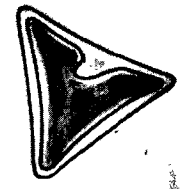
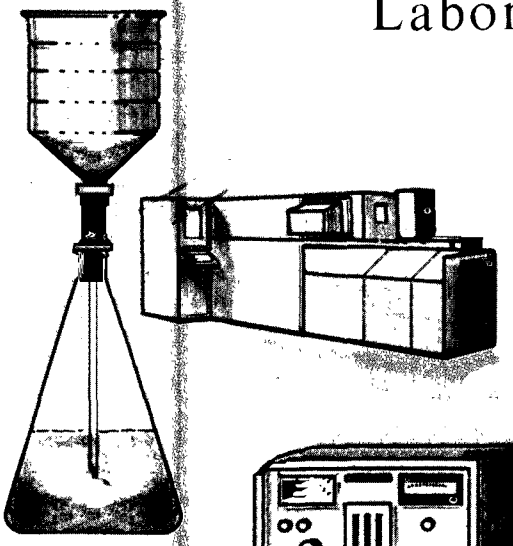
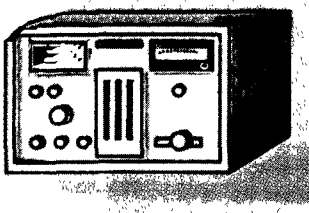
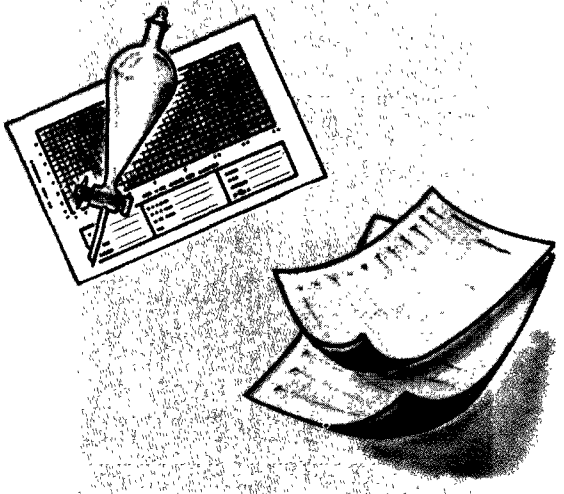
the National Water Quality Network operating manual



For Participating Laboratories







U.S. DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
Public Health Service

REVISED JUNE 1963

N A T I O N A L W A T E R Q U A L I T Y N E T W O R K

O P E R A T I N G M A N U A L

A Guide for Laboratories Participating in Sampling
and Analytical Activities of the
National Water Quality Network

Revised June, 1963

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Bureau of State Services
Division of Water Supply and Pollution Control
Basic Data Branch

Water Quality Section
1014 Broadway
Cincinnati 2, Ohio

TABLE OF CONTENTS

Page

SECTION I

THE NATIONAL WATER QUALITY NETWORK 1

Laboratory Analyses 2
Sampling 6

SECTION II

GENERAL INSTRUCTIONS 7

Sampling Schedules 8
Shipping Instructions 9
Assistance with Sampling, Laboratory, and Other Operational Problems 9
Addresses and Phone Numbers of Regional Offices 11

SECTION III

ORGANICS SAMPLING BY CARBON ADSORPTION METHOD 13

Types of Sampling Equipment in Use 13
Description of Carbon Adsorption Column 13
Presettling, Prefilter, and Backwash 13
Installations with Manual Backwash 15
Installations with Automatic Backwash 18
Pumping Systems 22
Precautions 22
Collection of Sample 23
Use of Carbon Column Data Sheet 23
Shipping 25

SECTION IV

COLLECTION OF SAMPLES FOR RADIOACTIVITY MEASUREMENTS 27

SECTION V

COLLECTION OF SAMPLE FOR PLANKTON ANALYSIS 29

SECTION VI

MEMBRANE FILTER DELAYED INCUBATION PROCEDURE 31

Supplies and Equipment 31
Sample Volume and Filtration 35
Shipping 39

SECTION VII

	Page
CHEMICAL AND PHYSICAL ANALYSES	43
Preliminary Remarks	43
Temperature	45
Dissolved Oxygen (DO)	46
pH	52
Biochemical Oxygen Demand (BOD)	54
Chemical Oxygen Demand (COD)	56
Chlorine Demand - 1 hour and 24 hour	59
Ammonia Nitrogen (NH_3/N)	63
Chlorides	66
Alkalinity (as $CaCO_3$)	69
Total Hardness (as $CaCO_3$)	70
Color	72
Turbidity	73
Sulfates	75
Phosphates	77
Total Dissolved Solids	83

