, however, essential to the adequate interpretation and application of test results.

5 The test is best used for local application. Generalizations should be made with great caution.

6 Field observations should be made of results of application over a significant period of time.

7 Careful distinction should be made between fish mortality due to a physiological toxicant, and that due to lack of DO.

8 A uniform testing procedure is essential to effective action in water pollution control.

B Routine Procedure for Static Tests

1 Test organisms should be fish or other organisms of local significance.

a The most sensitive species available should be selected, but:

b They should be species which are amenable to captivity.

c They should be accurately identified.

d They should be relatively uniform in size. Individuals less than 3 inches in length are usually most convenient.

e They should be healthy and thoroughly acclimated to the laboratory.

f A careful record should be kept of their origin, handling, and condition.

2 Test water should preferably be taken from the receiving stream just above the discharge being evaluated or in a lake or estuary, beyond the influence of the discharge.

a If this is unsuitable, cleaner but similar waters from a more remote station may be substituted.

b Artificial "standard" waters are not recommended for general use, although many formulae have been proposed.

c In estuarine situations, a series of tests (marine grid) should be run, using waters of high and low salinities as characteristic of the region.

3 Other experimental conditions

a Temperature. The tests should be performed at a uniform temperature in the upper part of the expected summer range, e.g., 25 ± 2°C for warm water fish, and 15 ± 2°C for cold water species.

b Test containers should be of glass, widemouthed "pickle jugs" or battery jars are satisfactory. Five and one gallon sizes are both useful, but the larger size is required for conclusive results.

c Artificial aeration should not be used to maintain the dissolved oxygen concentration. If this falls below approximately 4 or 5 ppm at any time during the test, fewer fish should be used per container or an auxiliary oxygenation procedure invoked that is designed to avoid undue loss of volatile toxicants.

d The number of test animals should not be less than 10 per concentration for reliable conclusions; these may be distributed between two or more containers.

e Ratio of fish to solution. There should be not more than one gram of fish per liter of test solution.

4 Experimental procedure

a All dilutions for a given run should be prepared from the same sample.

b Duration. Tests should be run for at least 48 hours, preferable 96.

c Dead fish should be removed as soon as observed. Survivors should be counted and recorded each 24 hours.

d Feeding during the test should be avoided.

e Experimental concentrations. Any appropriate series of concentrations may be used. A logarithmic series such as is suggested in Table I is very convenient.

TABLE I

A Guide to the Selection of Experimental Concentrations, Based on Progressive Bisection of Intervals on a Logarithmic Scale.

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
10.0	----	----	----	----
----	----	----	----	8.7
----	----	----	7.5	----
----	----	----	----	6.5
----	----	5.6	----	----
----	----	----	----	4.9
----	----	----	4.2	----
----	----	----	----	3.7
----	3.2	----	----	----
----	----	----	----	2.8
----	----	----	2.4	----
----	----	----	----	2.1
----	----	1.8	----	----
----	----	----	----	1.55
----	----	----	1.35	----
----	----	----	----	1.15
1.0	----	----	----	----

Effluents of unknown, mixed, or variable composition are usually best expressed as percent by volume; while pure substances, or specific analyzable components are usually expressed as milligrams per liter (ppm). A control or reference tank containing dilution water only (with no toxicant) is essential, to demonstrate that all experimental organisms would have survived had it not been for the toxicant being tested.

f Expression of results. The measure of relative toxicity is the tolerance limit (symbol: TL). The time of exposure "t" must be shown along with the percentage of fish surviving (written as a postscript). For example, a 96 hour TL50 (optional: $TL50^{96\,hr}$) of a toxic substance is that concentration in which 50% of the experimental organisms survive for 96 hours. (Figure 1)

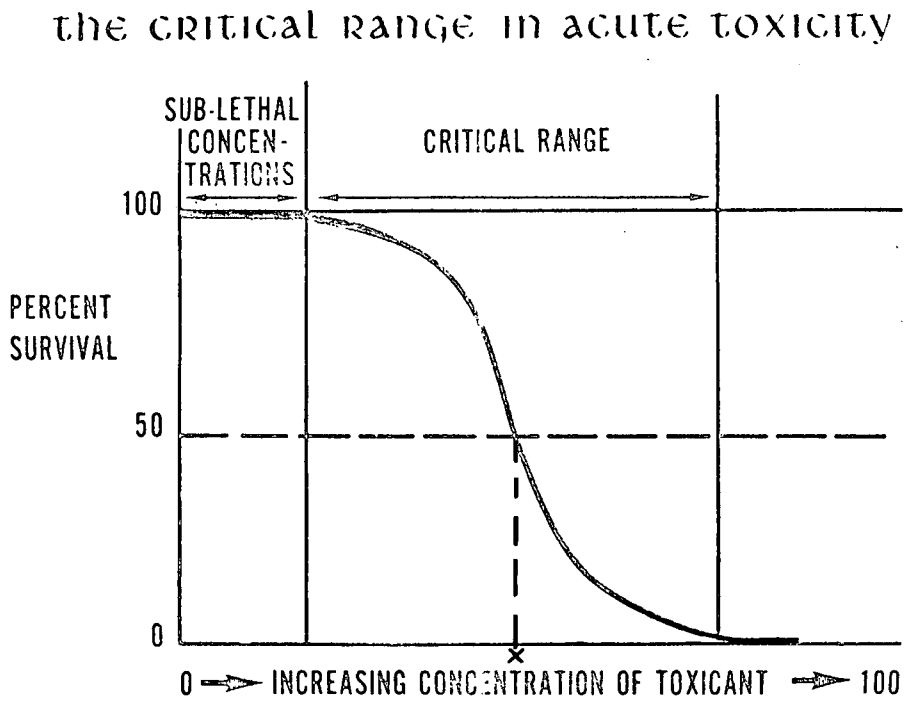

Figure 1
THE CRITICAL RANGE
X = $TL50^t$ Concentration

1) A $TL50^t$ is the equivalent of a median tolerance limit (TL_m^t).

2) This is analogous to the LC_{50} (concentration survived by 50% of the population) of the toxicologist, but is more universally usable with the parameters encountered in the water environment, some of which (such as temperature) cannot be expressed as "concentrations."

3) TL50's for 96 hours or less are arbitrarily referred to as measures of "acute" toxicity, while TL50's for longer periods of time are variously referred to as sub-acute, chronic, etc.

C Special Problems of Static Tests

1 Unaerated aquaria with finite quantities of toxicant are not always satisfactory (static tests).

a The toxicant may be volatile.

b Toxic materials may be masked by a high BOD.

c The toxicant may be progressively adsorbed on container walk, fish slime, metabolized or otherwise changed so that actual concentrations in tanks change with time.

2 Standards or requirements other than those involving toxicity per se may be involved.

3 Preliminary and concurrent investigations

a Obtain all available information about unknown to be tested.

b Does the material lend itself to this type of test?

c Run feasible on the spot analyses including DO.

d Significant quantities of solutions removed from test containers for analysis should be replaced with similar volume of same dilution.

4 Wastes with a high BOD or COD

a Suggested preliminary tests:

1) Set up two identical exploratory tests.

2) Aerate one but not the other.

3) If great difference develops between them, special procedures are indicated.

b Oxygenation or aeration of dilution water before making dilutions may help.

c Renewal of solutions at stated intervals (12, 24, or 48 hours) is approved. Fish are not harmed by being carefully transferred from one container to another. It is useful where:

1) Initial DO is adequate but slowly exhausted.

2) Toxicant is volatile, progressively adsorbed, precipitated, or otherwise changed.

D Continuous Flow Procedures

1 Continuous flow procedures imply the continuous or periodic renewal of the solutions in the experimental containers, at the same time maintaining the stated concentrations (including control). The variety of devices and flow plans to accomplish this are almost infinite, two general principals will be outlined below: assaying and monitoring.

2 Continuous flow bioassay, general advantages (Figure 2)

a Materials with moderate oxygen demands may be tested.

b Materials which degrade or are volatile may be tested.

c Due to the constant removal of metabolic and other wastes, and the constant supply of fresh oxygenated water, fish may be fed and so maintained over a longer period of time. Containers must of course be maintained in reasonably clean condition.

E Test Concentrations and End Points for Continuous Flow Assays

1 Test concentrations are in general less restricted than for static tests. They need not be so high as to insure achieving the desired end point in 48 or 96 hours, although they may be so set if desired.

2 Geometric type series of concentrations are still desirable (See Table 1).

3 Sub-lethal levels may be tested over entire life histories of organisms to determine long range effects.

4 In general, the setup should be prepared, calibrated and operated for several days, or until the concentrations have become chemically and physically stabilized before introducing the fish or other experimental organisms.

F Total Fish Weight and Liquid Volume in Continuous Flow Assays

In general, the constant renewal of test solution might appear to make possible testing more or larger fish in less water. Actually, flow-through volume and total weight of fish must be so related that adequate oxygen is maintained. Furthermore, over the longer periods of time involved, "lebensraum" (or territory) must be taken into account. Organisms must not be crowded to the extent that aggressive behavior and other ecological competitive factors are introduced.

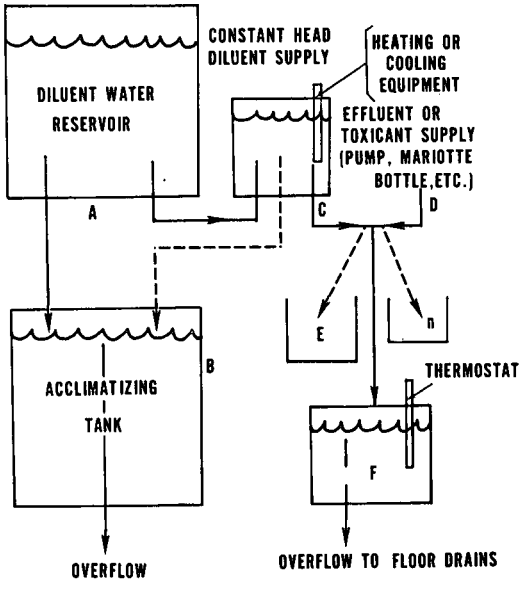

Figure 2

BASIC SETUP FOR CONTINUOUS FLOW BIOASSAY

E to n represents one of several exposure tanks containing a graded series of dilutions of the toxicant, including one control with none.

G End Points or Reactions to be Evaluated by Continuous Flow Assays

1 The original and traditional end point of biological evaluations such as those discussed here was the death of the organism. This was simple, direct, and unequivocal. Current practice, however, often involves much more sophisticated reactions such as reduction in the reproductive capacity, or a change in the breathing rate (movement of gills).

H Special Problems of Flow Through Bioassays

1 Due to the physical requirements of maintaining stated concentrations of chemicals over long periods of time, laboratory setups are usually complicated and always require attention and maintenance.

2 The problem of disease control frequently develops in populations held over a long period of time.

3 Water and/or power failure may jeopardize an assay experiment after months of time have been expended.

4 The expense of a long continued test may not be justified by the result.

5 The above points demonstrate that in general, flow through bioassays are not adapted to day-to-day routine toxicity determinations.

III REPORTING INTERPRETATION AND APPLICATION OF BIOASSAY RESULTS

A Reporting

1 Reports should include an orderly tabulation of all pertinent data such as:

a The type of setup used and duration of test

b Identity of experimental animals

c Their source, history, average size and condition, and number used per concentration

d Source of, and chemical and physical analysis of experimental dilution water

e Experimental temperature

f Volumes of experimental liquid in each container

g Records of routine analyses such as DO and pH

h Records of chemical analyses of toxicants in experimental tanks

i $TL50^t$ or other end point, and data from which it was determined.

B Interpretation and Application

1 The $TL50^t$ is an estimate of the mid-point of the critical concentration range the interval between the highest concentration at which all test animals survive, and the lowest at which they all die (Figure 1).

2 The final step is to extrapolate from this well established mid concentration to a safe concentration well below the "critical concentration range." Extrapolating or rather: "application factors" to accomplish this are still under development and will probably not be fully developed for many years. Available data indicate that these factors must be variable according to the toxicant in question acting in combination with the receiving water in question, and considering the entire aquatic community.

3 For a more complete discussion, see FWPCA Water Quality Criteria (Reference No. 9) pp. 55-72.

4 Other considerations

a Radioactive wastes must be evaluated with regard to their chemical toxicity as well as their radioactivity.

b Sub-acute levels of many toxicants such as lead, arsenic, cadmium, etc. may exert a low level chronic toxicity over a long period of time.

c "Safe levels" of a waste in regard to toxicity to aquatic life may still exceed standards of other types such as color, organic content, suspended solids, etc.

IV BIOMONITORING AS COMPARED TO BIOASSAY (Figure 3)

A Bioassay is (as stated above) the evaluation of the effects of stated concentrations of the test material for given periods of time.

B Biomonitoring is the use of organisms to detect change in an effluent (surveillance). It operates continuously and indefinitely.

C Bioassays typically involve relatively small flows and employ often especially prepared (perhaps repeatedly prepared) batches of experimental material, while biomonitoring typically involves larger flows, from operating industries or other installations.

D Bioassays basically determine:

1 Is the substance deleterious, and if so:

2 How deleterious is it?

E Biomonitoring is useful to

1 Demonstrate the continuous suitability of an effluent (or a predetermined dilution thereof) for the survival of the test organism.

2 Detect a change (usually deleterious) in the biological acceptability of the effluent.

3 To detect a change in the effect of a mixture of the effluent and the receiving water on the test organism (i.e. to detect a change in the receiving water).

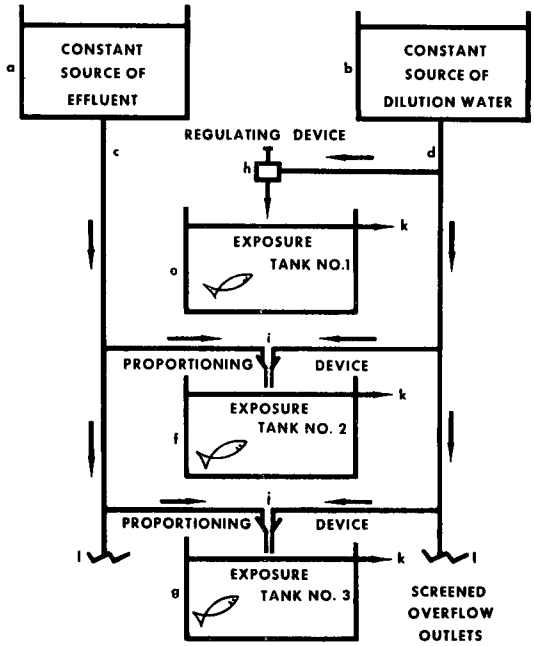

Figure 3
BASIC SETUP FOR BIOMONITORING

F Biomonitoring was originally effective only with relatively fast acting materials, or in situations where large changes might occur rather quickly (as for example, the accidental (?) dumping of a vat of waste pickle liquor). Recent developments in the field of biotelemetry now make it feasible to "wire" a fish with electrodes (like the astronauts) and so to immediately record electronically any sudden or subtle change in the effluent which affects the physiological parameters being monitored on the live fish.

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This outline was prepared by H.W. Jackson, Chief Biologist, National Training Center, Water Programs Operations, EPA, Cincinnati, OH 45268.

SPECIAL APPLICATIONS AND PROCEDURES FOR BIOASSAY

I INTRODUCTION

A The report of the Council on Environmental Quality (1970) repeatedly stresses the need for the development of predictive, simulative, and managerial capabilities to combat air and water pollution. The last capability depends on the first two.

B The standard static jar fish bioassay, which uses death as a response, enables one to predict the toxicity of a particular waste to fish. One limitation of this procedure is that it uses a grab sample which represents the quality of the waste at only one point in time. The water used to make the dilutions is also taken at one point in time. At the actual industrial site, the quality of the waste and the river water vary through time. A composite waste sample partially overcomes this limitation, but may mask variations that are biologically important.

C One could put fish in a continuous flow of waste diluted with river water, but then there is one further limitation of the standard bioassay: death is used as the response. In order to prevent damage to organisms, it is necessary to have an early warning of dangerous conditions, so that corrective action can be taken. In other words, symptoms of ill health, which occur before death, must be detected if there is to be time for diagnosis treatment.

II METHODS AND MATERIALS

A Fish Movement Patterns

1 Fish movement patterns can be monitored using the technique of light beam interruption described in detail by Cairns, et al. (1970). Dawn and dusk are simulated by a motor-driven dimming unit which gradually increases the intensity of the room lights over a half-hour period starting at 6:30 a.m. and gradually decreases the intensity to 0 over a half-hour period starting at 6:30 p.m. The cumulative movement of each of six bluegill sunfish, a single fish per tank, is recorded every hour throughout a test except during the simulated sunrise and sunset when an additional record is made on the half hour. Each day is divided into four intervals; first half day, second half day, first half night and second half night (Table I). Before any statistical analysis can be performed, recordings for day 1 must be completed. After the cumulative movement for day 1 is recorded, statistical analyses are performed after the completion of each disignated time interval. For example, the cumulative movement recorded hourly for each fish during day 1, first half day values are compared to the cumulative movement recorded hourly for each fish during day 2, first half day values.

2 Based on the results of 20 laboratory experiments "stress detection" is defined as the presence of two or more abnormal movement patterns recorded during the same time interval.

B Fish Breathing

1 Breathing rates may be determined from polygraph recordings of breathing signals. The fish are tested in plexiglas tubes through which dechlorinated tap water or some toxic solution is metered at a flow rate of approximately 100 ml/min. Breathing signals are detected by three platinum wire electrodes placed in the water; an active electrode, an indifferent electrode, and a ground. The test chambers and methods of acclimating the fish are described in more detail by Cairns, et al. (1970) The photoperiod is the same as that for the fish movement study.

2 The fish are placed in test chambers by 6:00 p.m. and the recordings began at 6:00 a.m. the next day to allow the fish to recover overnight from handling. Toxic solutions are introduced at 10:00 a.m. after the experimental fish have been exposed to water containing no added

toxicant for periods of one to six days. Each experimental fish thus serves as its own control. In addition, one or two fish are never exposed to the toxicant and serve as controls throughout each experiment. In one experiment, using zinc as the toxicant, reported in Table VI, six control fish were exposed to water containing no added zinc for four days.

a Preliminary evidence suggested that the data could be analyzed by separating the experimental day into four periods; a period from 6:00 to 8:00 a.m. when the breathing rates changed markedly, a period from 9:00 a.m. to 5:00 p.m. when the rates were comparatively high, another period of rapid change from 6:00 to 8:00 p.m., and a night period from 9:00 p.m. to 5:00 a.m. when the rates were comparatively low (Sparks, et al., 1970).

b Bluegills increase their breathing rates when exposed to zinc (Cairns, et al., 1970). An individual fish was thus considered to have shown a response each time its breathing rate during a time period exceeded the maximum breathing rate observed during the corresponding period of the first day, before any zinc was added. A response was scored for each value on the second day that was higher than the first day maximum for the comparable period. The control periods (before any zinc was added) and the experiment where no zinc was added at all were used to determine how many false detections this method of analysis would produce. The experimental periods (after zinc was added) determined how quickly the method of analysis could detect zinc concentrations in water.

c Zinc concentrations were determined daily by atomic absorption spectrophotometry.

III RESULTS

A Fish Movement Patterns

1 Table 1 shows the results of one continuous flow experiment carried out for 20 days. During this experiment fish were exposed to zinc on day 7 from 1:00 p.m. until 7:00 p.m. at which time the flow was returned to normal dilution water. The zinc concentrations reached their maximum at 7:00 p.m. and atomic absorption analyses on effluent samples collected at this time showed the following concentrations: tank one, 13.32; tank two, less than 0.08; tank three, 11.39; tank four, 12.72; tank five, 13.32; and tank six, 12.59 mg/l Zn^{++}. The results show that these concentrations of zinc developing over the six hour interval of exposure were insufficient to cause a detectable change in the movement patterns of the fish. By 8:30 a.m. of day 8 the effluent zinc concentrations were less than 0.30 in all cases.

2 To determine the percent survival and recovery patterns of the fish once stress detection occurred, zinc flow was reinitiated at 1:00 p.m. on day 13 of this experiment. Between 8:00 and 9:00 p.m. on day 13 the zinc concentration in the effluent reached a maximum of: 7.51 for tank one; less than 0.05 for tank two; 7.49 for tank three; 7.52 for tank four; 7.49 for tank five; and 7.54 mg/l for tank six. The concentrations remained near the above values until the statistical analyses showed "stress detection" during the first half night values on day 14 (Table 1). As soon as stress detection occurred the flow was returned to normal dilution water. At 10:00 a.m. on day 15 zinc analyses showed all effluent concentrations to be less than 0.70 mg/l Zn^{++}. Stress detection continued to be registered for two consecutive time intervals following the initial detection, but after that no stress detection was registered and the frequency of abnormal patterns returned to prestress levels within 48 hours. In this experiment

as with all others in which dilution water containing zinc was replaced with dilution water minus zinc at that time of stress detection all fish survived!

3 The results from the series of experiments at progressively lower zinc concentrations indicate that the lowest detectable concentration is between 3.65 (Table II) and 2.93 mg/l zinc (Table III) for a 96-hour exposure.

B Fish Breathing

1 Table IV shows the breathing rates of five fish on days 1, 2, and 7 of experiment 8. The first four fish were exposed to a measured zinc concentration of 4.16 mg/l, beginning at 10 a.m. on day 7. The fifth fish served as a control and was not exposed to any added zinc. The amplitude of the breathing signals decreased every night, and the breathing rates for fish 2, in particular, could not be determined during some portions of the dark period (7:30 p.m. - 7:00 a.m.). The maximum breathing rates for each fish during each period of the first day are circled. The breathing rate of any fish during a time period of day 2 or day 7, which is greater than the maximum breathing rate recorded for that fish during the corresponding time period of the first day has a rectangle drawn around it. The total number of fish showing increased breathing is given at the bottom of each column. On day 2, fish 2 showed increased breathing on just two occasions. In contrast after zinc was added on day 7, three and four experimental fish at a time showed increased breathing.

2 Table V summarizes the results of successive comparisons of the first day maximal breathing rates to breathing rates on subsequent days (SCM method of analysis), for experiment 8. During the control period before any zinc was added there were 15 occasions when a single experimental fish responded, and three occasions when two experimental fish responded at the same time. At no time during the control period did more than two fish show responses together. After the zinc was introduced, all four of the exposed fish showed responses simultaneously on five occasions, and three fish showed responses during the same time interval on 19 occasions. If the criterion for detection of water conditions potentially harmful to fish were two or more responses during the same time period, then three false detections would have occurred before any zinc was added, and 4.16 mg/l zinc would have been correctly detected eight hours after it was introduced. If the detection criterion were three or more responses during the same time period, then no false detections would have occurred and the zinc would still have been correctly detected after eight hours.

3 The lowest zinc concentration tested was 2.55 mg/l. Using a detection criterion of simultaneous responses by three fish, this concentration was detected 52 hours after the zinc was added, with no false detections occurring during the four hours before zinc was added (Table VI). The responses of six control fish that were exposed to dilution water containing no added zinc are also shown for comparison. Note that there was no tendency toward increased breathing rates through time in the control fish, and that no more than one control fish showed an increased breathing rate during one time period.

4 Table VII summarizes information on three experiments that indicates the effectiveness of the SCM method of analysis when different criteria for detection are used. Changing the criterion for detection from one to three responses per time period generally increases the lag time and decreases the number of false detections. The lag time is the time from the addition of zinc to the first detection. A false detection is one occurring before any zinc is added to the water.

IV DISCUSSION

A The experiments described above show that the movements and breathing rates of bluegill

sunfish can be used to detect sublethal concentrations of zinc. The criterion for detection is a certain number of fish showing an arbitrarily defined response in breathing rate or activity during one time period.

B In choosing a specific criterion for detection, the risk of not detecting stressful conditions soon enough must be weighed against the risk of false detections, and the choice would probably be determined by the nature of the pollutant. If a pollutant is easily detected by the biological monitoring system, is slow-acting, and if the toxic effects are reversible, then the criterion for detection might be responses by 3/4 of the test fish, to avoid the false detections that would necessitate expensive remedial action or a temporary shut-down. On the other hand, an industry that produces an effluent containing a fast-acting toxicant whose effects are irreversible would probably use a criterion that leads to rapid detection (responses by 1/4 to 1/2 of the test fish), and would have to go to the expense of installing holding ponds or recycling facilities to accommodate a relatively high number of false detections. Alternatively, a safety factor could be introduced by metering proportionally more waste into the dilution water delivered to the test fish than is delivered to the stream. The safety factor could be determined by growth and reproduction experiments with fish.

C In an actual industrial situation water and waste qualities are apt to vary unpredictably, and it would certainly be desirable to have a redundant detection system. It is conceivable that some harmful combination of environmental conditions and waste quality would be detected by monitoring one biological function, but not by monitoring another. It is also possible that excessive turbidity would disrupt the light beams of the movement monitor, and not affect the breathing monitor; or that an excessive concentration of electrolytes would affect the electrodes of the breathing monitor, but not affect the activity monitor. Therefore, the activity monitor and the breathing monitor have been combined in our laboratory for further experiments (Fig. 1).

D The rate of data acquisition and analysis could be greatly speeded up if the monitoring system were automated as shown in Figure 2. The sampling rate would be controlled by a minicomputer which could receive data from the movement monitor and the polygraph via a multiplexer as often as every minute. The minicomputer would be programmed to perform statistical analyses every 10 minutes, for example, and output the results on a teleprinter.

E Figure 3 shows how the fish monitoring units would be used at an actual industrial site. A monitoring unit would be located on each waste stream in the plant and on the combined waste stream. The experimental fish in each unit would be exposed to waste diluted with water from the river above the plant, and control fish would be exposed to upstream water alone (Fig. 4). The information from each monitoring unit could be analyzed by a central data processor, and when there was a warning response, the industry could tell which waste stream was at fault. If the problem was outside the plant, the control fish would show responses.

F Figure 5 shows how the in-plant monitoring systems would be integrated into a river management system. The in-plant monitoring units are shown as squares, and in addition to supplying information to each industry, the monitoring units also inform the control center. In such a system, there are several alternative damage prevention measures that could be used, in addition to whatever measures, such as shunting wastes to a holding pond or recycling wastes for further treatment, are available to each industry. If the monitoring units at Industry 2 indicate that toxic waste conditions are developing, then the control center might have Industry 1 hold its waste until the danger of combining wastes from Industry 1 and 2 in the river were alleviated by control measures at Industry 2. Alternatively, the control center might call for a release of water from the upstream dam to dilute the effluent from industry.

G It is likely that "fish sensors" in continuous monitoring units at industrial sites can warn of developing toxic conditions in time to forestall acute damage to the fish populations in streams. In conjunction with stream water quality standards for chronic exposure, such biological monitoring systems should make it possible for healthy fish populations to co-exist with industrial water use.

ACKNOWLEDGEMENT

This research was supported by grants 18050 EDP and 18050 EDQ from the Water Quality Office, Environmental Protection Agency.

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This outline was prepared by John Cairns, Jr. and Richard E. Sparks, Center for Environmental Studies and Department of Biology, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

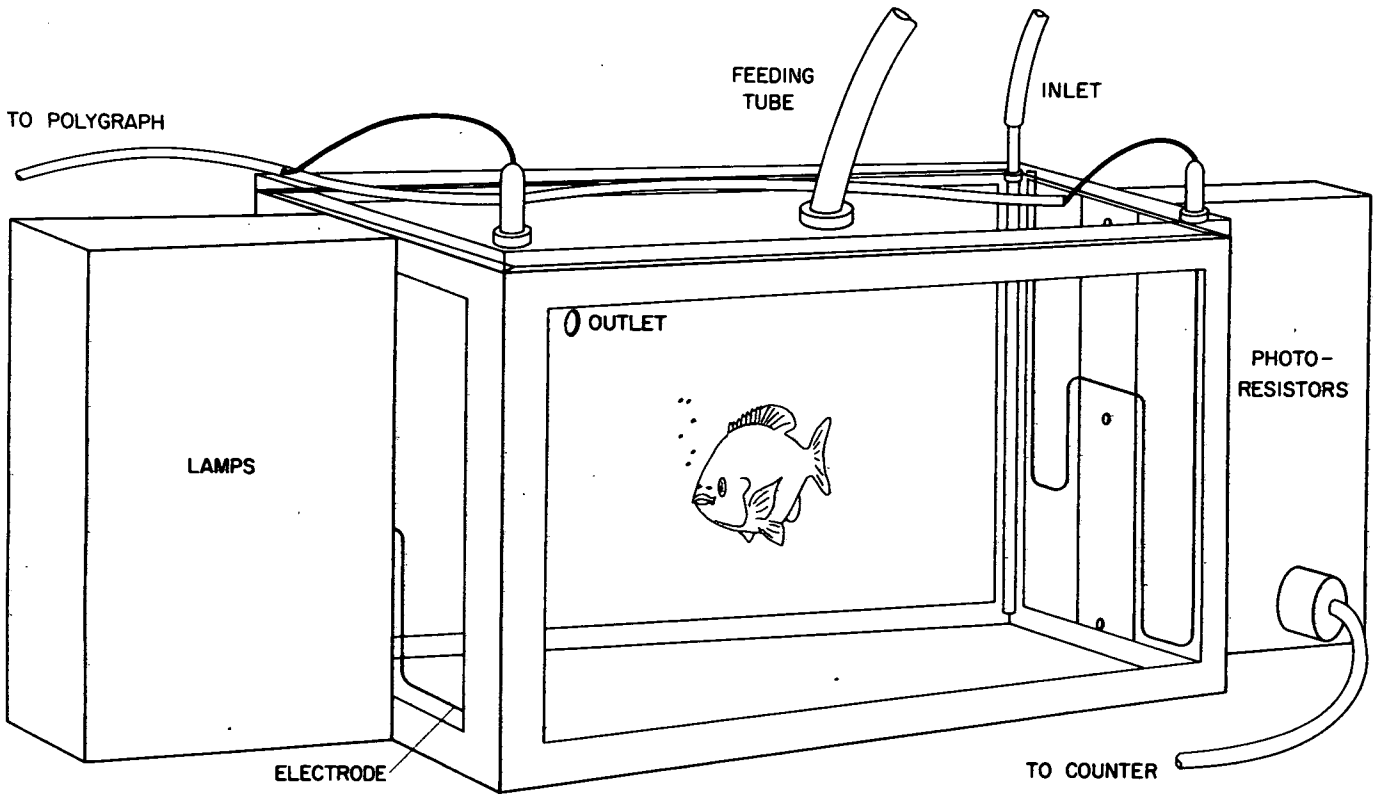


Figure 1. Test chamber for monitoring system, showing the electrodes for recording fish breathing and the light-beam system for recording fish movement.

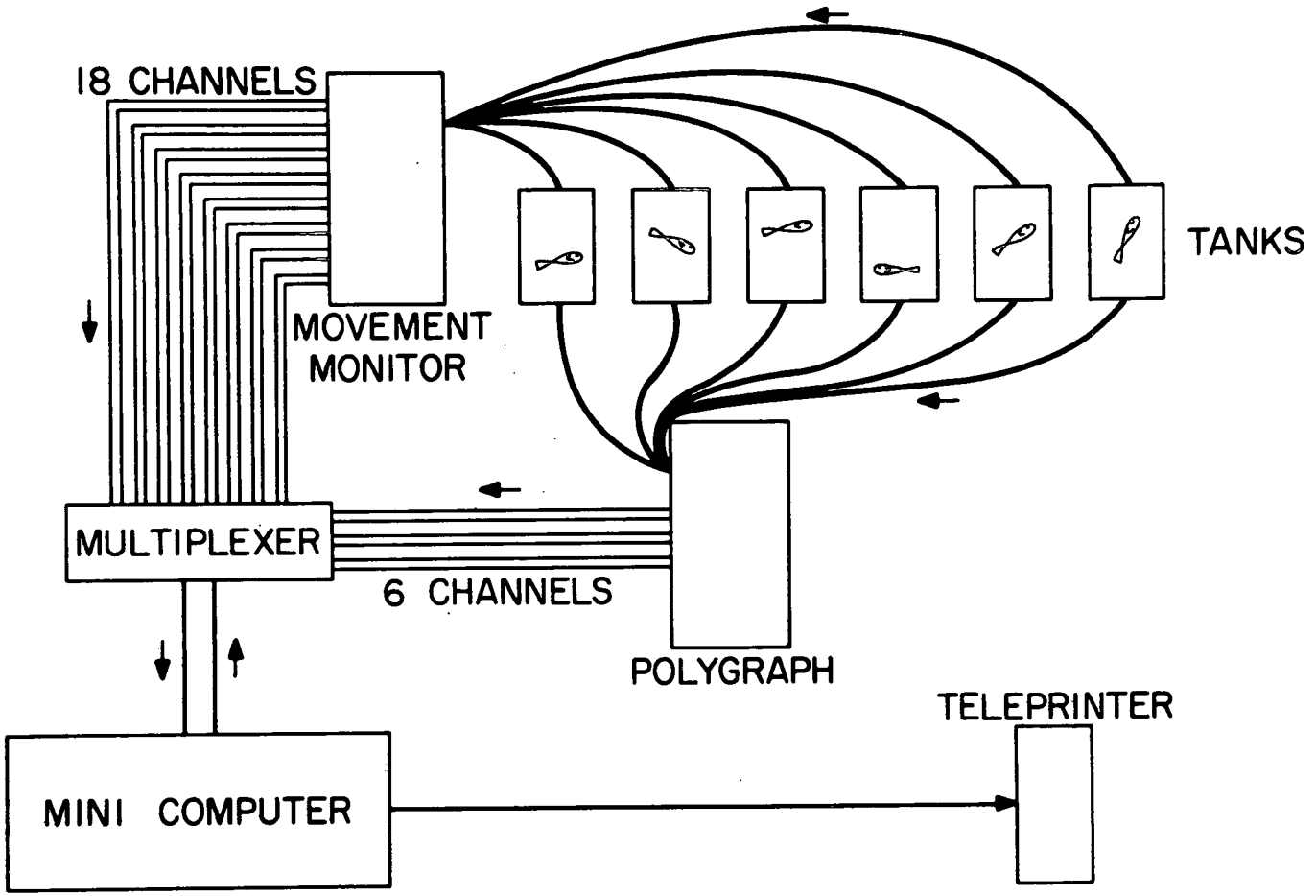


Figure 2. An automated fish monitoring unit.

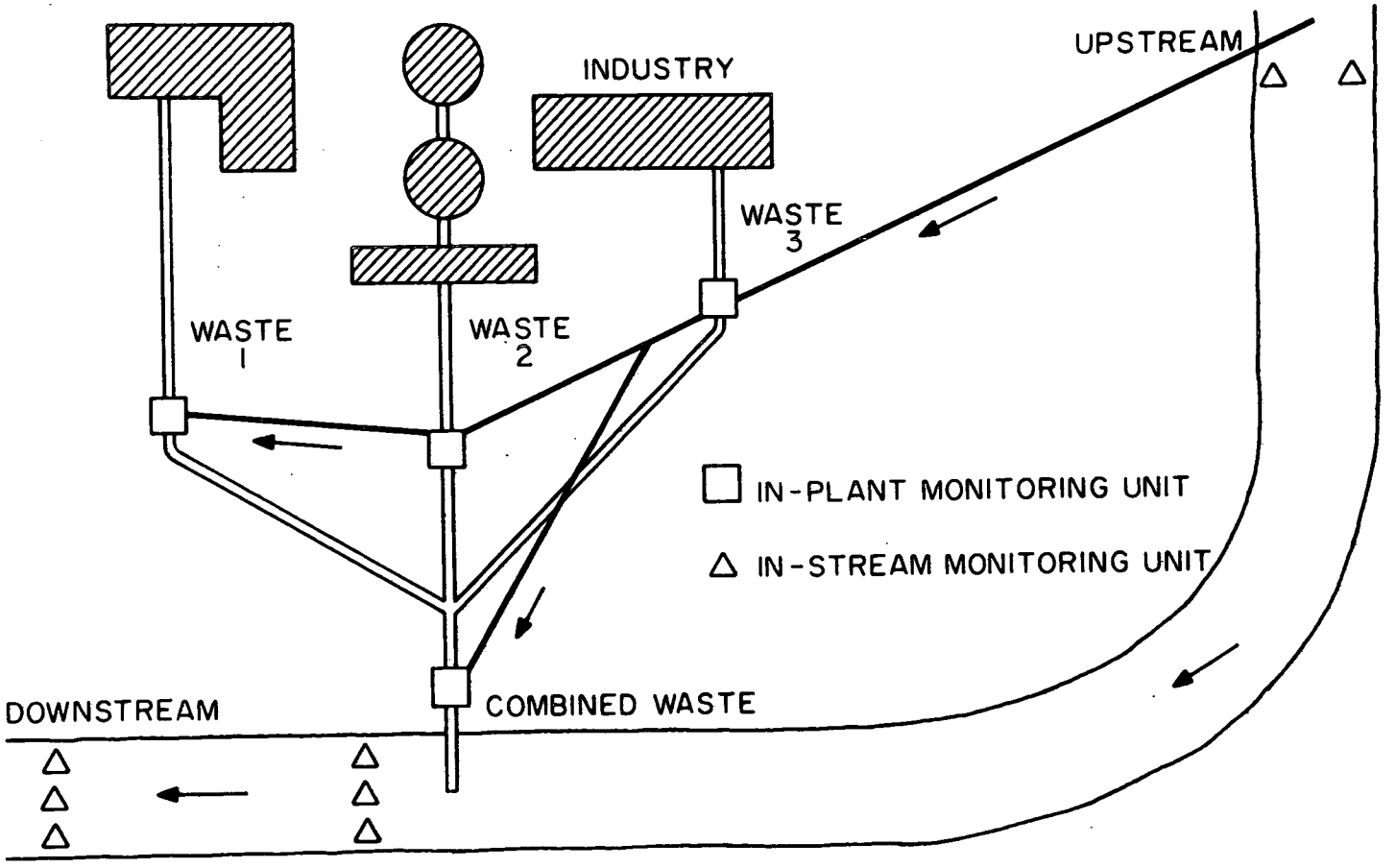


Figure 3. Arrangement of fish monitoring units at an industrial site.