SECTION VIII

HANDLING OF ANALYTICAL DATA	84
Reporting of Results	84
Presentation of Results	86

LIST OF FIGURES

	Page
Regions and Regional Offices	12
Carbon Adsorption Column and Shipping Container	14
Details of Sand Prefilter	16
Schematic Diagram of Piping Installation for Sand Prefilter and Carbon Filter	17
Carbon Adsorption Unit Model H_2O-MIC with Pre-Sand Filter and Automatic Backwash	19
Carbon Adsorption Unit, Model H_2O-M2C with Pre-settling Tank and Auxiliary Equipment in Shelter	20
Schematic Flow Diagram - Organics Sampling Apparatus	21
Sample Report Form for Carbon Filter Data	24
Single Bottle and Shipping Container for Water Samples for Radioactivity	28
Twinpak Bottles and Shipping Container Used when 1-liter Sample is Provided for Radioactivity and 1-liter Sample for Chemical Analysis at Cincinnati	28
Plankton Bottle and Shipping Container	30
Filtration Apparatus and Shipping Container for Coliform Samples	33
Preparation of m-Endo Broth	36
Dilution Chart for Membrane Filtrations	39
Placing Membrane on Pad Soaked with Preservative Medium	41
Sample Report Form for Delayed Incubation Test	44

LIST OF FIGURES

	Page
Nomograph for Preparation of 0.025N Thiosulfate from 1.00 N Thiosulfate	51
Nomograph for Preparation of 0.0141N Mercuric Nitrate from 0.141N Mercuric Nitrate	70
Sample Report Form for Chemical Analysis	87

SECTION I

THE NATIONAL WATER QUALITY NETWORK

THE NATIONAL WATER QUALITY NETWORK was established by the Public Health Service in 1957. It is operated in cooperation with state, local and other federal agencies having related responsibilities for the collection, interpretation and dissemination of basic data on chemical, physical, and biological water quality as it relates to water pollution prevention and control.

The overall objectives of the Network are to provide:

a. Information pertaining to the effect of changes in water use and development on water quality at key points in river systems;

b. continuing information on the nature and extent of pollutants affecting water quality;

c. data that will be useful in the development of comprehensive water resources programs;

d. data that will assist state, interstate and other agencies in their water pollution control programs and in the selection of sites for legitimate water uses.

As of April, 1963, there were 125 sampling locations in the Network. Each location satisfies one or more of the following criteria:

a. Major waterway used for public water supply, propagation of fish and wildlife, recreation, agricultural, industrial and other legitimate uses;

b. interstate, coastal and international boundary waters;

c. waters on which activities of the Federal Government may have an impact.

With its selection as one of the network of key stations, the participating laboratory occupies a unique position. Data collected at this and other Network stations will serve as a foundation for the evaluation of water pollution control

progress, both on a state and national level. The data will also reflect trends in water quality over the years, and thus provide an intelligence service on the quality of water resources of the nation. Finally, the participating laboratory will be a connecting link or reference point in intrastate or river basin pollution abatement programs.

LABORATORY ANALYSES

The analyses to be carried out have been selected on the basis of emerging and foreseeable problems in water quality management, as described below:

Radioactivity

Interest is rapidly growing in routine monitoring of water for radioactivity. With the development of nuclear power reactors and other peacetime atomic energy uses this interest will become even more intense. State and interstate agencies and municipalities are becoming increasingly concerned about establishing such programs. Experience with this Network will, it is hoped, encourage and stimulate more effective state and local programs in radiation monitoring.

Organic Chemicals

Studies conducted during the past decade have shown that products of our chemical technology, particularly organic contaminants, are being recovered from waterways in more and more locations as chemical plants increase in size and number, and as their products are increasingly used in the home, in industry, and in agriculture. Synthetic detergents, pesticides of all kinds, and other petro-chemicals are examples of these contaminants. An increasing number of reports of water damages from these pollutants is being made. Damages that can occur from trace amounts of contaminants include unpleasant tastes and odors, off-tastes in fish, fish kills, foaming, water treatment difficulties, and interference with recreational uses of water. It is important to assess the kinds and quantities of such wastes in our surface waters for the protection of all legitimate water uses.