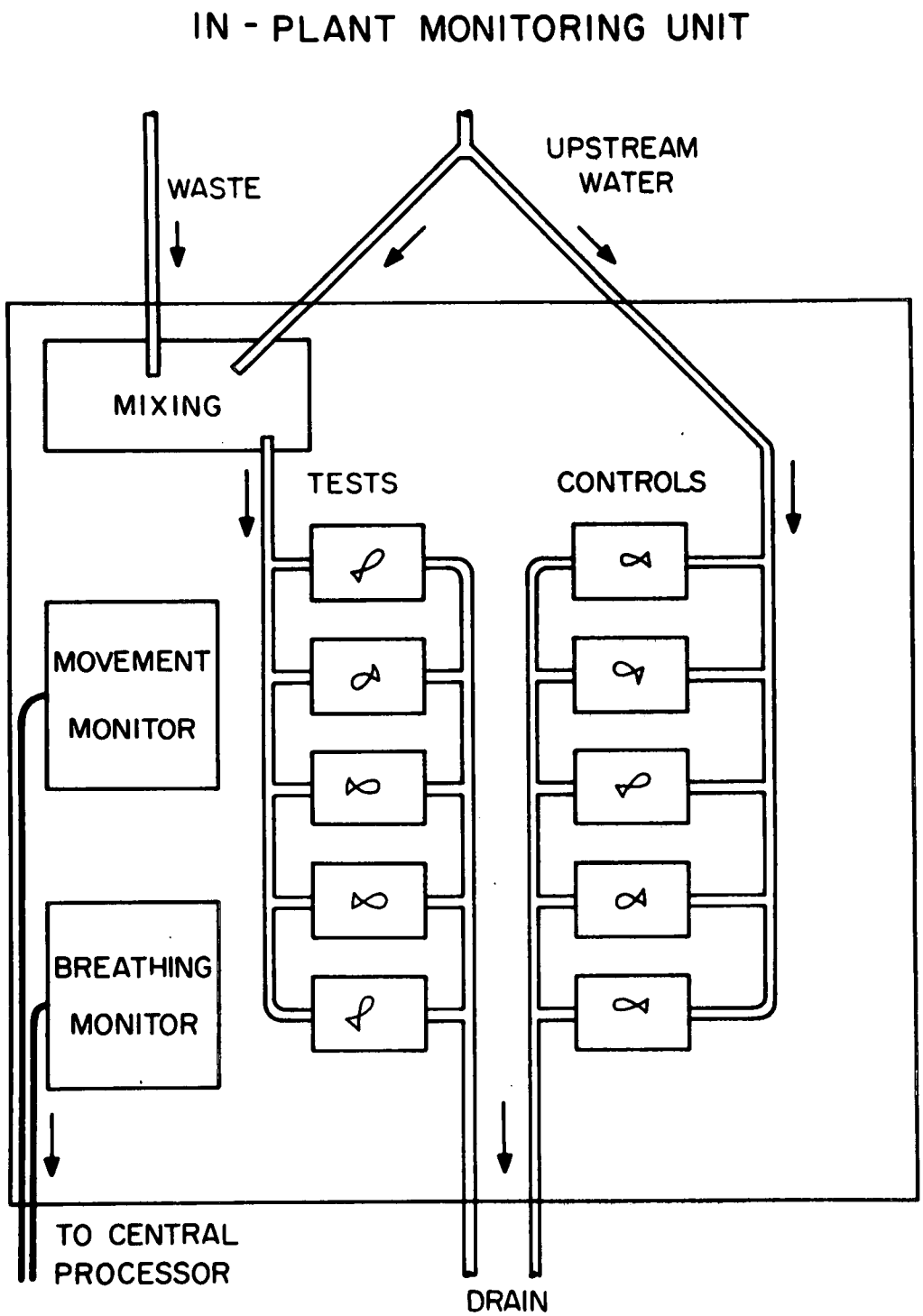


Figure 4. Detail of a single fish monitoring unit, showing how the experimental fish are exposed to waste diluted with upstream water and the control fish are exposed to upstream water alone.

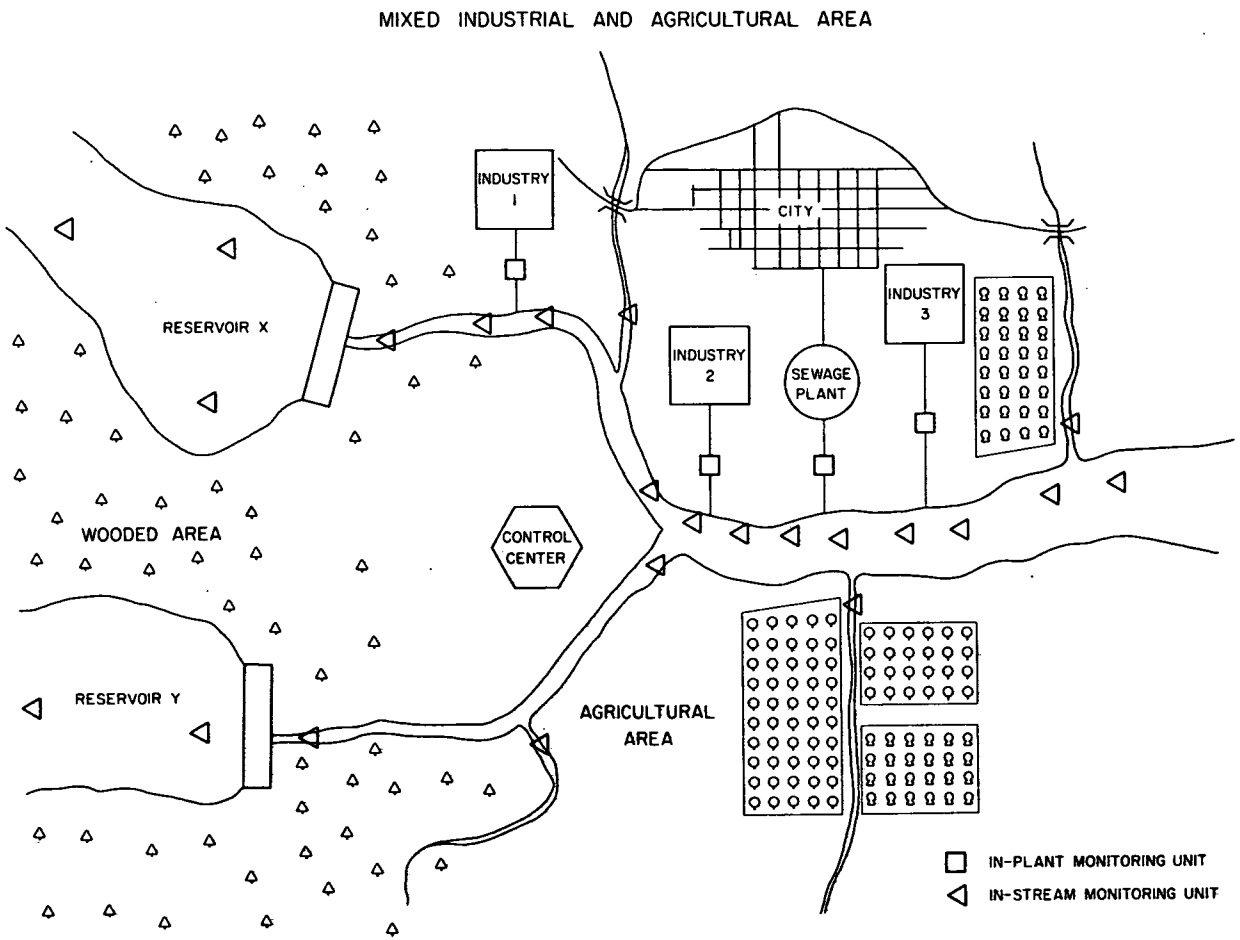


Figure 5. Use of in-plant monitoring units in a river management system.

THE USE OF BIO-ASSAYS: CASE HISTORIES

I USE FOR CONTROL OF INDUSTRIAL WASTES

Bio-assays can be used effectively for many purposes in industrial operations.

A The toxicity of final effluents and the probable effects on receiving waters can be determined.

Examples:

1 A large rayon plant released effluent into a highly valued recreational stream which effectively destroyed aquatic life. While this could be shown by examining the stream biota, conventional physical and chemical tests (temp., pH, DO, BOD, coliforms, etc.) gave no evidence of serious pollution. Bio-assays showed this effluent could be highly toxic to fish under minimum river flow conditions and helped in locating the major toxic component zinc. Attention to the elimination of zinc in the treatment process brought about recovery of this river in a short time.

2 A number of effluents from different industries were entering a receiving water which was itself of little or no consequence from the aquatic life standpoint. Toxicity, which built up in this basin, was suspected of causing difficulty in waters of recreational importance into which this basin drained. Bio-assays were made on effluents to evaluate contributions of toxicity. The following results illustrate how contributions of toxicity can be directly shown.

B Toxicity may be traced to process effluents, which may considerably reduce volumes requiring treatment.

Examples:

1 Samples of an effluent from a by-product coke plant appeared to vary greatly in toxicity. A study was made to evaluate the sources of toxicity in this plant. Figure 1 shows the toxicity of the various process effluents and their contribution to the final effluent. It can be readily seen that a large percentage of toxicity is contained in several small volume effluents. If other means of disposal were found for these process effluents the toxicity entering the receiving water would be greatly reduced.

2 Bio-assays at a zirconum separations plant determined that some process effluents were highly toxic and must be eliminated from the receiving stream for protection of aquatic life. Other effluents which made up a larger volume could be released safely if first mixed (lagooned) and released in a regulated volume according to stream flows.

Effluent	Number Samples	Flow cfs	Median Tolerance Limit (TL_m) % Concentration		Dilution Volume cfs
			Range	Average	
A	3	20.6	37 -42	40	32
B	7	17.4	4.4-16	9.1	174
C	7	10.5	13.5-28	20	42
D	8	2.8	4.0-24	9.6	26
E	14	9.85	2.9-22.5	11.0	80

C The effectiveness of treatment processes may be established.

Example:

1 Bio-assays were used to evaluate the effectiveness of two different treatment methods in the removal of toxicity from aircraft washing wastes.

D When locating new plants, the quantity of dilution water necessary or the degree of treatment of the wastes may be ascertained in advance of construction.

Example:

1 Bio-assays of pilot plant wastes from a synthetic rubber plant indicated difficulties in waste disposal at a proposed location for a new plant. Failure to work out satisfactory treatment methods caused the abandonment of this location.

2 Bio-assays of wastes from a similar facility indicated the feasibility of a proposed location for air force photographic laboratory. Removal of silver and mixing of the process wastes greatly decreased toxicity.

E Leakage, spills, or other losses of chemicals into waste streams may be detected and located.

Example:

1 Samples of effluent from a petrochemical plant were found to be highly toxic which led to a careful check of process and sewer systems. Certain imperfections in the system were found and corrected. Later samples indicated the toxicity had been greatly reduced.

F Effluents may be continuously monitored by means of continuous flow bio-assays.

G Modified bio-assays may be used to study the effect of chemicals in producing tastes in fish flesh.

Example:

1 A large chemical company is studying the effect of effluents containing chlorinated benzenes and phenols on production of tastes in fish flesh.

II OTHER USES

A Toxic concentrations of insecticides, algicides and herbicides can be established.

Examples:

1 Runoff from an area treated with dieldrin was found toxic to fish.

2 Fish toxicity studies are routinely made when screening potential algicides.

B Highly toxic contaminants in drinking water supplies can be detected.

Example:

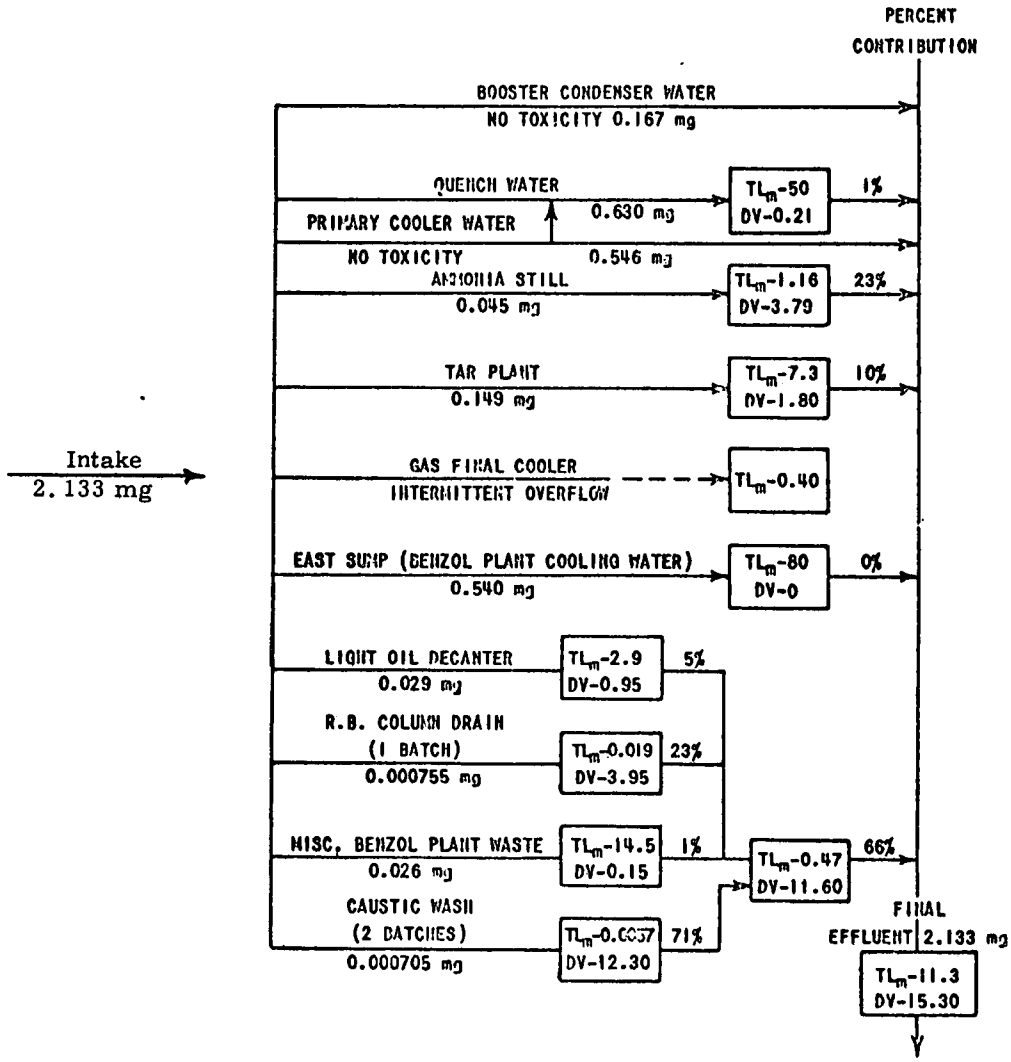
1 Detection of possible CW and BW contaminants.

C May be used as an analytical tool for measuring concentration of toxic chemicals.

Example:

1 A time concentration relationship was established and used in estimating the concentration of rotenone remaining and the effectiveness of various water treatment processes in the removal of rotenone from water.

FIGURE 1



SCHEMATIC DIAGRAM SHOWING TOXICITY OF MAJOR COKE PLANT WASTES DISCHARGED TO SEWER DURING AN 8 HOUR PERIOD

TL_m's in % Dilution volumes (DV) in millions of gallons per 8-hour period. Since intake water actually had a TL_m of 60% and a DV of 1.42 mg, water from another source was used in these tests.

D Used in the development of selective fish poisons.

Example:

1 Screening of various chemicals for lamprey control in the Great Lakes area.

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This outline was prepared by C. Henderson, Biologist, FWQA, Colorado River Project Laboratory, Salt Lake City, Utah.

IV CONDUCTING THE SURVEY

	Outline Number
Sampling in Water Quality Studies	24
Sample Handling - Field Through Laboratory	25
Flow Measurement	26
Tracing Natural Waters	27

SAMPLING IN WATER QUALITY STUDIES

I INTRODUCTION

A Objective of Sampling

1 Water quality characteristics are not uniform from one body of water to a another, from place to place in a given body of water, or even from time to time at a fixed location in a given body of water. A sampling program should recognize such variations and provide a basis for interpretation of their effects.

2 The purpose of collection of samples is the accumulation of data which can be used to interpret the quality or condition of the water under investigation. Ideally, the sampling program should be so designed that a statistical confidence limit may be associated with each element of data.

3 Water quality surveys are undertaken for a great variety of reasons. The overall objectives of each survey greatly influence the location of sampling stations, sample type, scheduling of sample collections, and other factors. This influence should always be kept in mind during planning of the survey.

4 The sampling and testing program should be established in accordance with principles which will permit valid interpretation.

a The collection, handling, and testing of each sample should be scheduled and conducted in such a manner as to assure that the results will be truly representative of the sources of the individual samples at the time and place of collection;

b The locations of sampling stations and the schedule of sample collections for the total sampling program should be established in such a manner that the stated investigational objectives will be met; and

c Sampling should be sufficiently repetitive over a period of time to provide valid data about the condition or quality of the water.

B Sample Variations

Interpretation of survey data is based on recognition that variations will occur in results from individual samples. While it is beyond the scope of this discussion to consider the implications of each in detail, the following can be identified as factors producing variations in data and should be considered in planning the sampling program.

1 Apparent variations

a Variations of a statistical nature, due to collection of samples from the whole body of water, as contrasted with examination of all the water in the system.

b Variations due to inherent precision of the analytical procedures.

c Apparent variations are usually amenable to statistical analysis.

2 True differences

a Variations of a cyclic nature

Diurnal variations, related to alternating periods of sunlight and darkness.

Diurnal variations related to waste discharges from communities.

Seasonal variations, related to temperature and its subsequent effects on chemical and biological processes and interrelationships.

Variations due to tidal influences, in coastal and estuarine waters.

b Intermittent variations

Dilution by rainfall and runoff.

Effects of irregular or intermittent discharges of wastewater, such as "slugs" of industrial wastes.

Irregular release of water from impoundments, as from power plants.

c Continuing changes in water quality

Effects downstream from points of continuous release of wastewater.

Effects of confluence with other bodies of water.

Effects of passage of the water through or over geological formations of such chemical or physical nature as to alter the characteristics of the water.

Continuing interactions of biological, physical, and chemical factors in the water, such as in the process of natural self-purification following introduction of organic contaminants in a body of water.

II LOCATION OF SAMPLING STATIONS

A The Influence of Survey Objectives

Much of the sampling design will be governed by the stated purpose of the water investigation. As an example of how different objectives might influence sampling design, consider a watercourse with points A and B located as indicated in Figure 1.

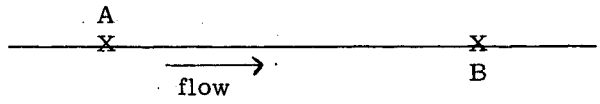


Figure 1

Point A can be the point of discharge of wastes from Community A. Point B can be any of several things, such as an intake of water treatment plant supplying Community B, or it might be the place where the river crosses a political boundary, or it may be the place where the water is subject to some legitimate use, such as for fisheries or for recreational use.

1 Assume that the objective of a water quality investigation is to determine whether designated standards of water quality are met at a water plant intake at Point B. In this case, the objective only is concerned with the quality of the water as it is available at Point B. Sampling will be conducted only at Point B.

2 Alternately, consider that there is a recognized unsatisfactory water quality at Point B, and it is alleged that this is due to discharges of inadequately treated wastes, originating at Point A. Assume that the charge is to investigate this allegation.

In this case the selected sampling sites will include at least three elements:

a At least one sampling site will be located upstream from Point A, to establish base levels of water quality, and to check the possibility that the observed conditions actually originated at some point upstream from Point A.

b A site or sites must be located downstream from Point A. Such a site should be downstream a sufficient distance to permit adequate mixing in the receiving water.

c Sampling would be necessary at Point B in order to demonstrate that the water quality is in fact impaired, and that the impairment is due to influences traced from Point A.

B Hydraulic Factors

1 Flow rate and direction

a In a survey of an extended body of water it is necessary to determine the rate and direction of water movement influences selection of sampling sites. Many workers plan sampling stations representing not less than the distance water flows in a 24-hour period. Thus, in Figure 1, intervening sampling stations would be selected at points representing the distance water would flow in about 24 hours.

b In a lake or impoundment direction of flow is the major problem influencing selection of sampling stations. Frequently it is necessary to establish some sort of grid network of stations in the vicinity of the suspected sources of pollution.

c In a tidal estuary, the oscillating nature of water movement will require establishment of sampling stations in both directions from suspected sources of pollution.

2 Introduction of other water

a In situations in which a stream being studied is joined by another stream of significant size and character, sampling stations will be located immediately above the extraneous stream, in the extraneous stream above its point of juncture with the main stream, and in the main stream below the point of juncture.

b Similar stations will be needed with respect to other water discharges, such as from industrial outfalls, other communities, or other installations in which water is introduced into the main stream.

3 Mixing

a Wherever possible, one sampling point at a sample collection site is used in stream surveys. This usually is near the surface of the water, in the main channel of flow.

b In some streams mixing does not occur quickly, and introduced water moves downstream for considerable distances below the point of confluence with the main streams. Example: Susquehanna River at Harrisburg, where 3 such streams are recognizable in the main river. Preliminary survey operations should identify such situations.

When necessary, collect separate samples at two or more points across the body of water.

c Similarly, vertical mixing may not be rapid. This is noted particularly in tidal estuaries, where it may be necessary to make collections both from near the bottom and near the surface of the water.

d Collection of multiple samples from a station requires close coordination with the laboratory, in terms of the number of samples that can be examined. Some types of samples may be composited. The decision must be reached separately for each type of sample.

C Types of Analytical Procedure

1 Samples collected for physical, chemical, and bacteriological tests and measurements may be collected from the same series of sampling stations.

2 Sampling stations selected for biological (ecological) investigation require selection of a series of similar aquatic habitats (a series of riffle areas, or a series of pool areas, or both). The sites used by the aquatic biologist may or may not be compatible with those used for the rest of the survey. Accordingly, in a given stream survey, the stations used by the aquatic biologist usually are somewhat different from the stations used for other examinations.

D Access to Sampling Stations

For practical reasons, the sampling site should be easily reached by automobile if a stream survey, or by boat if the survey is on a large body of water. Highway bridges are particularly useful, if the sample collector can operate in safety.

III FACTORS IN SCHEDULING OF SAMPLING PROGRAMS

A Survey Objectives

B Time of Year

1 In short-term water quality investigations, particularly in pollution investigations, there often is need to demonstrate the extremes of pollution effects on the aquatic environment. For this reason, many short-term surveys are conducted during the warmer season of the year, at such times as the water flow rate and volume is at a minimum and there is minimum likelihood of extensive rainfall.

2 In a long-term investigation, sampling typically is conducted at all seasons of the year.

C Daily Schedules

As shown in an introductory paragraph, water quality is subject to numerous cyclic or intermittent variations. Scheduling of sample collections should be designed to reveal such variations.

1 In short-term surveys it is common practice to collect samples from each sampling site at stated intervals through the 24-hour day, continuing the program for 1 - 3 weeks. Sampling at 3-hour intervals is preferred by many workers, though practical considerations may require extension to 4- or even 6-hour intervals.

2 In an extended survey there is a tendency to collect samples from each site at not more than daily intervals, or even longer. In such cases the hour of the day should be varied through the entire program, in order that the final survey show cyclic or intermittent variations if they exist.

3 In addition, sampling in tidal waters requires consideration of tidal flows. If samples are collected but once daily, many workers prefer to make the collections at low slack tide.

4 In long-term or any other survey in which only once-daily samples are collected, it is desirable to have an occasional period of around-the-clock sampling.

IV IDENTIFICATION OF SAMPLING SITES

A River Mile System

The FWPCA method of identifying points on a water course is by counting river miles from the mouth (or junction with a larger stream) back to the source. This should not be confused with other systems, such as those in which the river mile is started at the source of the stream and proceeds to the mouth of the stream or confluence with another body of water.

B STORET System

The STORET System is a computer-oriented data processing system used by FWPCA for storage, retrieval, and analysis of water quality data collected by federal, state, local, and private agencies.

The system includes a complex system - based on the river mile system - for identifying sampling locations on all rivers and streams in the United States. A recent addition to the system introduces a location procedure based on geographic coordinates; this procedure is especially adapted to location of sampling stations in large bodies of water such as lakes and impoundments.

Not all locations have been coded at this time, although the coding systems have been established. The interested worker should consult Public Health Service Publication No. 1263, "The Storage and Retrieval of Data for Water Quality Control," 1963.

V SAMPLE COLLECTION

A Types of Samples

1 "Grab" sample - a grab sample is usually a manually collected single portion of the wastewater or stream water. An analysis of a grab sample shows the concentration of the constituents in the water at the time the sample was taken.

2 "Continuous" sample - when several points are to be sampled at frequent intervals or when a continuous record of quality at a given sampling station is required, an automatic or continuous sampler may be employed.

a Some automatic samplers collect a given volume of sample at definite time intervals; this is satisfactory when the volume of flow is constant.

b Other automatic samplers take samples at variable rates in proportion to changing rates of flow. This type of sampler requires some type of flow measuring device.

3 "Composite" sample - a composite sample is the collection and mixing together of various individual samples based upon the ratio of the volume of flow at the time the individual samples were taken to the total cumulative volume of flow. The desired composite period will dictate the magnitude of the cumulative volume of flow. The more frequently the samples are collected, the more representative will be the composite sample to the actual situation. Composite samples may be obtained by:

a Manual sampling and volume of flow determination made when each sample is taken.

b Constant automatic sampling (equal volumes of sample taken each time) with flow determinations made as each sample is taken.

c Automatic sampling which takes samples at pre-determined time intervals and the volume of sample taken is proportional to the volume of flow at any given time.

B Type of Sampling Equipment

1 Manual sampling

a Equipment is specially designed for collection of samples from the bottom muds, at various depths, or at water surfaces. Special designs are related to protection of sample integrity in terms of the water characteristic or component being measured.

b For details of typical sampling equipment used in water quality surveys, see outlines dealing with biological, bacteriological, and chemical tests in this manual.

c Manual sampling equipment has very broad application in field work, as great mobility of operation is possible, at lower cost than may be possible with automatic sampling equipment.

2 Automatic sampling equipment

Automatic sampling equipment has several important advantages over manual methods. Probably the most important consideration is the reduction in personnel requirements resulting from the use of this equipment. It also allows more frequent sampling than is practical manually, and eliminates many of the human errors inherent in manual sampling.

Automatic sampling equipment has some disadvantages. Probably the most important of these is the tendency of many automatic devices to become

clogged when liquids high in solids are being sampled. Individual portions of composite samples are usually quite small which may in some cases be disadvantageous. In using automatic samplers, sampling points are fixed, which results in a certain loss of mobility as compared to manual methods.

Automatic sampling equipment should not be used indiscriminately; some types of samples - notably bacteriological, biological, and DO samples - should not be composited. In cases of doubt, the appropriate analyst should be consulted.

a Compositing samplers

1) Jar and tube sampler - this type samples effectively when flow is nearly constant. As water drains from the upper carboy, the vacuum created syphons waste into the lower one. The rate-of-flow is regulated by the pinch clamp to fill the lower carboy during the sampling period. (See Figure 2)

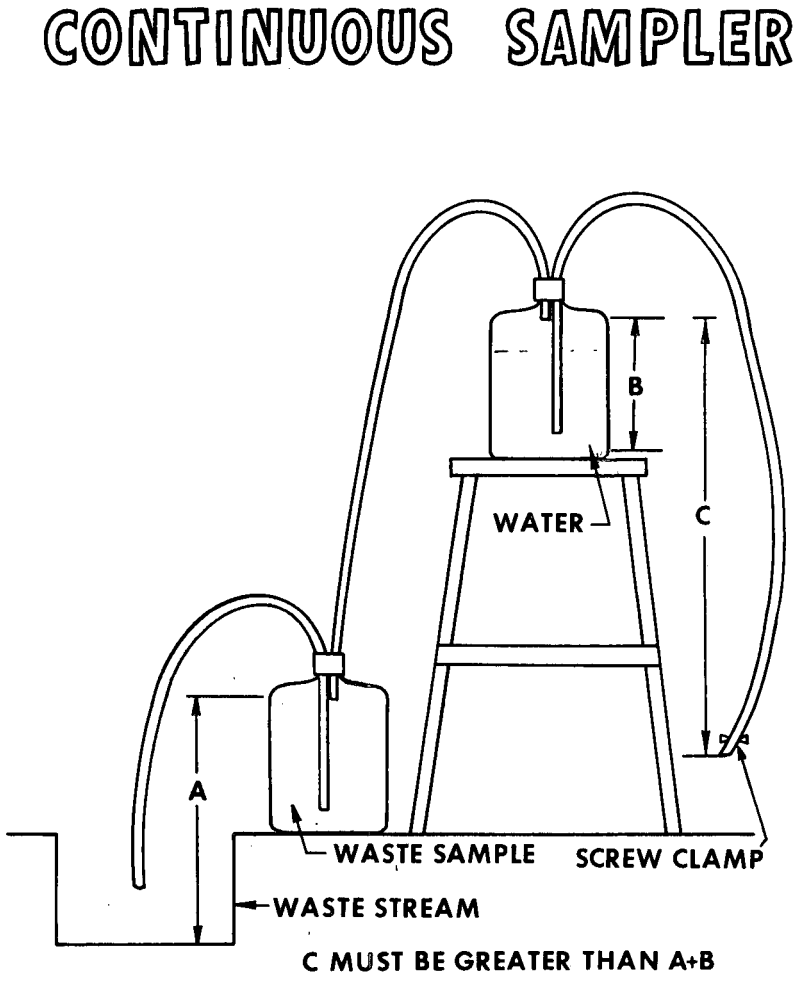


Figure 2

2) Scoop type

a) Rotating scoop

This device consists of a power driven scoop mounted upstream from a weir. The scoop is so designed and mounted that the sample volume grabbed on each rotation of the scoop is proportional to the flow, as governed by the head on the weir. The scoop may be rotated at a constant speed or timed to sample at fixed time intervals.

b) Revolving wheel with cups (Figure 3)

This device consists of a power driven wheel or disc mounted upstream from a weir. A number of freely suspended buckets are mounted at varying distances from the axis so that increased flow will cause more buckets to be filled, thereby giving a sample proportionate to flow. Both this device and the rotating scoop sampler can, of course, be used for non-proportionate sampling.

c) Bucket elevators

This device may consist of a single bucket alternately lowered into and raised out of the waste stream, or it may consist of a series of buckets on an endless chain passing through the waste stream. In either case, it will include a tripping mechanism to cause the bucket or buckets to spill into a sampling funnel. Both types may be operated continuously or timed for intermittent operation. This method is not well adapted to proportionate sampling.

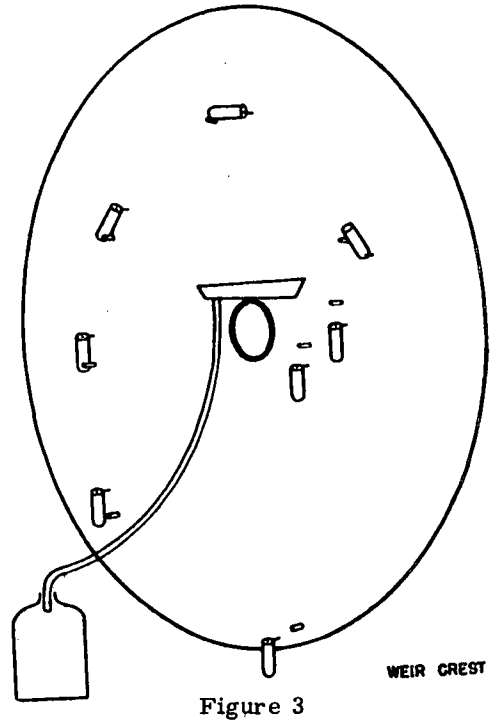


Figure 3
WHEEL WITH BUCKETS

3 Pumps

a) Chemical feed pumps have been found useful for sampling, because of their ability to meter out small doses of liquids. A timing mechanism may be used to make the pump run for longer periods during heavy flow, thereby allowing collection of the sample in proportion to flow. These pumps are usually provided with adjustable stroke and variable speed features which allow variation of the volume of sample being pumped. Figure 4 illustrates a battery operated pump.

b) Automatic shift sampler (Figure 5)

Figure 5 shows the automatic shift sampler. It consists first of a Randolph or other "squeegee-" type pump unit.

The 2-rpm gear motor drives the pump at between 1 and 2 rpm through the spring-loaded adjustable-pitch pulley and adjustable motor-base arrangement.

We use 1/8-in. (.32-cm) ID or 1/4-in. (.64-cm) ID polyethylene tubing for sample intake from the waste stream. The sample flow is delivered to the distributor via a 3/16-in. (.48-cm) ID Tygon tube which is supported loosely by a wire attached to the framework.

Operation of the distributor is very simple. The 1-rpm clock motor powers the chain-and-sprocket drive which turns a threaded bolt. Rotation of the bolt moves the discharge tube down the plastic trough at a rate equal to one division every eight hours. With the 10 sample-jar receivers the timer can be set on Friday, and the 9 week-end shift samples can be picked up on Monday.

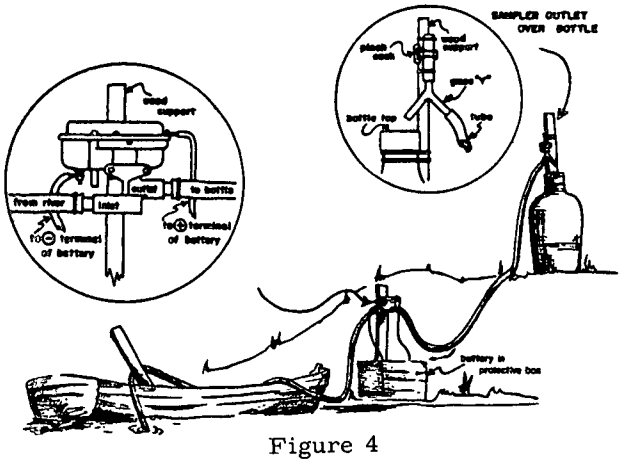
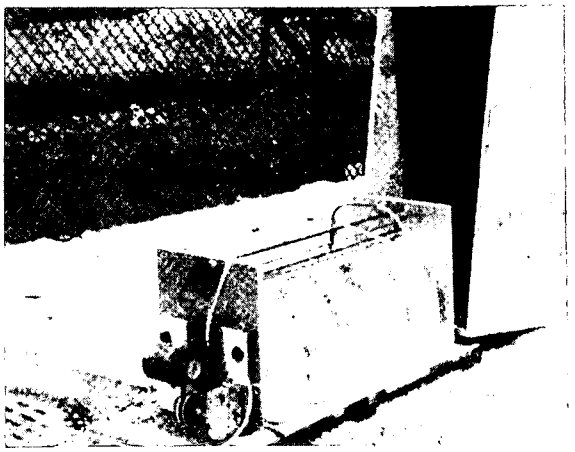


Figure 4
BATTERY OPERATED PUMP



4) Solenoid-valve arrangements

A solenoid valve employed in connection with a timing device may be used for withdrawing waste from a pipe under pressure. Used in connection with a pump such devices may be employed in sampling free flowing streams. (See Figures 6 and 7.)

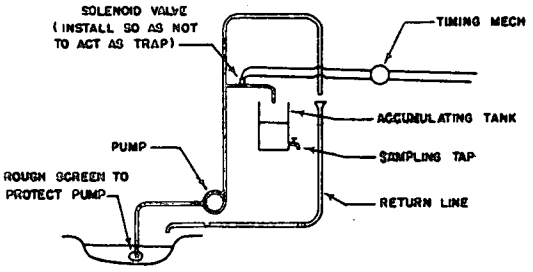


Figure 6
PUMP - SOLENOID VALVE - TIMER TYPE SAMPLER

5) Vacuum operated

In its simplest form, the vacuum is created by a suitably mounted siphon. It collects the sample at a uniform rate and is not suitable for use when proportional sampling is required.

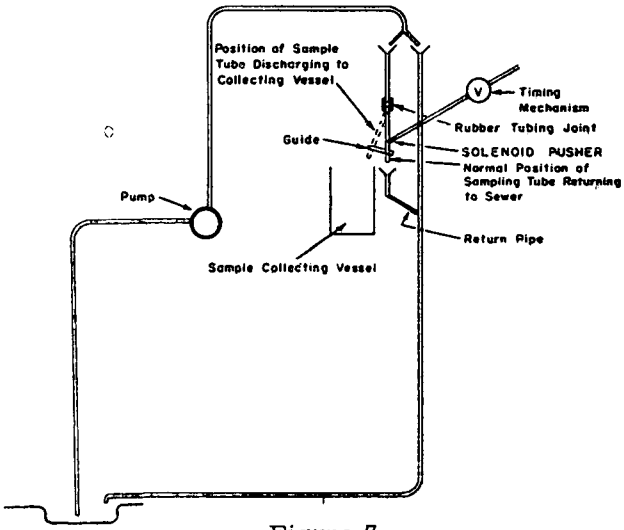


Figure 7
PUMP - SOLENOID-DIVERTER - TIMER TYPE SAMPLER

6) Air vent control

This type of device is illustrated in Figure 8. The rate of sample collection is controlled by the bubbling mechanism. It is not suitable for use when proportionate sampling is required.

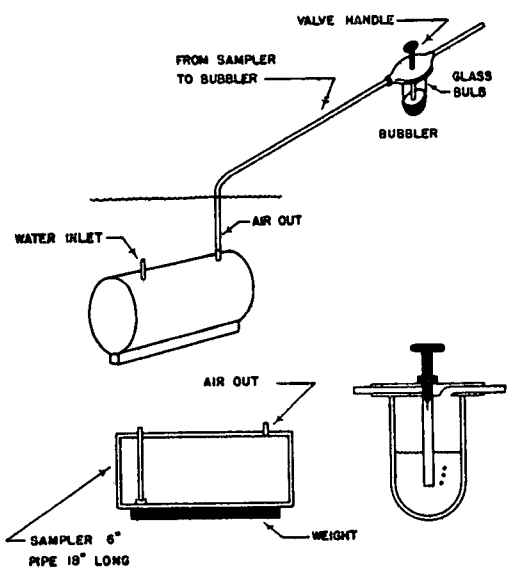


Figure 8
AIR RELEASE TYPE SAMPLER

7) Drip sampler

Two types of this device are illustrated in Figures 9 and 10. Both devices are simple methods of obtaining a composite sample at a fairly constant rate.

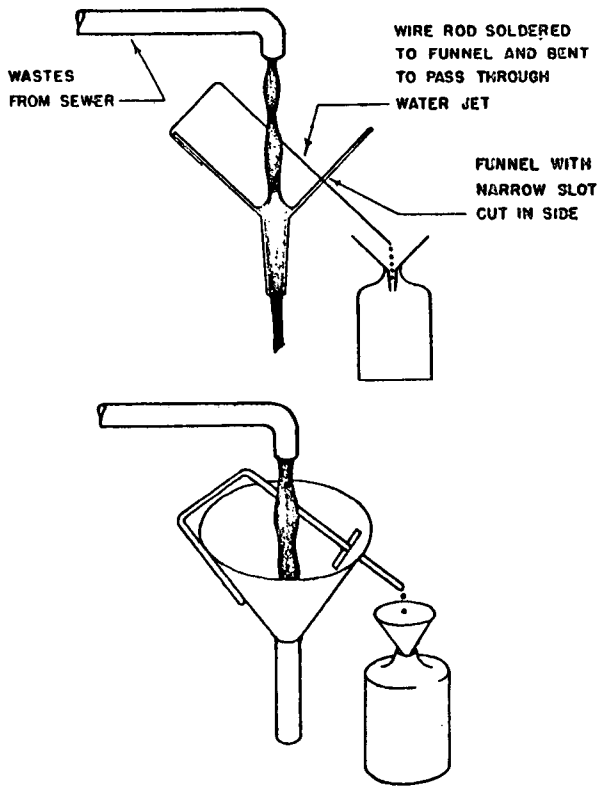


Figure 9
FUNNEL AND ROD DIVERTER

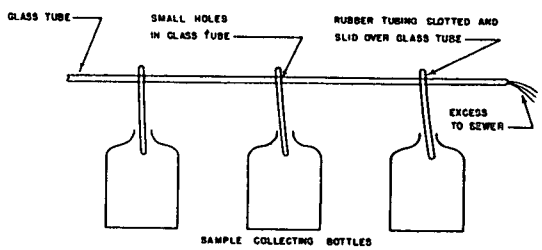


Figure 10
DRIP TUBE SAMPLERS

b Continuous recording equipment

Instruments have been developed which provide direct measurement of temperature, pH, conductivity, color, and dissolved oxygen. Such instruments may be equipped for continuous recording. Instruments of this type are quite expensive and their installation is often difficult. They are best adapted to permanent installations, although good portable non-recording instruments are available for the measurement of temperature, pH, and conductivity.

VI SOME CONSIDERATIONS IN SAMPLING OPERATIONS

All procedures in care and handling of samples between collection and the performance of observations and tests are directed toward maintaining the reliability of the sample as an indication of the characteristics of the sample source.

A Sample Quantity

1 Samples for a series of chemical analyses requires determination of the total sample volume required for all the tests, and should include enough sample in addition to provide a safety factor for laboratory errors or accidents. Many workers collect about twice the amount of sample actually required for the chemical tests. As a rule of thumb, this is on the order of 2 liters.

2 Bacteriological samples, in general, are collected in 250 - 300 ml sterile bottles; approximately 150 - 200 ml of samples is adequate in practically all cases.

B Sample Identification

1 Sample identification must be maintained throughout any survey. It is vital, therefore, that adequate records be made of all information relative to the source of the sample and conditions under which the collection was made. All information must be clearly understandable and legible.

2 Every sample should be identified by means of a tag or bottle marking, firmly affixed to the sample bottle. Any written material should be with indelible marking material.