The measurement of the trace concentrations of organic contaminants requires the use of special techniques since our common procedures lack the needed sensitivity and specificity. Concentration of the contaminants by means of a carbon adsorption column followed by solvent elution

and organic analyses presently offers our best means of measuring the segment of organics of most interest. The chloroform and alcohol extractable materials along with separated groups provide a tangible material that can be analyzed and stored for future reference. Infrared characterization of the extractable materials makes it possible to screen these substances for specific compounds. Gas chromatographic analysis is also employed in these identifications.

Differences in the relative adsorbability on carbon of various organic compounds found in surface waters, as well as the decrease in column adsorption efficiency in heavily polluted waters make it inadvisable to consider results as strictly quantitative.

Biological Populations

Natural waters support a variety of organisms ranging in size from bacteria and minute diatoms to fish. If the water quality deteriorates, the populations change. Those forms of life least affected, or in some cases benefited by water quality deterioration, will find less competition and may develop in very large numbers. Therefore, the presence of large numbers of organisms representing only a few of the more tolerant species is indicative of pollution. Conversely, waters supporting a large variety of organisms in few to moderate numbers is typical of good water quality.

Plankton, microscopic or barely visible plant and animal forms that have limited locomotion in water, comprise an important group for study in relation to water quality. Some of these impart objectionable tastes and odors to water, while others are troublesome because they clog sand filters in water treatment systems. Plankton populations that respond to the water quality changes brought about by pollution are useful in detecting water quality characteristics.

Studies are made of the animal life in the stream and lake bottoms. These bottom-dwelling forms are called benthos. They usually remain in one place and are subjected to water that passes over them. If the water quality and bottom is suitable they grow, reproduce, and provide important food for fish. Water of adverse quality will, however, destroy some or most of the forms. Benthic life varies greatly in ability to survive water quality changes. A study of the

kinds of life and their relative numbers is useful in detecting both improvement or deterioration of water quality.

Fish require water that contains adequate oxygen and is nontoxic. They must also have suitable food consisting of either plankton, benthos, or small fish that have fed upon plankton or benthos. Fish, like other aquatic life, vary in their sensitivity to pollution. Observations of the kinds of fish, their numbers, and rates of growth are useful in evaluating suitability of water for this purpose.

Coliforms

The presence of these organisms in water is direct evidence of the presence of sewage. The degree of contamination of the water by these organisms will be of interest to the municipality using the stream for its source of water. The delayed membrane filter technique will be used to carry out this test, as it is the most reliable method available whereby samples can be shipped long distances without deterioration.

Chemical and Physical Parameters

There are many standard chemical and physical measurements that can be made on water. Those of significance to the establishment of water quality vary with the purposes for which the water is to be used. The determinations selected below are of basic value to most water uses. They have, therefore, been included in the Network program. In certain locations other determinations, of local significance, may be added as the program develops. The measurements the Network reports for each station are listed below in the order in which they appear on the Field Form (PHS 2845-1, Revised, 6-59).

1. Temperature
2. Dissolved Oxygen
3. pH
4. Biochemical Oxygen Demand
5. Chemical Oxygen Demand
6. Chlorine Demand-1 hour
7. Chlorine Demand-24 hours
8. Ammonia Nitrogen
9. Chlorides
10. Alkalinity
11. Total Hardness
12. Color
13. Turbidity
14. Sulfates
15. Phosphates
16. Total Dissolved Solids

A copy of the Field Form appears on page 87.

The laboratory facilities of the Water Quality Section in Cincinnati are equipped to perform the determinations numbered 9 through 16. It is necessary for the participating laboratories, however, to run the analyses numbered 1 through 8 since these measurements change with time.

The Water Quality Section will assist individual laboratories in every way possible, by furnishing expendable equipment and prepared reagents and by personal visits, if necessary, that these determinations may be available from each Network station. All data collected at each sampling point will be freely exchanged among the Public Health Service, the participating laboratory, and the state agency responsible for water pollution control.

In many cases where laboratories are well equipped they are able to perform all of the requested analyses. Thirty-five of the 125 Network stations are reporting all 16 of the requested determinations.

Reference Samples

In a national program wherein analytical results originate from a multitude of laboratories it is essential that laboratory data be comparable as to precision and accuracy. The Reference Sample activity is a means by which this objective can be achieved.