3 Minimum information on the sample label should include identification of the sample site, date and time of collection, and identification of the individual collecting the sample.

4 Supplemental identification of samples is strongly recommended, through maintenance of a sample collection logbook. If not included on the sample tag (some prefer to duplicate such information) the logbook can show not only the sample site and date and hour of collection, but also the results of any tests made on site (such as temperature, pH, dissolved oxygen). In addition, the logbook should provide for notation of any unusual observations made at the sampling site, such as rainfall, direction and strength of unusual winds, or evidence of disturbance of the collection site by human or other animal activity.

C Care and Handling of Samples

1 As a general policy, all observations and tests should be made as soon as possible after sample collection.

a Some measurements require performance at the sampling site, such as temperature, light intensity (if determined), flow-rate, etc.

b Some tests are best made at the sampling site because the procedures are simple, rapid, and of acceptable accuracy. This may include such determinations as pH and conductivity.

c Some additional determinations, such as alkalinity, hardness, dissolved

oxygen, and turbidity may be made in the field, provided that ease, convenience, and reliability of results are acceptable for the purposes of the study.

2 Samples to be analyzed in the laboratory require special protection to assure that the quality measured in the sample represents the condition of the source. Many samples, especially those subjected to biological analysis, require special preservation, protection, and handling procedures. In case of doubt, the appropriate analyst should be consulted. Most common procedures for sample protection include:

a Examination within brief time after collection.

b Temperature control.

c Protection from light.

d Addition of preservative chemicals.

Applications of these sample protective procedures are along the following lines:

3 Early examination of sample

Applicable to all types of samples.

4 Temperature control

a All biological materials for examination in a living state should be iced between collection and examination.

b Bacteriological samples, according to "Standard Methods" should be maintained at the same temperature as the source of the sample between collection and starting the laboratory tests. Most survey workers, however, continue to ice samples and start laboratory tests within 6 hours after collection.

c Chemical samples often require icing.

Samples for dissolved oxygen can be maintained several hours if kept iced, and protected from the light. BOD samples can be held several hours in an iced condition.

Quick freezing will permit retention of many samples for up to several months prior to laboratory examination.

5 Protection from light

a Any constituent of water which may be influenced by physiochemical reactions involving light should be protected. DO samples brought to the iodine stage, for example, should be protected from light prior to titration.

b In addition, any water constituent (such as dissolved oxygen) which may be influenced by algal activity should be protected from light.

6 Addition of chemical preservatives

a Bacteriological samples never should be "protected" by addition of preservative agents. The only permissible chemical additive is sodium thiosulfate, which is used to neutralize free residual chlorine, if present.

b Samples for biological examination should be protected by chemical additives only under specific direction of the principal biologist in a water quality study. Limited applications of chemical preservatives are discussed in the biology outlines in this manual.

c For chemical tests, preservatives are useful for a number of water components. The following examples are cited:

Nitrogen and phosphorus analyses: The addition of 1 ml concentrated H_2SO_4/liter of sample will retard biological activity, which otherwise might alter the concentration of these constituents. However, it should be noted that some procedures for these determinations will require

subsequent neutralization of the sample.

Metals: The addition of 1 - 5 ml of acid (HCl, HNO_3, or H_2SO_4) prevents precipitation of the metal in the container. The choice of acid depends on what other analyses are to be made on the sample (e.g. HCl would not be used to preserve a sample which later will be analyzed for chlorides).

COD and ABS: Addition of 1 ml sulfuric acid per liter of sample is suggested.

In general, samples requiring retardation of biological activity can be temporarily preserved by addition of chloroform; tests should be run as soon as possible, however.

Determination of ratio of volatile to suspended solids can be delayed up to 6 months if 2% formaldehyde is added.

Cyanide determinations may be delayed temporarily through addition of alkali to the sample. A few pellets of sodium hydroxide are sufficient.

Sulfide analysis may be delayed up to as much as 6 months by addition of 2 ml/liter of sample of 2N solution of zinc acetate.

Phenol analysis can be delayed temporarily by acidification to below pH 4.0 with phosphoric acid and preservation with 1 gram $CuSO_4$ per liter of sample.

REFERENCES

1 Standard Methods for the Examination of Water, Sewage and Industrial Wastes. 12th Ed. A.P.H.A. 1965.

2 Planning and Making Industrial Waste Surveys. Ohio River Valley Water Sanitation Commission.

3 Industry's Idea Clinic. Journal of the Water Pollution Control Federation. April, 1965.

This outline was prepared by H.L. Jeter, Director, National Training Center, WPO, EPA, Cincinnati, OH 45226 and P.F. Atkins, Jr., formerly Sanitary Engineer, FWPCA Training Activities, SEC.

SAMPLE HANDLING - FIELD THROUGH LABORATORY

I PLANNING A SAMPLING PROGRAM

A Factors to Consider:

1 Locating sampling sites

2 Sampling equipment

3 Type of sample required

a grab
b composite

4 Amount of sample required

5 Frequency of collection

6 Preservation measures, if any

B Decisive Criteria

1 Nature of the sample source

2 Stability of constituent(s) to be measured

3 Ultimate use of data

II REPRESENTATIVE SAMPLES

If a sample is to provide meaningful and valid data about the parent population, it must be representative of the conditions existing in that parent source at the sampling location.

A The container should be rinsed two or three times with the water to be collected.

B Compositing Samples

1 For some sources, a composite of samples is made which will represent the average situation for stable constituents.

2 The nature of the constituent to be determined may require a series of separate samples.

C The equipment used to collect the sample is an important factor to consider. ASTM[1] has a detailed section on various sampling devices and techniques.

D Great care must be exercised when collecting samples in sludge or mud areas and near benthic deposits. No definite procedure can be given, but careful effort should be made to obtain a representative sample.

III SAMPLE IDENTIFICATION

A Each sample must be unmistakably identified, preferably with a tag or label. The required information should be planned in advance.

B An information form preprinted on the tags or labels provides uniformity of sample records, assists the sampler, and helps ensure that vital information will not be omitted.

C Useful Identification Information includes:

1 sample identity code
2 signature of sampler
3 signature of witness
4 description of sampling location detailed enough to accommodate reproducible sampling. (It may be more convenient to record the details in the field record book).
5 sampling equipment used
6 date of collection
7 time of collection
8 type of sample (grab or composite)
9 water temperature
10 sampling conditions such as weather, water level, flow rate of source, etc.
11 any preservative additions or techniques
12 record of any determinations done in the field
13 type of analyses to be done in laboratory

IV SAMPLE CONTAINERS

A Available Materials

1 glass
2 plastic
3 hard rubber

B Considerations

1 Nature of the sample - Organics attack polyethylene.

2 Nature of constituent(s) to be determined - Cations can adsorb readily on some plastics and on certain glassware. Metal or aluminum foil cap liners can interfere with metal analyses.

3 Preservatives to be used - Mineral acids attack some plastics.

4 Mailing Requirements - Containers should be large enough to allow extra volume for effects of temperature changes during transit. All caps should be securely in place. Glass containers must be protected against breakage. Styrofoam linings are useful for protecting glassware.

C Preliminary Check

Any question of possible interferences related to the sample container should be resolved before the study begins. A preliminary check should be made using corresponding sample materials, containers, preservatives and analysis.

D Cleaning

If new containers are to be used, preliminary cleaning is usually not necessary.

If the sample containers have been used previously, they should be carefully cleaned before use.

There are several cleaning methods available. Choosing the best method involves careful consideration of the nature of the sample and of the constituent(s) to be determined.

1 Phosphate detergents should not be used to clean containers for phosphorus samples.

2 Traces of dichromate cleaning solution will interfere with metal analyses.

E Storage

Sample containers should be stored and transported in a manner to assure their readiness for use.

V SAMPLE PRESERVATION

Every effort should be made to achieve the shortest possible interval between sample collection and analyses. If there must be a delay and it is long enough to produce significant changes in the sample, preservation measures are required.

At best, however, preservation efforts can only retard changes that inevitably continue after the sample is removed from the parent population.

A Functions

Methods of preservation are relatively limited. The primary functions of those employed are:

1 to retard biological action
2 to retard precipitation or the hydrolysis of chemical compounds and complexes
3 to reduce volatility of constituents

B General Methods

1 pH control - This affects precipitation of metals, salt formation and can inhibit bacterial action.

2 Chemical Addition - The choice of chemical depends on the change to be controlled.

Mercuric chloride is commonly used as a bacterial inhibitor. Disposal of the mercury-containing samples is a problem and efforts to find a substitute for this toxicant are underway.

To dispose of solutions of inorganic mercury salts, a recommended procedure is to capture and retain the mercury salts as the sulfide at a high pH. Several firms have tentatively agreed to accept the mercury sulfide for re-processing after preliminary conditions are met.[4]

3 Refrigeration and Freezing - This is the best preservation technique available, but it is not applicable to all types of samples. It is not always a practical technique for field operations.

C Specific Methods

The EPA Methods Manual[2] includes a table summarizing the holding times and preservation techniques for several analytical procedures. This information also can be found in the standard references[1, 2, 3] as part of the discussion of the determination of interest.

VI METHODS OF ANALYSIS

Standard reference books of analytical procedures to determine the physical and chemical characteristics of various types of water samples are available.

A EPA Methods Manual

The Analytical Quality Control Laboratory, Office of Research and Monitoring, Environmental Protection Agency, has published a manual of analytical procedures to be used in Office of Water Programs laboratories for the analysis of water and wastes. The title of this manual is "Methods for Chemical Analysis of Water and Wastes" (1971).

For some procedures, the analyst is referred to Standard Methods and/or to ASTM Standards.

B Standard Methods

The American Public Health Association, the American Water Works Association and the Water Pollution Control Federation prepare and publish a volume describing methods of water analysis. These include physical and chemical procedures. The title of this book is "Standard Methods for the Examination of Water and Wastewater", 13th edition, 1971.

C ASTM Standards

The American Society for Testing and Materials publishes an annual "book" of specifications and methods for testing materials. The "book" currently consists of 33 parts. The part applicable to water is a book titled, "Annual Book of ASTM Standards, Part 23, Water; Atmospheric Analysis".

D Other References

Current literature and other books of analytical procedures with related information are available to the analyst.

VII ORDER OF ANALYSES

The ideal situation is to perform all analyses shortly after sample collection. In the practical order, this is rarely possible. The allowable holding time for preserved samples is the basis for scheduling analyses.

A The allowable holding time for samples depends on the nature of the sample, the stability of the constituent(s) to be determined and the conditions of storage.

1 For some constituents and physical values, immediate determination is required, e.g. dissolved oxygen, pH.

2 Using preservation techniques, the holding times for other determinations range from 6 hours (BOD) to 7 days (COD). Metals may be held up to 6 months.[2]

3 The EPA Methods Manual[2] includes a table summarizing holding times and preservation techniques for several analytical procedures. This information can also be found in the standard

references[1, 2, 3] as part of the discussion of the determination of interest.

4 If dissolved concentrations are sought, filtration should be done in the field if at all possible. Otherwise, the sample is filtered as soon as it is received in the laboratory. A 0.45 micron membrane filter is recommended for reproducible filtration.

B The time interval between collection and analysis is important and should be recorded in the laboratory record book.

VIII RECORD KEEPING

The importance of maintaining a bound, legible record of pertinent information on samples cannot be over-emphasized.

A Field Operations

A bound notebook should be used. Sample information written in it would include:

1 Sample identification records (See Part III)

2 Any information requested by the analyst as significant

3 Details of sample preservation

4 A complete record of data on any determinations done in the field. (See B, next)

5 Shipping details and records

B Laboratory Operations

Samples should be logged in as soon as received and the analyses performed as soon as possible.

A bound notebook should be used. Preprinted data forms provide uniformity of records and help ensure that required information will be recorded. Such sheets should be permanently bound.

Items in the laboratory notebook would include:

1 sample identifying code
2 date and time of collection
3 date and time of analysis
4 the analytical method used
5 any deviations from the analytical method used
6 data obtained during analysis
7 quality control checks used
8 any information useful to those who interpret and use the data
9 signature of the analyst

IX SUMMARY

Valid data can be obtained only from a representative sample, unmistakably identified, carefully collected and stored. A skilled analyst, using reliable methods of analyses and performing the determinations within the prescribed time limits, can produce data for the sample. This data will be of value only if a written record exists to verify sample history from the field through the laboratory.

REFERENCES

1 ASTM Standards, Part 23, Water; Atmospheric Analysis.

2 Methods for Chemical Analysis of Water and Wastes, EPA-AQCL, 1971, Cincinnati, OH 45268.

3 Standard Methods for the Examination of Water and Wastewater, 13th edition, APHA-AWWA-WPCF, 1971.

4 Dean, R., Williams, R. and Wise, R., Disposal of Mercury Wastes from Water Laboratories, Environmental Science and Technology, October, 1971.

This outline was prepared by A. Donahue, Chemist, National Training Center, DTTB, MDS, OWP, EPA, Cincinnati, OH 45268.

FLOW MEASUREMENT

I INTRODUCTION

Flow measurements are among the more important data collected during a water quality survey. Such measurements are used to interpret data variations, calculate loadings, and expedite survey planning. If the analysis of survey data involves estimation of loads, the accurate measurement of discharge assumes a level of importance equal to that of laboratory and analytical results.

In the following discussion, procedures for measurement of stream flow and waste discharge are described. Some of these procedures are used in long-term, very detailed water quality and supply studies; others are more suited to short-term pollution surveys.

II PLANNING

A Station Location

Four factors influence location of gauging or flow measurement stations:

1 Survey objectives

2 Physical accessibility

3 Characteristics of the stream bed

4 Hydrologic effects

Survey objectives represent the major influence on station location; depending upon objectives, gauging stations may be located above and/or below confluences and outfalls.

Physical accessibility determines the ease and cost of installation and maintenance of the station. The characteristics of the stream bed may greatly influence the obtainable accuracy of measurement. For instance, rocky bottoms greatly reduce the accuracy of current meters. Sedimentation in pools behind control structures may influence stage-discharge relationships. Hydrologic variations in stream flow may cause washout or bypass of the gauging station. In the Southwest, flash floods have been known to wash out or bypass gauging stations by assuming different channels of flow.

B Methodology

Choice of a specific measurement procedure is dependent upon at least three considerations:

1 The relation between obtainable and desired accuracy

2 Overall cost of measurement

3 The quantity of flow to be measured

Ideally, discharge measurements should be reported to a specific degree of accuracy; the gauging procedure greatly influences this accuracy. The influence of overall cost on the gauging program is readily apparent. Extensive, detailed studies are usually characterized by high costs for automatic instrumentation and low personnel cost; the opposite is usually true for less detailed studies. The range of flows to be measured (within acceptable accuracy) is, of course, not known prior to the survey. However, experienced personnel usually can make reasonable estimates of expected flows from visual observations and other data, and may recommend appropriate gauging procedures. In this regard, experienced personnel always should be consulted.

III MEASUREMENT

A Streams, Rivers, and Open Channels

1 Current Meter

The current meter is a device for measuring the velocity of a flowing body of water. The stream cross section is divided into a number of smaller sections, and the average velocity in each section is determined. The discharge is then found by summing the products of area and velocity of each section.

2 Stage-discharge relationships

Large flows usually are measured by development of and reference to a stage-discharge curve; this procedure has long been used by the U. S. Geological Survey. Such gauging stations are composed of a control structure located downstream of the location of measurement and some type of water level indicator which identifies the height of the water surface above a previously determined datum.

Location of the control structure so that reliable measurements of flow will be obtained at all river stages is particularly important. The water level may be continuously recorded by an automatic recorder located in a wet well or may be indicated directly on a staff gauge located at the bank of the river. Such stations must be calibrated by measurement of flow by velocity-area methods (current meter) at all expected stages of river flow.

3 Weirs

A weir may be defined as a dam or impediment to flow, over which the discharge conforms to an equation. The edge or top surface over which the liquid flows is called the weir crest. The sheet of liquid falling over the weir is called the nappe. The difference in elevation between the crest and the liquid surface at a specified location, usually a point upstream, is called the weir head. Head-discharge equations based on precise installation requirements have been developed for each type of weir. Weirs so installed are called standard weirs. Equations for non-standard installations or unusual types may be derived empirically.

Weirs are simple, reliable measurement devices and have been investigated extensively in controlled experiments. They are usually installed to obtain continuous or semi-continuous records of discharge. Limitations of weirs include difficulty during installation, potential siltation in the weir pond, and a relatively high head requirement, 0.4 - 2.0 feet. Frequent errors in weir installation include insufficient attention to standard installation requirements and failure to assure completely free discharge of the nappe.

a Standard suppressed rectangular weir

This type of weir is essentially a dam placed across a channel. The height of the crest is so controlled that construction of the nappe in the vertical direction is fully developed. Since the ends of the weir are coincident with the sides of the channel lateral contraction is impossible. This weir requires a channel of rectangular cross section, other special installation conditions, and is rarely used in plant survey work. It is more commonly used to measure the discharge of small streams.

The standard equation for discharge of a suppressed rectangular weir (Francis equation) is:

$$Q = 3.33\ LH^{3/2}$$

where

Q = discharge, cfs
L = length of the weir crest, feet
H = weir head, feet

The performance of this type of weir has been experimentally investigated more intensively than that of other weirs. At least six forms of the discharge equation are commonly employed. The standard suppressed weir is sometimes used when data must be unusually reliable.

b Standard contracted rectangular weir

The crest of this type of weir is shaped like a rectangular notch. The sides and level edge of the crest are so removed from the sides and bottom of the channel that contraction of the nappe is fully developed in all directions. This weir is commonly used in both plant surveys and measurement of stream discharge.

The standard equation for discharge of a contracted rectangular weir (corrected Francis equation) is

$$Q = 3.33\ (L - 0.2H)H^{3/2}$$

where

Q = discharge, cfs
L = length of the level crest edge, feet
H = weir head, feet
0.2H = correction for end contractions as proposed by Francis

c Cipolletti weir

The Cipolletti weir is similar to the contracted rectangular weir except that the sides of the weir notch are inclined outward at a slope of 1 horizontal to 4 vertical. Discharge through a Cipolletti weir occurs as though end contractions were absent and the standard equation does not include a corresponding factor for correction.

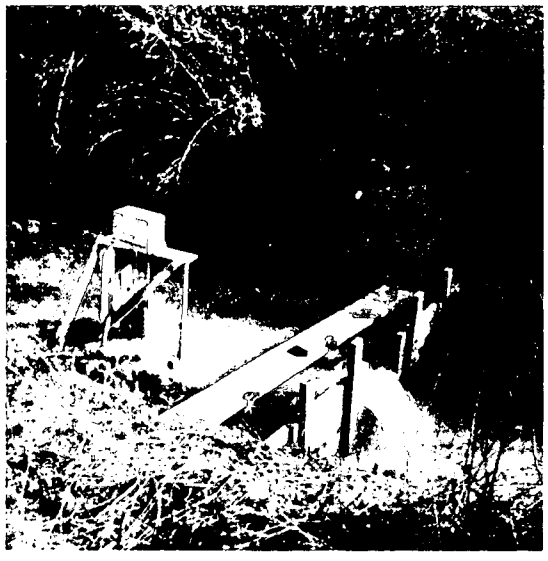


Figure 1. STANDARD CONTRACTED RECTANGULAR WEIR

The standard equation for discharge through a Cipolletti weir is

$$Q = 3.367\ LH^{3/2}$$

where

Q = discharge, cfs

L = length of the level crest edge, feet

H = weir head, feet

The discharge of a Cipolletti weir exceeds that of a suppressed rectangular weir of equal crest length by approximately 1 percent.

d Triangular weirs

The crest of a triangular weir is shaped like a V-notch with sides equally inclined from the vertical. The central angle of the notch is normally 60 or 90 degrees. Since the triangular weir develops more head at a given discharge than does a rectangular shape, it is especially useful for measurement of small or varying flow. It is preferred for discharges less than 1 cfs, is as accurate as other shapes up to 10 cfs, and is commonly used in plant surveys.

The standard equation for discharge of a 90° triangular weir (Cone formula) is

$$Q = 2.49H^{2.48}$$

where

Q = discharge, cfs
H = weir head, feet

Crest height and head are measured to and from the point of the notch, respectively.

e Accuracy and installation requirements

Quotations of weir accuracy express the difference in performance between two purportedly identical weirs and do not include the effects of random error in measurement of head. Weirs installed according to the following specifications should measure discharge within ± 5% of the values observed when the previously cited standard equations were developed.

1) The upstream face of the bulkhead and/or weir plate shall be smooth and in a vertical plane perpendicular to the axis of the channel.

2) The crest edge shall be level, shall have a square upstream corner, and shall not exceed 0.08 in (2 mm) in thickness. If the weir plate is thicker than the prescribed crest thickness the downstream corner of the crest shall be relieved by a 45° champfer.

3) The pressure under the nappe shall be atmospheric. The maximum water surface in the downstream channel shall be at least 0.2 ft. below the weir crest. Vents shall be provided at the ends of standard suppressed weirs to admit air to the space beneath the nappe.

4) The approach channel shall be straight and of uniform cross section for a distance above the weir of 15 to 20 times the maximum head, or shall be so baffled that a normal distribution of velocities exists in the flow approaching the crest and the water surface at the point of head measurement is free of disturbances. The cross-sectional area of the approach channel shall be at least 6 times the maximum area of the nappe at the crest.

5) The height of the crest above the bottom of the approach channel shall be at least twice, and preferably 3 times, the maximum head and not less than 1 foot. For the standard suppressed weir the crest height shall be 5 times the maximum head. The height of triangular weirs shall be measured from the channel bottom to the point of the notch.

6) There shall be a clearance of at least 3 times the maximum head between the sides of the channel and the intersection of the maximum water surface with the sides of the weir notch.

7) For standard rectangular suppressed, rectangular contracted, and Cipolletti weirs the maximum head shall not exceed 1/3 the length of the level crest edge.

8) The head on the weir shall be taken as the difference in elevation between the crest and the water surface at a point upstream a distance of 4 to 10 times the maximum head or a minimum of 6 feet.

9) The head used to compute discharge shall be the mean of at least 10 separate measurements taken at equal intervals. The head range of the measuring device shall be 0.2 - 1.5 feet.

The capacities of weirs which conform to these specifications are indicated in Table 1.

4 Parshall flume

The Parshall flume is an open constricted channel in which the rate of flow is related to the upstream head or to the difference between upstream and downstream heads. It consists of an entrance section with converging vertical walls and level floor, a throat section with parallel walls and floor declining downstream, and an exit section with diverging walls and floor inclining downstream. Plan and sectional views are shown in Figure 2. Advantages of the Parshall flume include a low head requirement, dependable accuracy, large capacity range, and self cleaning capability. Its primary disadvantage is the high cost of fabrication; this cost may be avoided by use of a prefabricated flume. Use of prefabricated flumes during plant surveys is becoming increasingly popular.

a Standard equations

The dimensions of Parshall flumes are specified to insure agreement with standard equations. Table of dimensions are available from several sources [3, 4]. For flumes of 6 inch to 8 foot throat width the following standard equations have been developed.

1) 6 inch throat width

$$Q = 2.06\ H_a^{1.58}$$

2) 9 inch throat width

$$Q = 3.07\ H_a^{1.53}$$

TABLE 1 DISCHARGE OF STANDARD WEIRS

Crest Length (Feet)	Contracted Rectangular* Weir (discharge-cfs)		Suppressed Rectangular* Weir (discharge-cfs)		Cipolletti* Weir (discharge-cfs)		90° Triangular* Weir (discharge-cfs)	
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
1.0	.590	.286	.631	.298	.638	.301		
1.5	1.65	.435	1.77	.447	1.79	.452		
2.0	3.34	.584	3.65	.596	3.69	.602		
2.5	5.87	.732	6.30	.744	6.37	.753		
3.0	9.32	.881	10.0	.893	10.1	.903		
3.5	13.8	1.03	14.8	1.04	15.0	1.05		
4.0	19.1	1.18	20.4	1.19	20.6	1.20		
4.5	25.6	1.33	27.5	1.34	27.8	1.35		
							6.55	.046
5.0	28.8	1.48	30.6	1.49	30.9	1.51		
6.0	34.9	1.78	36.7	1.79	37.1	1.81		
7.0	41.0	2.07	42.8	2.08	43.3	2.11		
8.0	47.1	2.37	48.9	2.38	49.5	2.41		
9.0	53.2	2.67	55.0	2.68	55.7	2.71		
10.0	59.3	2.97	61.1	2.98	62.0	3.01		

* $H \geq 0.2$ ft, $H \leq 1.5$ ft, $H \leq 1/3$ L

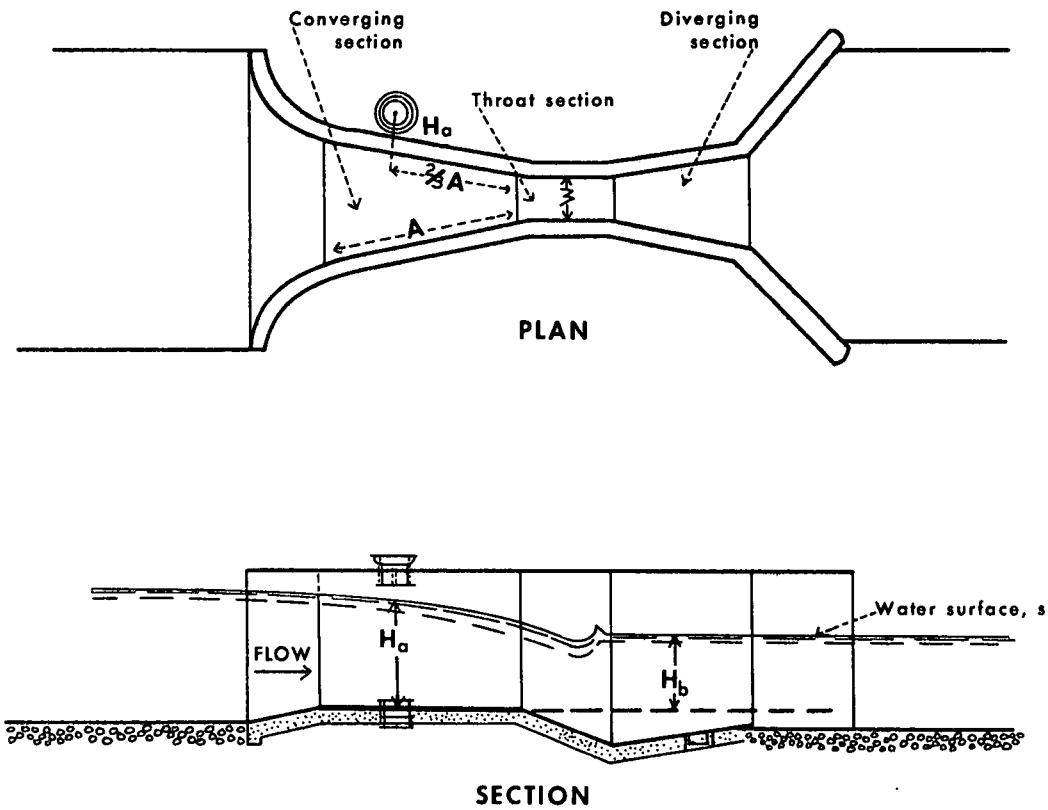


FIGURE 2 PARSHALL FLUME

3) 1 to 8 foot throat width

$$Q = 4WH_a^{1.522W^{0.026}}$$

where

Q = free-flow discharge, defined as that condition which exists when the elevation of the downstream water surface above the crest, H_b, does not exceed a prescribed percentage of the upstream depth above the crest, H_a. The prescribed percentage of submergence is 60 percent for 6 and 9 inch flumes and 70 percent for 1 to 8 foot flumes

W = throat width, feet

H_a = upstream head above the flume crest

b Head loss

The head required by a Parshall flume is greater than (H_a - H_b) because H_a is measured at a point in the converging section where the water surface has already begun to decline. Table 2 indicates the total head requirements of standard Parshall flumes. These losses should be added to the normal channel depth to determine the elevation of the water surface at the flume entrance. No head losses are indicated for discharge-throat width combinations for which H_a is less than 0.2 ft. or greater than 2/3 the sidewall depth in the converging section.

c Accuracy and installation requirements

A Parshall flume will measure discharge within ± 5% of the standard value if the following conditions are observed.

1) The dimensions of the flume shall conform to standard specifications.

2) The downstream head, H_b, shall not exceed the recommended percentage of the upstream head, H_a.

TABLE 2 HEAD LOSS IN STANDARD PARSHALL FLUMES UNDER FREE DISCHARGE

Discharge (cfs)	Head Loss, Feet, in Flume of Indicated Width							
	1 foot	2 feet	3 feet	4 feet	5 feet	6 feet	7 feet	8 feet
0.5	.08							
1.0	.14	.09	.06					
2.5	.26	.16	.12	.10	.08	.07	.06	.05
5.0	.42	.27	.20	.16	.13	.12	.10	.09
10.0	.70	.45	.34	.27	.22	.19	.17	.15
30.0			.70	.56	.47	.40	.35	.30
50.0					.68	.57	.49	.41

$H_a \geq 0.2$, $H_a \leq 2.0$

3) The upstream head shall be measured in a stilling well connected to the flume by a pipe approximately 1-1/2 inches in diameter.

4) The flume shall be installed in a straight channel with the centerline of the flume parallel to the direction of flow.

5) The flume shall be so chosen, installed, or baffled that a normal distribution of velocities exists at the flume entrance.

5 Tracer materials

Techniques, materials, and instruments are presently being refined to permit accurate measurement of instantaneous or steady flow with several tracer materials. Measurements are made by one of two methods:

a Continuous addition of tracer

b Slug injection

With the first method, tracer is injected into a stream at a continuous and uniform rate; with the second a single dose of tracer material is added. Both methods depend on good transverse mixing and uniform dispersion throughout a stream. The concentration of tracer material is measured downstream from the point of addition. When continuous addition is employed, flow rates are calculated from the equation:

$$q \cdot C = (Q + q)\, c$$

in which q = rate of tracer addition to the stream at concentration, C, Q = the stream flow rate, and c = the resulting concentration of the stream flow combined with the tracer. For the slug injection method

$$Q = \frac{S}{\bar{c}\ \Delta t}$$

in which Q = the stream discharge, S = the quantity of tracer added, $\bar{c}$ = the weighted average concentration of tracer material during its passage past the sampling point, and Δt = the total time of the sampling period. Disadvantages of tracer methods include mixing, natural adsorption and interference, and high equipment costs.

6 Floats

Floats may be used to estimate the time of travel between two points a known distance apart. The velocity so obtained may be multiplied by 0.85 to give the average velocity in the vertical. Knowing the mean velocity and the area of the flowing stream, the discharge may be estimated. Floats should be employed only when other methods are impractical.

B Pipes and Conduits

1 Weirs and Parshall flumes

Weirs and Parshall flumes are commonly installed in manholes and junction boxes and at outfalls to measure flow in pipes. All conditions required for measurement of open channel flow must be observed.

2 Tracer materials

These methods are popular for measurement of pipe flow because they do not require installation of equipment or modification of the flow. These are especially convenient for measurement of exfiltration and infiltration.

3 Depth-slope

If the depth of the flowing stream and the slope of the sewer invert are known, the discharge may be computed by means of any one of several formulas.

a Manning formula

$$Q = \frac{1.486}{n}\ A\ R^{2/3} S^{1/2}$$

where

Q = discharge, cfs

n = roughness coefficient

A = area of flow, sq. ft.

R = hydraulic radius, ft.

= area divided by wetted perimeter, ft.

S = slope, ft. per ft.

b Chezy formula

$$Q = CA\sqrt{RS}$$

where

Q = discharge, cfs

C = friction coefficient

A = area of flow, sq. ft.

R = hydraulic radius, ft.

= area divided by wetted perimeter, ft.

S = slope, ft. per ft.

4 Open end pipe flow

The following methods can be employed when other more precise means are not practical. They can be employed, however, only when there is free discharge to the air.

a Coordinate method (Figures 3, 4, and 5)

Discharge may be computed by the following formula:

$$Q\ (\text{gpm}) = \frac{1800\ AX}{Y}$$

where

A = cross sectional area of liquid in the pipe (sq. ft.)

X = distance between the end of the pipe and the vertical gauge in ft., measured parallel to the pipe.

Y = vertical distance from water surface at the end of the pipe to the intersection of the water surface with the vertical gauge, in ft.

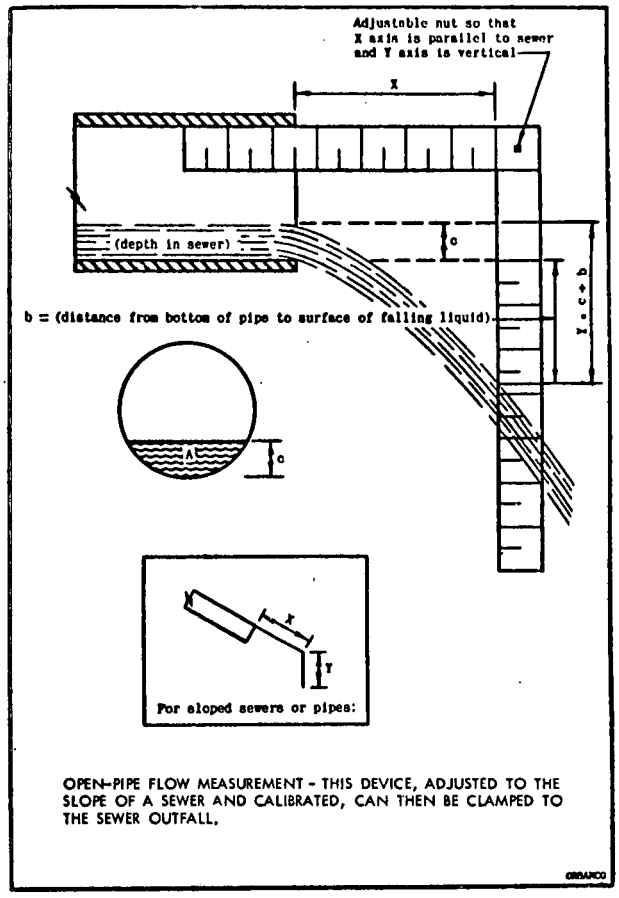


Figure 3

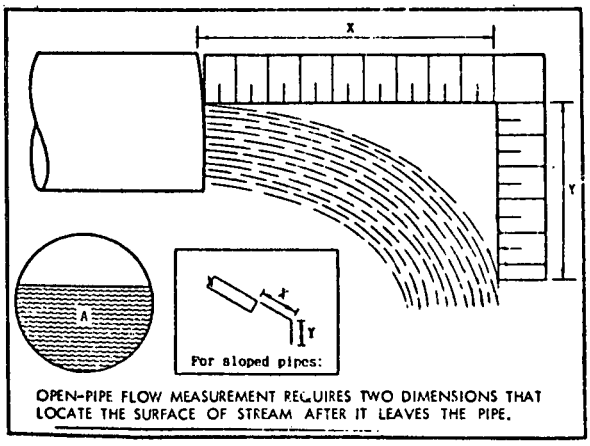


Figure 4

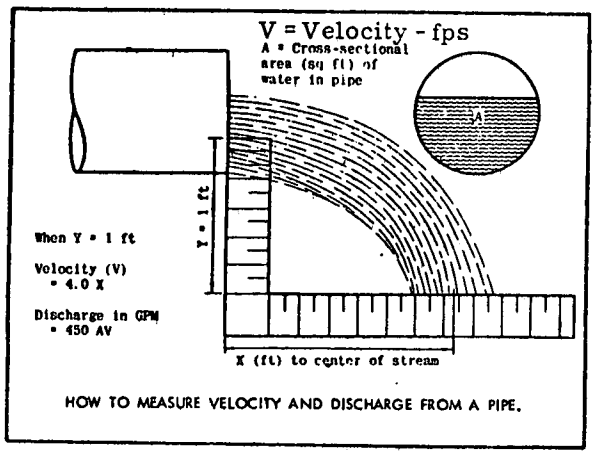


Figure 5

b California pipe flow method (Figure 6)

This method may be used only for horizontal pipes having free discharge. If the pipe is not horizontal, a connection must be made to one that is. The horizontal length must be not less than 6 times the diameter of the pipe. Discharge may be computed by the following formula:

$$Q\ (\text{gpm}) = T \times W$$

$$\text{where } T = 3{,}900\ (1 - \frac{a}{d})^{1.88}$$

$$W = d^{2.48}$$

where a and d are measured in feet

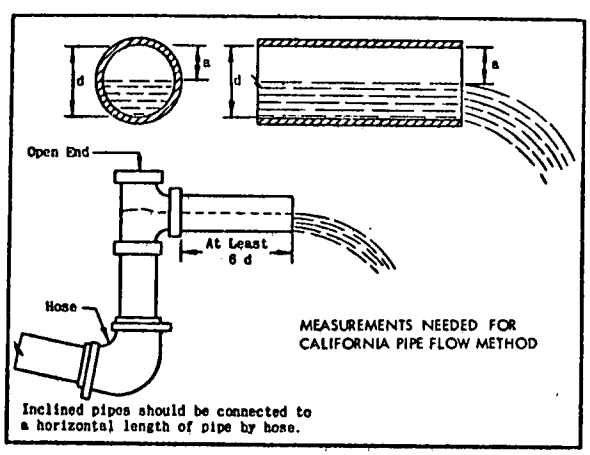


Figure 6

C Head Measuring Devices

Several of the above gauging methods require the measurement of water level in order that discharge may be determined. Any device used for this purpose must be referenced to some zero elevation. For example, the zero elevation for weir measurements is the elevation of the weir crest. The choice of method is dependent upon the degree of accuracy and the type of record desired.

1 Hook gauge

The hook gauge measures water elevation from a fixed point. The hook is dropped below the water surface and then raised until the point of the hook just breaks the surface. This method probably will give the most precise results when properly applied.

2 Staff gauge

The staff gauge is merely a graduated scale placed in the water so that elevation may be read directly.

3 Plumb line

This method involves measurement of the distance from a fixed reference point to the water surface, by dropping a plumb line until it just touches the water surface.

4 Water level recorder

This instrument is used when a continuous record of water level is desired. A float and counterweight are connected by a steel tape which passes over a pulley. The float should be placed in a stilling well. A change in water level causes the pulley to rotate which, through a gearing system, moves a pen. The pen traces water level on a chart which is attached to a drum that is rotated by a clock mechanism. When properly installed and maintained, the water level recorder will provide an accurate, continuous record.

ACKNOWLEDGMENT:

Certain portions of this outline contains training material from prior outlines by P.E. Langdon, A.E. Becher, and P.F. Atkins, Jr.

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TRACING NATURAL WATERS

I INTRODUCTION

The validity of water pollution studies is dependent upon an ability to describe the actual time and space situation of a pollutant as it blends with the natural receiving water. This understanding is important in order to predict the subsequent effects of the pollutant on the receiving water and subsequent users or to detect the sources of pollution.

The nature of this blending is dependent upon the physical and chemical properties of both the pollutant and the receiving water as well as the mixing and flow characteristics of the receiving channel, basin, or aquifer. Tracing is an attempt to approximate the actual motion and mixing of this blend as it moves through the channel, basin or aquifer.

Although there has been scant reference to tracers in texts there has been rapidly increasing number of technical articles describing their use in recent years. A comprehensive compilation of early radioactive tracer studies may be found in the report of the "Time of Flow Studies, Ottawa River, Lima, Ohio"[1] one of the early attempts to compare various tracer techniques under similar field conditions. Several reports (see Bibliography) have discussed the use of dyes during the early 1960's.

More refined and extensive tracer investigations may be expected as experience is gained and as more complex studies arise. A water quality agency should develop competence in at least one tracer technique and would be wise to be capable in some others as well.

II PURPOSES

Tracer applications are still in a highly developmental stage. One finds many words or phrases to suggest similar field findings. In broad terms these measurements are concerned with indications of mass movement, blend mixing, and flow direction. Basically, tracers are used to determine:

A Flow Rates

1 In freshwater channels or lakes such terms as passage time, time of travel, time of flow, flow quantity or flow volume are used.