This is accomplished by preparation of a large volume of a standard sample into which the desired constituents are measured very accurately. Similar portions of the sample are then mailed to each of the participating laboratories, along with a report form and complete instructions for analysis. When the analytical results are returned to the Water Quality Section, a second report is returned to the responding laboratory showing how its results compare with the true results. Whenever possible, comments concerning sources of error and means of correction are included. When all the groups have reported, a final review and summary of all the data is distributed to all Network agencies.

These samples are distributed periodically and past experience has shown that this mechanism leads to increased proficiency of the participants. In addition, it has served to point up routine errors within a laboratory that would otherwise have gone unnoticed.

SAMPLING

All samples are to be of raw waters. All samples are to be collected from the flowing stream or from the raw water intake prior to any treatment, including sedimentation, prechlorination, etc. Samples for determination of radioactivity, organic chemicals, plankton populations, and coliforms are to be shipped to the Water Quality Section at Cincinnati for analysis. The chemical analyses will be performed by the participating laboratories on samples collected at the same time. Procedures for collection, shipment and analyses of samples are given in subsequent sections of this manual.

All sampling containers, shipping cases, and other materials will be provided and all shipping charges will be paid by the Public Health Service. Carbon adsorption columns, packed with carbon, will be furnished in individual shipping containers. Containers and shipping cases will be provided for the remaining samples.

Cooperating laboratories are encouraged to develop laboratory competence in the analyses, especially in those determinations that must be performed immediately. The Public Health Service will furnish all possible assistance through training, methods, consultation, reference samples, loan of equipment, and other resources that may be available.

SECTION II

GENERAL INSTRUCTIONS

Routine collection of samples for shipment to the Water Quality Section will be carried out according to detailed instructions for collection and shipment presented in subsequent sections of this manual. The program includes the following:

a. Radioactivity Sample - weekly:

A 1-liter sample should be taken weekly.

b. Chemical Sample - weekly:

A 1-liter sample should be taken weekly at the same time the radiological sample is taken. Since many stations perform all the chemical measurements, a weekly chemical sample need not be sent to the Water Quality Section. In cases where the analytical work is performed by the Water Quality Section, a "TWIN-PAK" container is provided by which two 1-liter samples may be shipped together (see Section VII: Page 45 , paragraph 4).

c. Coliform Sample - weekly:

This sample should be collected on the same day as the chemical and radiological samples are taken. Note that this sample should not be taken on a Thursday or Friday. Membrane filtration and mailing of this sample to the Water Quality Section should be done as quickly as possible after collection.

d. Plankton Populations Sample - semi-monthly:

Requires a 5½-pint sample. Collect on the same day as the chemical and radiological samples are taken.

e. Carbon Adsorption Sample - monthly:

Start carbon adsorption mechanism on the same day that a sample is collected for the chemical and radiological sample.

f. Chemical Oxygen Demand Sample - weekly and monthly:

The determination is to be performed weekly whenever possible. For those laboratories that cannot perform this test, a sample bottle is supplied in the shipping box with the carbon adsorption sample. This sample should be collected on the next sample day after the carbon unit is put into operation, and a portion of the sample should be placed in the bottle.

Note: This bottle will not appear in the box when a station performs the test weekly at the collection point.

SAMPLING SCHEDULES

Weekly and monthly sampling schedules should be set by each participating agency to fit in best with normal routine operations. Once the schedule is established, however, it should be followed as closely as plant operations permit. The preferred days are Monday, Tuesday, or Wednesday. Thursday samples for coliform arrive either too late on Friday for processing or are not delivered until the following Monday. Friday samples for coliform are also unsatisfactory since extended time in the mail causes a large percentage of these to be unreliable, especially during warm seasons of the year.

First sample day of each month,

1. Collect chemical and radiological samples, mail to Cincinnati. Analyze chemical sample and mail results.

2. Collect,filter, and mail the membrane filter coliform sample.

3. Start the carbon adsorption run.

4. Collect and ship the plankton sample.

Second sample day of the month,

1. Same as first sample day.

2. Same as first sample day.

3. Collect COD samples and place in carbon column shipping box (if applicable).

Third sample day of each month,

1. Same as first sample day.

2. Same as first sample day.

3. Remove carbon column and ship to Cincinnati. (This may be done on any day that the carbon adsorption run is completed).

4. Collect and ship plankton sample.

Fourth sample day of each month,

1. Same as first sample day.

2. Same as first sample day.

Fifth sample day of each month,

If the month has five sample days, repeat the fourth week's schedule. If the sample day coincides with a holiday, sample on the first workday following the holiday.