2 In estuaries such terms as rate of renewal, flushing rate, drift velocity, mass transfer or net (tidal) drift are used. The tidal fluctuation imposes a need for consideration of flow reversal effects.

3 In subsurface waters such terms as recharge rate, flow rate and residence time are used. Related factors such as basin capacity, porosity and permeability are determined.

B Flow Direction

1 In estuaries

a Direction of flow relative to tidal phases which do not necessarily correspond to slack conditions.

b Obscure current circulation as influenced by the interlated factors of tides, winds, Coriolis forces, topography and density gradients.

2 In ground water

a Aquifer may flow contrary to initial superficial impression.

b Hydrostatic conditions may change and reverse normal flow direction.

C Mixing Patterns

1 Short circuit effects

a Eddying - primarily the result of surface channel and basin configuration.

b Stratification - primarily due to temperature and density differences.

c Inter-connections - between aquifers in ground water as well as solution channels and open fractures.

2 Distribution phenomena

a Dispersion of colloidal, soluble and suspended substances

b Diffusion of temperatures or gaseous substances

III TYPES OF STUDIES

Tracers are used in many situations, including:

A Treatment Plant Units

B Closed Conduits

C Open Channels

D Large Water Bodies

E Hydraulic Models

F Subsurface Aquifers

G Subsurface Basins

IV TYPES OF TRACERS

Materials used for tracers include:

A Floats

1 Surface (wooden and plastic devices as well as fruit). Influenced by wind action and debris.

2 Sub-surface "drogues". Apparent direction must be carefully evaluated.

B Salts

1 Common salt - hard to detect when less than 1 mg/l.

2 Brackish and freshwater mixing in estuaries and coastal aquifers.

3 Ammonium chloride. (See Table 1)

C Dyes, such as:

1 Rhodamine series - See section VI

2 Pontacyl Brilliant Pink B - most stable of fluorescent dyes. Rather expensive dye.

3 Fluorescein - very inexpensive. Fluoresces very near natural stream background level.

4 Uranine - fluoresces near stream background level.

D Radioactive substances, such as: (see Table 2) AEC must approve all experiments. AEC has published tables on permissible concentrations in unrestricted areas.[13]

1 Rubidium-86

2 Iodine-131

3 Tritium (H^3) gives best overall performance in subsurface[6] tracing.

4 Krypton-85 - used recently in gas transfer measurement in laboratory and stream studies.[12]

E Waste return characteristics; significant built-in factors such as:

1 Silt - understandably dependent upon velocity and obstructions.

2 Foam - ABS will foam at levels as low as 1 - 5 mg/l depending on hardness.

Table 1. SUBSURFACE NONRADIOISOTOPE FLUID TRACERS

Tracer	Form	Test conditions	Remarks
Chloride Dextrose Fluorescein Dye	NaCl Sugar	Lab: Columns of sand and sandy loam.	Chloride most rapid. Fluorescein far from satisfactory.
Chloride Dextrose Fluorescein Dye	NaCl Sugar	Field: 4 feet thick aquifer of sand and gravel, 90 feet below surface.	Fluorescein considered best of dyes. Chloride in the large conc. required caused density currents.
Dextrose Ammonia Fluorescein Dye Boron	Sugar Chloride H_3BO_3	Field: Added in Conc. of 10,000 ppm, 500 ppm, 50 ppm, and 200 ppm respectively into a 4 foot thick sand horizon at 2,100 feet below surface in McKean County, Pennsylvania.	Adsorption observed: dextrose - little or none, boron - slight (conc. dropped 30%) ammonia - moderate, fluorescein - strong (moved at rate about 1/10 that of flood water). Greenburg[33] found that borax in Hanford fine sandy loam penetrated only 2 feet.
Boron	$Na_2B_4O_7 \cdot 10H_2O$ H_3BO_3	Field: Injection into input wells. Dilution factor ~5.	Limit of detection is reached after 10^3 dilution.
Thiocyanate	NH_4SCN Alkali-Metal SCN	Field: Water flooding.	Dilution possible 10^5.
Rhodamine B		Field: Karst topography.	Dye not detected after 6×10^6 dilution.
Oxygen-18 Deuterium	H_2O HDO		Variations resulting from seasonal fluctuations are useful to study climate. (Also useful in meteorology and glaciology).

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Table 2. SUBSURFACE RADIOISOTOPE FLUID TRACERS - FIELD TESTS[6]

Tracer	Half-life	Form	Test conditions	Remarks
H^3	12.5 y.	HTO	Karst groundwater	Useful results up to 30 km distance.
			Chalk River soil, undisturbed, but penetrated with driven piezometers.	Fluorescein dye traveled only about 3/4 as fast as tritium.
			Glaciofluvial sand and gravel, various till soils, and fissures and channels.	Chromium complex traveled as fast as tritium.
S^{35}	89.d	Na_2SO_4	Chalk River soil at waste disposal site.	Lags behind tritium indicating some interaction with the soil. In soil containing appreciable amounts of gypsum there would be exchange and loss of S^{35}.
I^{131}	8 d.	Iodine, carrier free	4 feet thick aquifer of sand and gravel, 90 feet below surface.	Should be used with several ppm stable iodine carrier.
I^{131} Co^{60}	8 d. 5.2 y.	KI EDTA - (Co) and $K_3Co(CN)_6$	Tracer compounds used with carriers KI, EDTA-(Na) and $K_3Co(CN)_6$. Limestone aquifer consisted of some argillaceous material and marly dolomite. Single-well pulse technique.	Co^{60} complex unsuitable in this aquifer. $K_3Co^{60}(CN)$ appeared to be most suitable of tracers tested in limestone aquifer.
Br^{82}	36 h.	NH_4Br	Aquifers in alluvium and permeable strata in calcareous marl series.	Br^{82} satisfactory under these conditions.
Rb^{86}	19 d.	RbCI	Groundwater direction at reservoir site in Egypt.	Tracer detectable 7 miles from injection after 5 d.
I^{131} P^{32}	8 d. 14 d.	NaI Na_2HPO_4	Single pulse tracing at dam site for Jesenitz Reservoir on Odrava River in Czechoslovakia.	Detected very high subterranean water velocity necessitating sealing of porous layer.
I^{131} Br^{82} Na^{24}	8 d. 36 h. 15 h.	NaI NaBr NaCI	Single pulse tracing at dam site on arges River in Roumania.	Determined direction and velocity of flow of subsurface water.

Reproduced with permission of Isotopes, Inc.

3 Acid - severe effects upon total stream ecology.

4 Temperature - infra-red filming techniques reveal 1°C temperature differences.

5 Lignins - "Orzan" is a commercial product based upon these non-degrading materials.

6 Dyes - prevalent in textile wastes.

F Biota, various techniques possible with:

1 Mammals

2 Fish

3 Shellfish

V DESIRABLE CHARACTERISTICS

Ideally a tracer should be:

A Biologically innocuous to human and aquatic life, with special reference to

1 Acute toxicity

2 Long-term toxicity

3 Carcinogenic effects

4 Genetic effects

B Stable or persistant despite the effects of

1 Stream chemical constituents

2 Bacteria

3 Sunlight

4 Adsorption

5 Temperature

6 Wind action

7 Inherent decay

8 Channel obstructions

9 Stratification

C Readily detectable either

1 Visually and/or

2 Instrumentally despite dilution or background effects;

D Representative: coincide with the real waste and stream blend under study: this involves miscibility and specific gravity characteristics similar to the blend.

E Economic: this involves careful evaluation of the costs for

1 Materials

2 Material preparation, and release - ease of handling

3 Detection equipment

4 Detection technique and recording - convenience in operation

5 Stream deterioration

F Esthetically agreeable: inoffensive to:

1 Taste

2 Sight - conflict with easy detection

VI ELEMENTS OF A TRACER STUDY - USING RHODAMINE DYES (Currently in widespread use for surface studies.)

A Rhodamine Dyes

1 Available from American Cyanamid, DuPont, Allied Chemical and General Aniline.

2 Price $4.95 per pound except Rhodamine WT which is $10.00 per pound.

3 Specific gravity of 0.99 to 1.12 depending on the proportions of Alcohol, Ethylene Glycol, Acetic Acid, and Water used as solvents in preparing the solution.

4 Solutions normally 15%, 20%, 30%, or 40% dye by weight.

5 pH 1.0 to 9.0.

6 Peak wavelength of adsorption at 525-556μ and of fluorescence at 548-585μ are not normally found in natural waters.

7 Detectable to 0.5 μg/l with continuously sampling and recording equipment.

8 Visibly red to approximately 1.0 mg/l.

9 Rapid dispersion when dropped in water.

10 Subject to some destruction by light, but much less than experienced with fluorescein.

11 Destroyed by agents such as hypochlorite. Rhodamine WT is more resistant.

12 Essentially non-toxic.

B Measuring Equipment

1 Available from Turner Associates, Beckman Instruments, Inc., American Instrument Co., Inc.

2 Price as low as $1,000 for photofluorometer complete or $500 for unit to modify a spectrophotometer.

3 Available for individual grab sample analysis or continuous analysis of sample pumped through instrument.

4 Automatic recorders available.

5 Will measure several dyes (fluorescein, rhodamine, etc.)

C Fluorometer Calibration

The instrument should be calibrated before and after a study. The calibration is a function of temperature (about 2.3%/°C) so two or more runs with temperatures covering the expected range of the study water are desirable. Also it is advisable to make a calibration with the study water. This will check for background and any difference in fluorescent characteristics. A few helpful hints are:

1 Pumping a known concentration sample, from a plastic bag immersed in a constant temperature water bath, through the meter is a convenient calibration procedure. Continuous dousing with a concentrated solution into the bag will give various instrument readings through the detectable ranges.

2 Flush the system with methyl or butyl alcohol solution before each calibration to remove traces of dye.

3 Bubbles in the flow cuvette will cause erratic readings.

4 The fluorometer door is not light tight, so the instrument should be draped and used out of intense light to prevent erroneous high readings.

5 The sample lines on a continuous flow system will transmit light through the instrument door causing erroneous high readings. Taping these tubes with black electrical tape for about one foot will alleviate problem.

D Study Procedures

1 Select objectives which then dictate:

a Length of time to be studied

b Release point

c Monitoring locations and schedules

2 Determine physical properties of affected area.

a Probable net flows

b Total water volumes

c Probable water temperature

d Natural fluorescent background

e Salinity

f Suspended solids

3 Estimate required quantities of dye

4 Calibrate fluorometers

5 Conduct mock run to test equipment

6 Public relations

7 Release and monitor dye

8 Process and interpret data

9 Report

VIII DISPERSION STUDY COMPUTATIONS

A Most Dispersion Equations are Normalized Solutions of Ficks Second Law

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2}$$

c = concentration, x = distance,
t = time, D_x = diffusion coefficient

B Hydraulic Model Studies of the Fate of Pollution

From instantaneous release compute steady state nonconservative pollutant distribution

$$C_{(xy)} = \int f(t) + g(t)$$

where f(t) represents concentration function and g(t) = decay function

C Coastal Water Dispersion Study, Hilo Bay, Hawaii[9]

1 From instantaneous release measure concentration profile during slack water

2 Using these measurements and a two dimensional dispersion model compute D_x and D_y.

3 Two dimensional model

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} - \bar{U} \frac{\partial c}{\partial x} - \bar{V} \frac{\partial c}{\partial y}$$

$\bar{U}$ = velocity in x direction

$\bar{V}$ = velocity in y direction

Normalized solution:

$$C = \frac{W_D}{2\pi\sigma_x\sigma_y} \exp - \frac{1}{2}\left[\left(x - \frac{ut^2}{\sigma_x}\right) + \left(y - \frac{vt^2}{\sigma_y}\right)\right]$$

D Channel Studies

1 From instantaneous release compute longitudinal dispersion coefficient

2 Measure time-concentration profile at given station

3 This C vs. t curve fits equation

$$C = \frac{M}{A(4\pi Dt)^{\frac{1}{2}}} \exp - \frac{(x - ut)^2}{4\ Dt}$$

4 Take log of both sides

$$Ct^{\frac{1}{2}} = \log\left(\frac{M}{A4\pi D}\right) - \frac{(x - ut)^2}{4\ Dt} \log e$$

5 D can be determined from semi-log

plot of $Ct^{\frac{1}{2}}$ vs. $\frac{(x - ut)^2}{t}$

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V SURVEY EVALUATION AND REPORT

	Outline Number
Preparation of Survey Reports	28
Presentation of Data	29
Case Preparation and Courtroom Procedure	30

WATER QUALITY SURVEYS

PREPARATION OF SURVEY REPORTS

I TYPE OF REPORT

The type of stream survey report to be prepared depends on two basic factors. These are the purpose and the audience for whom intended.

A The Purpose of the Report

1 A report of findings or basic data

2 A report of existing causes and effects together with an explanation of how and why.

3 An exposition of existing causes and effects and a projection of conditions that reasonably may occur due to natural variations in stream flow and temperature.

4 A purpose similar to 3 above plus a prediction of the effects of population growth and industrial change.

5 The same purpose as 4 above plus an estimate of the need to protect water uses, and cause reduction in waste loads.

B The Specific Audience for Whom the Report Is Prepared

1 For the record - no expository purpose

2 Other technical agencies with competencies in the same field

3 Other technical agencies in other fields

4 Public officials supporting or opposing the recommendations of the report

5 The general public

C Both in style and content the report should be adequate to serve as a basis for action to accomplish the recommended objectives.

II ORGANIZATION OF REPORT

A Title, Authors, Contents

B Acknowledgement of Aid and Assistance

1 Can be included in a letter of transmittal or submission

2 Can be incorporated in a preface or foreword

3 Should include names of persons and of corporations, public and private, who assisted or aided the survey

C Authority

1 Source of Authority

2 Date of authorization

D Report Summary

1 A brief summary of the report and its recommendations generally precedes the report proper and should include three topics:

a Summary of specific findings

b Conclusions drawn from findings

c Recommendations in general terms.

2 Brevity is essential but not at the expense of clarity.

3 A very brief but lucid description of the stream section involved should be included.

4 This will be the only part of the report read by many of its audience. Consequently it should be drafted with the utmost care.

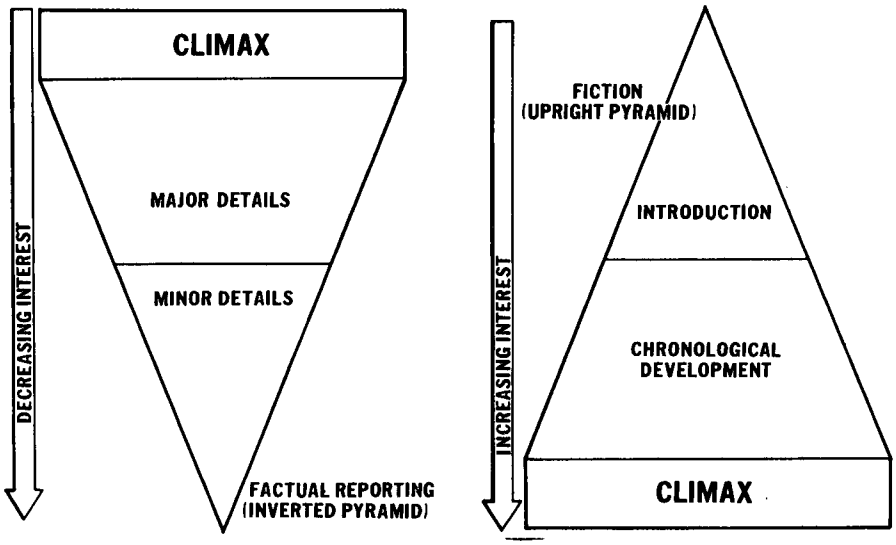


Figure 1

5 Figure 1 illustrates the principles of written communication format. It is important that technical reports be presented in factual report arrangement and NOT in one similar to that of fiction.

6 Figure 2 shows how the various portions of a survey report relate to the generalized factual report.

7 Recommendations, although briefly stated in general terms, should be couched in positive, unexaggerated language.

8 Cost estimates of compliance with recommendations is helpful but not essential.

9 Both tangible and intangible benefits may be listed briefly under conclusions.

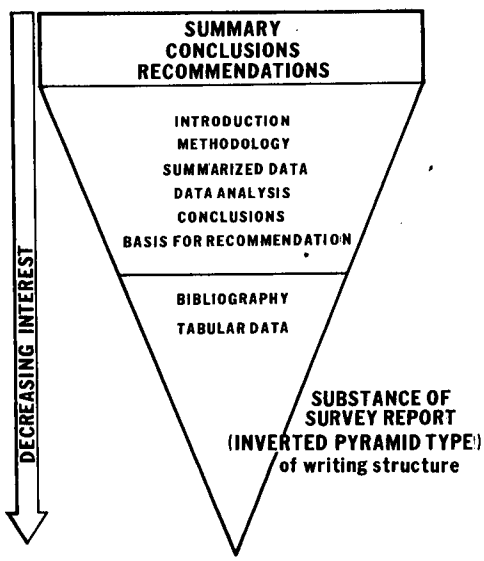


Figure 2

E INTRODUCTION

The body of the report should begin with a statement of the problem and a discussion of the reasons for and the location of the study.

1 Statement of the problem

a A description of the area, emphasizing pertinent features, should be included.

1) The inclusion of pertinent historical data is of value for audience orientation.

2) The relationship of this study to other current water resource studies.

3) Water use and economic data may be important.

b An area map is an absolute necessity.

1) Features included should be carefully selected and section of the stream involved should be emphasized.

2) Do not include unnecessary detail.

3) A general location map usually orients the reader to the area map.

2 Objectives of the Survey

a A statement of the purpose by listing the specific answers sought by the survey to address various aspects of the problem.

b The geographical and time scope of the objectives of the survey.

F Survey Methodology

A complete description of the methods of study employed is an important part of the record.

1 The time period of survey should be noted.

2 All sampling and gauging station locations should be identified by river mile.

3 Sampling and analytical methods

a Provide adequate description of all non-standard methods.

b An appendix for these descriptions may be required if they are lengthy.

4 Frequency of sampling

5 Description of laboratory types and locations

6 Hydrological methods employed for:

a Times of water travel

b Stream flow data

c Any waste flow measurements

G Survey Results

1 Sources of wastes

a Computed waste loads based on known contributing populations and industrial waste strength

b Results of sampling and gauging program

c Data summaries or displays suffice for text of report.

2 Stream data

a Summarized survey in the text

b Complete tabulations including time of collection and averages in appendix

3 Hydrological data

a Usually tabulated with analytical results both in the text and in appendices

b Time of water travel curve or curves

c Stream flow frequency charts

d Pertinent groundwater data

4 Aesthetic considerations are of real importance.

H Analysis and Interpretation of Data

1 Three fundamental procedures are required:

a Comparison of survey results and appropriate water quality criteria

b Projection of survey data to provide for comparison of stream conditions with water quality criteria under more adverse conditions

c Estimates of permissible wastes loads under present and future conditions.

2 Since this topic is the subject of other outlines it will not be further developed here.

3 A description of the methods of analysis and interpretation belong in the report.

a Necessary assumptions should be stated.

b All statistical methods used should be identified.

4 Results of analysis and interpretation are best presented in chart form insofar as possible, to support discussion and interpretation rationale.

I Conclusions

1 Focus of attention, much of it critical, is on this section of the report.

2 Clearness, conciseness, and positiveness are essential.

3 This section indicates reasoning that leads from findings to conclusions.

J Recommendations

1 This is the crux of the report and should answer the question, "What needs to be done to resolve problems delineated in the report?"

2 Cost estimates are highly desirable, if possible, and appropriate.

K Bibliography

1 Useful to the student and perhaps to future workers

2 Entails additional time and effort in assembling references in proper form

III TECHNIQUES AND TOOLS

A Prepare a Detailed Outline

1 This is an important step if the coverage of the report is to be complete and its arrangement logical. It is also a time-saver if properly done.

2 Topics to be included in the outline will become apparent from the foregoing discussion of report content.

B Words are Your Tools

1 Keep dictionary, thesaurus, and glossary available.

2 Define any vague terms or abbreviations.

3 Control superlatives and slang.

4 Avoid emphatics such as "it is to be noted" or "it is a well-known fact".

5 Limit intensive expressions, such as "extremely" or "undoubtedly."

6 Use active verbs when possible.

C Regularly review the report organization and development with a colleague.