SHIPPING INSTRUCTIONS

All samples, except the carbon adsorption samples, are to be shipped by mail or parcel post to:

U. S. Department of Health,Education, and Welfare
Public Health Service
1014 Broadway
Cincinnati 2, Ohio

Attn: Chief, Water Quality Section
National Water Quality Network

The carbon adsorption samples are to be shipped by Railway Express, Charges Collect, to the above address. See special comments regarding shipping instructions in Section III, page 25 .

ASSISTANCE WITH SAMPLING, LABORATORY, AND OTHER OPERATIONAL PROBLEMS

If questions or difficulties arise in connection with instructions and procedures outlined in this manual or any other phase of the Network operation, the participating

agency should contact the Water Quality Section in Cincinnati, Ohio, by telephone collect, or by other means of communication as indicated by the circumstances involved. Requests for assistance should be directed to:

Chief, Water Quality Section
National Water Quality Network
1014 Broadway
Cincinnati 2, Ohio

Telephone:

381-2200
Ext. 2925,
2926, or
2927.

Addresses and phone numbers for each of the USPHS Regional Offices are also listed on the following page. These are given because there is an appointed representative in each office to assist the Network participants in whatever way possible. Personnel at the Network stations are urged to contact these representatives as the circumstances demand expecially if it appears that assistance or information may be obtained more efficiently. A map showing the geographical areas of the respective Regions is included on page 12. Requests for assistance from the Network representative in the Regional Offices should be made through the Regional Program Director, PHS.

The addresses and phone numbers for the various regional offices are given on the following page.

Region I

120 Boylston Street
Boston 16, Massachusetts
Telephone: 617-482-6550

Region II

Room 1200, 42 Broadway
New York 4, New York
Telephone: 212-363-2523

Region III

700 E. Jefferson Street
Charlottesville, Virginia
Telephone: 703-296-5171

Region IV

Room 453, 50 Seventh St., N. E.
Atlanta 23, Georgia
Telephone: 404-876-5737

Region V

Room 712 New Post Office Bldg.
433 W. Van Buren Street
Chicago 7, Illinois
Telephone: 312-828-5250

Region VI

560 Westport Road
Kansas City 11, Missouri
Telephone: 816-221-7000

Region VII

Ninth Floor
1114 Commerce Street
Dallas 2, Texas
Telephone: 214-748-2721

Region VIII

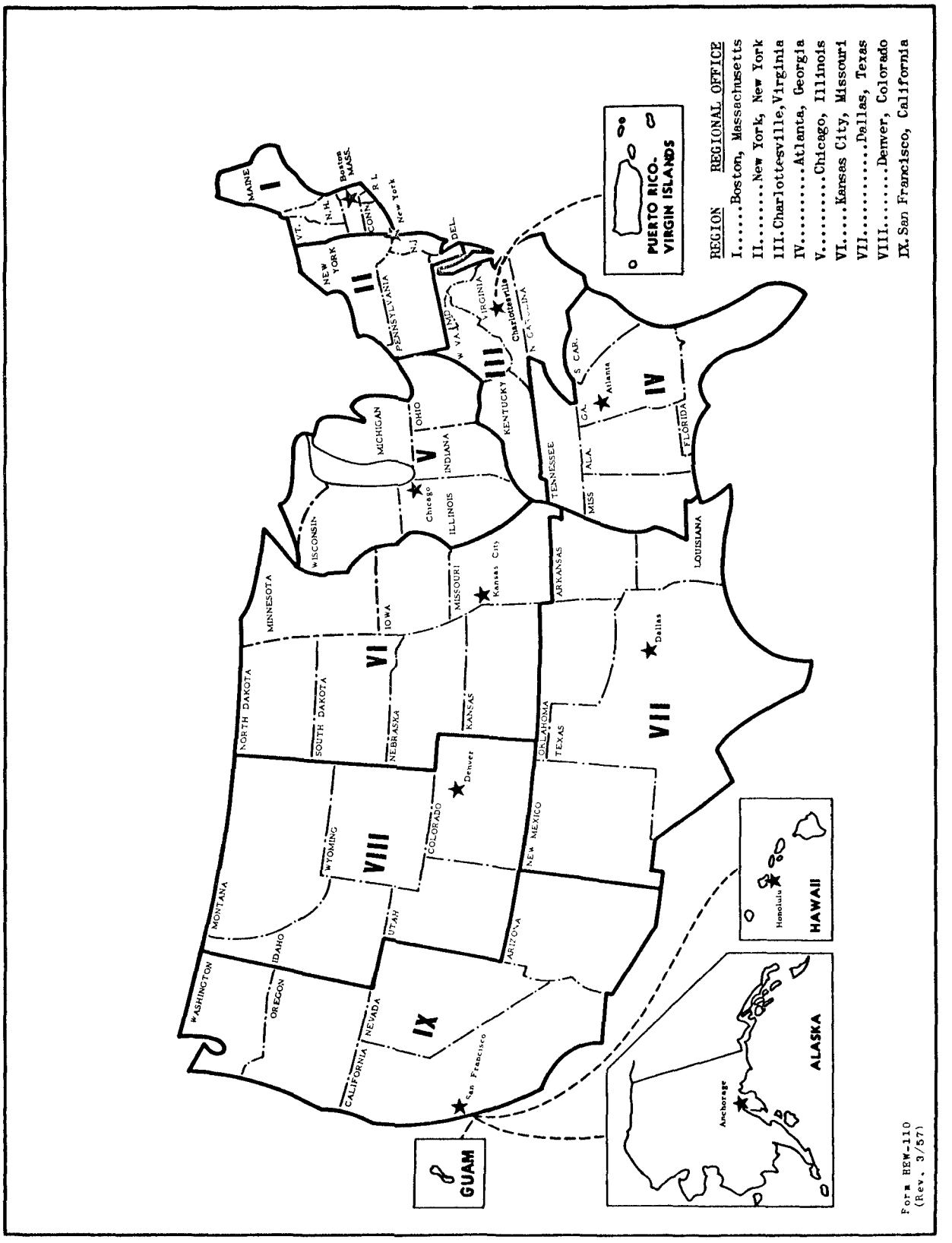
Room 551
621 Seventeenth Street
Denver 2, Colorado
Telephone: 303-534-1320