This outline was prepared by Staff Members, National Training Center, WPO, EPA, Cincinnati, OH 45268.

PRESENTATION OF DATA

I INTRODUCTION

The data collected during any water quality survey must ultimately be reduced to some simple, expressive form for presentation. Ideally, the data presentation should be easily understood by the least trained personnel as well as by the trained professional. The data presentation alone may determine the response to the survey.

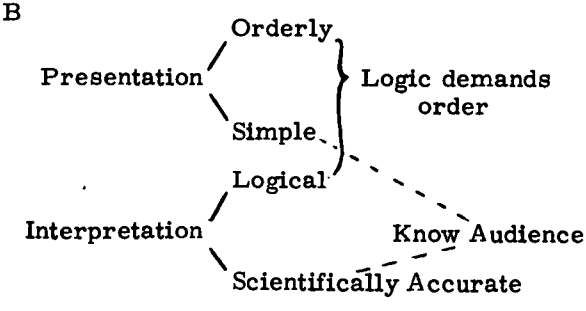
II ANALYSIS OF DATA

A Before one analyzes any information, the data must be set into logical order and the analyst must present the information to himself.

In developing this order, the analyst should keep in mind the objectives of the survey, and the variables encountered during the study.

The analyst's "private" presentation to himself enables him to evaluate or interpret the data in a logical and scientific manner.

B



III PRESENTATION OF DATA

This is one of the most important areas of report writing and unfortunately is often neglected or overlooked.

A Common Methods of Presenting Data

1 Single value

2 Single value plus related information

3 Graphic methods

B Single Value Approach

1 Methods commonly used

a Arithmetic mean

b Geometric mean

c Median value

d Mode value

2 Advantages of using single value approach

a Economical - engineering design criteria is often based on average values. In some instances minimum and maximum values are more critical.

b Instrumentation - advanced analytical techniques and instrumentation are accounting for the collection of tremendous amounts of information. The tendency is to compile this information on computers and use sophisticated statistical methods to arrive at representative mean values.

c Audience - since some readers (local, state or federal legislators) do not have the technical background or (especially), interest to read through many pages of numbers, it becomes convenient to summarize the numerous observations by using single representative values. In effect, the analyst is a salesman, his report being his product.

C Single Value Plus Related Information

1 Methods commonly used

a Single value plus maximum or minimum value

b Single value plus percentage range (usually 80%) of survey or laboratory results

c Single value plus standard deviations from the mean (depending upon degree of confidence required)

d Distribution and frequency distribution tables

2 Advantages of using single value plus related information.

a Eliminates some misinterpretation caused by extremely high or low results that occur rarely.

b Gives an idea of what type of distribution is occuring (normal, skewed, etc.)

c Average values are extremely useful but it is usually the maximum or minimum values that pose serious problems.

D Graphic Methods

One of the easiest, most attractive, and most efficient ways to present numerical information is by use of graphs.

1 Graphs commonly used

a Normal graph paper (Cartesian Coordinate paper) - This is the most generally used graph paper and is most useful in obtaining an idea of the trend the numerical observations are taking. This type of paper is most helpful in preliminary plotting of information to decide if semi-log, log-log or other types of functional graph paper would be more desirable to use.

b Functional graph paper (semi-log, log-log) - Use of this paper allows for the plotting of results in straight line fashion that would appear on normal graph paper (Cartesian Coordinate paper) as a curved line.

c Arithmetic or geometric (log) probability paper - this type of graph plots the normal frequency curve (Bell shaped curve) as a straight line.

d Nomograph - Used where complex equations or complicated mathematical manipulations and calculations are involved. Nomographs have been developed for numerous applications.

e Special graphs

1 3-dimensional diagrams

2 pie-diagrams

3 histograms, etc.

2 Desirable characteristics of graphs

a Fairly simple

b Be able to stand alone

c Graphs should be designed so they may be easily reproduced.

IV SUMMARY

The presentation of information is one of the first steps in report writing. It is one of the most important parts of any report and if properly handled can produce a report that is brief, understandable and useful to the reader. The manner in which results are presented (written or oral) may serve as a basis for judgment of the whole survey.

This outline was prepared by P. F. Atkins, Jr., Sanitary Engineer, formerly with Training Activities, Ohio Basin Region, FWQA.

CASE PREPARATION AND COURTROOM PROCEDURE

I TYPES OF PROCEEDINGS IN WHICH WATER QUALITY EVIDENCE MAY BE USED

A Administrative Proceedings

1 Rule making

a Setting up of regulations having general application, e.g., stream classifications and implementation plan target dates

b Factors of safety and absolute prohibitions may be appropriate

2 Adjudications

a Determinations by agency having expertise with respect to particular discharge or discharger, e.g., approval of plans and specs and time schedule of a particular discharger

B Court Actions

1 Civil in behalf of state or federal government

a Actions to compel action or suspension of action - nuisance, health hazard, etc., --including court action following federal conference --hearing procedure

b Violations of Water Quality Standards

c Violations of Effluent Standards or discharge permits

d Tort or contract actions relating to design and/or operation of treatment facilities

2 Criminal (dependent on content of applicable statutes)

a Discharge of specific materials

b Discharges from specific industries

c Littering

d Discharges harmful to fish and/or crustaceans

e Discharges harmful to specific types of receiving waters

f Discharges of poisons

NOTE--In some of these situations doing the act may constitute the violation; in others proof of intent or knowledge of effects may also have to be proved.

3 Private actions for damages or to compel action

a Alleged harm to plaintiff, e.g., pollution of stream killing animals

C Procedural Matters

1 See Attached sheet "Administrative and Court Proceedings" on Burden of proof, fact finding, and methods of presentation of evidence.

D Classes of Evidence - General Rules

1 Facts - direct

a The material was floating from the outfall.

2 Derived values - expert testimony - test results and/or opinion as to effects

a The D.O. was zero; the waterway was polluted; the plant can be built in 6 months.

3 Hearsay

a Joe told me

4 Relevancy

5 Admissibility vs. weight

a Even if admissible, the weight to be given is up to fact finder--credibility.

E Admissibility of Results of Sampling and Testing (Numbers)

1 Sampling

a Chain of custody

b Tags, etc.

c Containers

d Place and time

e Retention of samples (Proving that the sample represents what is at issue in the action (relevancy), that there has been no opportunity for tampering; and availability of portions for analysis by other side (non-transitory criteria)).

2 Analysis

a Who performed (Can identity of each participant be shown?)

b Admission through supervisor - custodian

c Scientific acceptance of method. Is there a particular method required to be used by the agency?

d Propriety of conduct

e Retention of bench cards and other indicia of results. (Your attorney can make arrangements to substitute copies for originals).

3 Tests

a Comparison with actual conditions

b Mathematical models - how can a computer be cross-examined?

F Admissibility of Expert Opinion on Causes and Effects

1 Who has special knowledge - and of what particular areas?

2 Indicators

3 Significance of numerical determinations or observations

4 Consistency with own prior publications and testimony

5 Have underlying facts been or need to be proved--first hand information of this and/or comparable situations.

6 Use of treatises

G Conduct on the Witness Stand

1 General

a On direct - know what counsel will ask and let him know generally what you will answer, but don't make it sound rehearsed.

b Use layman's language to extent possible.

c Listen to question and answer it to best of your ability.

d Speak so that court reporter, judge, jury, and counsel can hear you.

e Speak in language that will be understood; don't talk down.

f Answer only what you are asked --don't volunteer; however, answer with precision.

g There is nothing wrong with asking to have a question repeated or rephrased.

h There is nothing wrong with saying that you consulted with your attorney before you testified, but beware of the question "Did Mr. X tell you what to say?"

i There is nothing wrong with thinking out your answer before responding.

j You are not expected to know all the answers--if you do not know, admit it.

k Don't attempt to answer questions outside your area of personal knowledge (hearsay) or beyond your expertise. (Your may be an expert on conducting laboratory tests, but not on epidimeological inferences from results).

l Don't try to answer before the judge rules on objection.

m Show that you are an impartial dispenser of information and/or opinion, not a protagonist.

n Don't be afraid to admit what may appear to be damaging.

2 If you are testifying as an expert:

a Establish qualifications -- give information relevant to your area of expertise -- educational (including this course?), work, publications, number of times you have testified previously.

b Differentiate between physical facts (measurements and observations) and opinion (derived values).

c Be prepared to discuss theory (including assumptions) instruments used, techniques(including choice of a particular technique), physical limitations and errors, interferences.

d If experiments were conducted, be able to justify both as to theory and relevancy to this litigation.

e If you're being paid to testify, admit it.

3 Scientific personnel as advisers to counsel:

a Review and refamiliarize self with materials before you discuss with your attorney.

b Be in a position to present all facts known to you simply and concisely: Who, What, When, Where, and Why, How.

c Don't overlook facts and/or test results because you don't think they're important. Let attorney decide what he needs.

d Use of standard report forms

e Ability to recommend additional witnesses with needed specialized knowledge

f Ability to aid in cross-examination of other side's experts and reconcile opinions and/or results

g Be candid - sometimes better not to start a lawsuit or accept a settlement than lose in the end.

H Non-Verbal Presentation of Evidence

1 Exhibits - including photographs

2 Summaries

3 Business and/or government records

a Prepared contemporaneously and in usual course of activities

4 Pre-prepared direct examination

a Usually limited to actions before ICC, FPC, and other federal agencies.

I Criminal Procedure

1 Privilege Against Self Incrimination (available only to persons)

a Warning and suspects

b Effect of duty to report spills

c Effect of duty to obtain license or permit and/or furnish operating reports

d Immunity from prosecution

2 Double Jeopardy

3 Unreasonable search and seizure

a Available to persons and corporations

4 Procedures and need for arrest and search warrants -- possible cause

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This outline was prepared by David I. Shedroff, Enforcement Analyst, Office of Enforcement and General Counsel, Cincinnati Field Investigations Center, 5555 Ridge Avenue, Cincinnati, OH 45268.

Administrative & Court Proceedings, and Excerpts from Revised Draft of Proposed Rules of Evidence for the United States Courts can be found on the following pages.

ADMINISTRATIVE & COURT PROCEEDINGS

Court or Agency	Fact Finder	Burden of Proof	Comments
State Pollution Control Agency	Agency	As per statute - usually weight of evidence.	Hearing may be conducted by hearing examiner, agency member, or full agency. Appeal may be on facts and law or law alone, depending on statute.
Rule making-adjudication			
Federal Water Pollution Control Act			
Conference	Head of agency		Reports acceptable.
Hearing	Hearing Board		Specific testimony.
Court	Judge		Uses prior material, and may take additional testimony.
Court			
Civil Case -- - for money only	Judge or jury	Weight of evidence	
- injunction			
preliminary or temporary	Judge	Must show immediate harm or danger.	Must also show likelihood of success at final hearing - bond required for non-government plaintiff.
permanent	Judge	Usually clear and convincing.	"Balance Equities"
- administrative appeal	Judge - whether "arbitrary and capricious" or substantial evidence.		Sometimes have complete new trial.
Criminal case includes penalties	Jury unless waived.	Beyond reasonable doubt.	Proof of intent may be required.

Excerpts from Revised Draft of Proposed

RULES OF EVIDENCE FOR THE UNITED STATES COURTS

GENERAL PROCEDURES

Rule 102.

PURPOSE AND CONSTRUCTION

These rules shall be construed to secure fairness in administration, elimination of unjustifiable expense and delay, and promotion of growth and development of the law of evidence to the end that the truth may be ascertained and proceedings justly determined.

Rule 101.

PRELIMINARY QUESTIONS

(a) Questions of Admissibility Generally. Preliminary questions concerning the qualification of a person to be a witness, the existence of a privilege, or the admissibility of evidence shall be determined by the judge, subject to the provisions of subdivision (b). In making his determination he is not bound by the rules of evidence except those with respect to privileges.

(b) Relevancy Conditioned on Fact. When the relevancy of evidence depends upon the fulfillment of a condition of fact, the judge shall admit it upon, or subject to, the introduction of evidence sufficient to support a finding of the fulfillment of the condition.

Rule 615.

EXCLUSION OF WITNESSES

At the request of a party the judge shall order witnesses excluded so that they cannot hear the testimony of other witnesses, and he may make the order of his own motion. This rule does not authorize exclusion of (1) a party who is a natural person, or (2) an officer or employee of a party which is not a natural person designated as its representative by its attorney, or (3) a person whose presence is shown by a party to be essential to the presentation of his cause.

Rule 611.

MODE AND ORDER OF INTERROGATION AND PRESENTATION

(a) Control by Judge. The judge may exercise reasonable control over the mode and order of interrogating witnesses and presenting evidence so as to (1) make the interrogation and presentation effective for the ascertainment of the truth, (2) avoid needless consumption of time, and (3) protect witnesses from harassment or undue embarrassment.

(b) Scope of Cross-Examination. A witness may be cross-examined on any matter relevant to any issue in the case, including credibility. In the interests of justice, the judge may limit cross-examination with respect to matters not testified to on direct examination.

Rule 613.

PRIOR STATEMENTS OF WITNESSES

(a) Examining Witness Concerning Prior Statement. In examining a witness concerning a prior statement made by him, whether written or not, the statement need not be shown or its contents disclosed to him at that time, but on request the same shall be shown or disclosed to opposing counsel.

JUDICIAL NOTICE

Rule 201.

JUDICIAL NOTICE OF ADJUDICATIVE FACTS

(b) Kinds of Facts. A judicially noticed fact must be one not subject to reasonable dispute in that it is either (1) generally known within the territorial jurisdiction of the trial court or (2) capable of accurate and ready determination by resort to sources whose accuracy cannot reasonably be questioned.

(g) Instructing Jury. The judge shall instruct the jury to accept as established any facts judicially noticed.

RELEVANCE

Rule 401.

DEFINITION OF "RELEVANT EVIDENCE"

"Relevant evidence" means evidence having any tendency to make the existence of any fact that is of consequence to the determination of the action more probable or less probable than it would be without the evidence.

Rule 402.

RELEVANT EVIDENCE GENERALLY ADMISSIBLE;
IRRELEVANT EVIDENCE INADMISSIBLE

All relevant evidence is admissible, except as otherwise provided by these rules, by other rules adopted by the Supreme Court, by Act of Congress, or by the Constitution of the United States. Evidence which is not relevant is not admissible.

COMPETENCY OF WITNESSES

Rule 601.

GENERAL RULE OF COMPETENCY

Every person is competent to be a witness except as otherwise provided in these rules.

Rule 602.

LACK OF PERSONAL KNOWLEDGE

A witness may not testify to a matter unless evidence is introduced sufficient to support a finding that he has personal knowledge of the matter. Evidence to prove personal knowledge may, but need not, consist of the testimony of the witness himself. This rule is subject to the provisions of Rule 703, relating to opinion testimony by expert witnesses.

EXPERT TESTIMONY

Rule 702.

TESTIMONY BY EXPERTS

If scientific, technical, or other specialized knowledge will assist the trier of fact to understand the evidence or to determine a fact in issue, a witness qualified as an expert by knowledge, skill, experience, training, or education, may testify thereto in the form of an opinion or otherwise.

Rule 703.

BASES OF OPINION TESTIMONY BY EXPERTS

The facts or data in the particular case upon which an expert bases an opinion or inference may be those perceived by or made known to him at or before the hearing. If of a type reasonably relied upon by experts in the particular field in forming opinions or inferences upon the subject, the facts or data need not be admissible in evidence.

Rule 705.

DISCLOSURE OF FACTS OR DATA UNDERLYING EXPERT OPINION

The expert may testify in terms of opinion or inference and give his reasons therefore without prior disclosure of the underlying facts or data, unless the judge requires otherwise. The expert may in any event be required to disclose the underlying facts or data on cross-examination.

Rule 706.

COURT APPOINTED EXPERTS

(a) Appointment. The judge may on his own motion or on the motion of any party enter an order to show cause why expert witnesses should not be appointed, and may request the parties to submit nominations. The judge may appoint any expert witnesses agreed upon by the parties, and may appoint witnesses of his own selection. An expert witness shall not be appointed by the judge unless he consents to act. A witness so appointed shall be informed of his duties by the judge in writing, a copy of which shall be filed with the clerk, or at a conference in which the parties shall have opportunity to participate. A witness so appointed shall advise the parties of his findings, if any; his deposition may be taken by any party; and he may be called to testify by the judge or any party. He shall be subject to cross-examination by each party, including a party calling him as a witness.

HEARSAY

Rule 801.

DEFINITIONS

The following definitions apply under this Article:

(a) Statement. A "statement" is (1) an oral or written assertion or (2) nonverbal conduct of a person, if it is intended by him as an assertion.

(b) Declarant. A "declarant" is a person who makes a statement.

(c) Hearsay. "Hearsay" is a statement, other than one made by the declarant while testifying at the trial or hearing, offered in evidence to prove the truth of the matter asserted.

Rule 802.

HEARSAY RULE

Hearsay is not admissible except as provided by these rules or by other rules adopted by the Supreme Court or by Act of Congress.

Rule 803.

HEARSAY EXCEPTIONS: AVAILABILITY OF DECLARANT IMMATERIAL

The following are not excluded by the hearsay rule, even though the declarant is available as a witness:

(5) Recorded Recollection. A memorandum or record concerning a matter about which a witness once had knowledge but now has insufficient recollection to enable him to testify fully and accurately, shown to have been made when the matter was fresh in his memory and to reflect that knowledge correctly. If admitted, the memorandum or record may be read into evidence but may not itself be received as an exhibit unless offered by an adverse party.

(6) Records of Regularly Conducted Activity. A memorandum, report, record, or data compilation, in any form, of acts, events, conditions, opinions, or diagnoses, made at or near the time by, or from information transmitted by, a person with knowledge, all in the course of a regularly conducted activity, as shown by the testimony of the custodian or other qualified witness, unless the sources of information or other circumstances indicate lack of trustworthiness.

(18) Learned Treatises. To the extent called to the attention of an expert witness upon cross-examination or relied upon by him in direct examination, statements contained in published treatises, periodicals, or pamphlets on a subject of history, medicine, or other science or art, established as a reliable authority by the testimony or admission of the witness or by other expert testimony or by judicial notice. If admitted, the statements may be read into evidence but may not be received as exhibits.

IDENTIFICATION OF PERSONS AND SAMPLES

Rule 901.

REQUIREMENT OF AUTHENTICATION OR IDENTIFICATION

(a) General Provision. The requirement of authentication or identification as a condition precedent to admissibility is satisfied by evidence sufficient to support a finding that the matter in question is what its proponent claims.

(b) Illustrations. By way of illustration only, and not by way of limitation, the following are examples of authentication or identification conforming with the requirements of this rule:

(1) Testimony of Witness with Knowledge. Testimony that a matter is what it is claimed to be.

(3) Comparison by Trier or Expert Witness. Comparison by the trier of fact or by expert witnesses with specimens which have been authenticated.

(9) Process or System. Evidence describing a process or system used to produce a result and showing that the process or system produces accurate result.

ADMISSIBILITY AND PROOF OF SPECIAL MATTERS

Rule 406.

HABIT; ROUTINE PRACTICE

(a) Admissibility. Evidence of the habit of a person or of the routine practice of an organization, whether corroborated or not and regardless of the presence of eye-witnesses, is relevant to prove that the conduct of the person or organization on a particular occasion was in conformity with the habit or routine practice.

(b) Method of Proof. Habit or routine practice may be proved by testimony in the form of an opinion or by specific instances of conduct sufficient in number to warrant a finding that the habit existed or that the practice was routine.

Rule 612

WRITING USED TO REFRESH MEMORY

If a witness uses a writing to refresh his memory, either before or while testifying, an adverse party is entitled to have it produced at the hearing, to inspect it, to cross-examine the witness thereon, and to introduce in evidence those portions which relate to the testimony of the witness.

Rule 1006.

SUMMARIES

The contents of voluminous writings, recordings, or photographs which cannot conveniently be examined in court may be presented in the form of a chart, summary, or calculation. The originals, or duplicates, shall be made available for examination or copying, or both, by other parties at a reasonable time and place. The judge may order that they be produced in court.