Region IX (San Francisco, Calif.)

447 Federal Office Bldg.
Civic Center
San Francisco 2, California
Telephone: 415-552-2350

Region X (Portland, Oregon)

Room 570, Pittock Block
921 S. W. Washington
Portland 5, Oregon
Telephone: 503-226-3361



Form HEW-110
(Rev. 3/57)

SECTION III

ORGANICS SAMPLING BY CARBON ADSORPTION METHOD

The carbon adsorption method of organics sampling consists of the passage of up to 5,000 gallons of raw water at a rate of 1/4 to 1/2 gallon per minute through a carbon adsorption column. Following the sample run, the column is shipped to the Water Quality Section, Cincinnati, Ohio, for analysis.

TYPES OF SAMPLING EQUIPMENT IN USE

There are three types of carbon adsorption mechanisms in current use. The first and oldest of these consists of a piping arrangement that was originally assembled and installed at the sampling location. This device is referred to as the manual type installation and is discussed on page 15. The other two types are automatic sampling devices (designated H_2O-MIC and H_2O-M2C) prefabricated in the Water Quality Section Workshop and are shipped ready for installation. The M-1 is a panel unit equipped with automatic backwash device, designed for inside-the-plant use. The M-2 unit is similar to the M-1 unit, but is built into protective housing for operation in remote or outside-the-plant use.

Since a large number of the manual devices continue to operate with good efficiency, it is not anticipated that they will be replaced in the near future. A discussion of operating procedures for both types of equipment is therefore included in this section.

DESCRIPTION OF CARBON ADSORPTION COLUMN (CAC)

The CAC consists of a piece of pyrex glass pipe 3 inches in diameter and 18 inches long. The ends are fitted with brass plates and 3/4-inch galvanized nipples. A stainless steel screen is fixed in a neoprene gasket at both ends. The filter unit will arrive packed with activated carbon ready for use. The special shipping container provided should be used when returning the filter. The unit, with the shipping container is pictured on page 14.

PRESETTLING, PREFILTER, AND BACKWASH

River waters will frequently clog the CAC before the desired volume of water has been sampled. To prevent this, it is necessary to remove enough turbidity to permit the

required amount of water to pass through the unit. This may require a presettling tank and a prefilter containing sand and gravel.

Presettling Tank.

A standard hot water tank connected with the inlet at the bottom and outlet at the top, with a clean-out tap at the bottom, can serve as a presettling tank. The outlet connects to the prefilter containing sand and gravel. The hot water tank should be flushed at frequent intervals to prevent accumulation of solids. Open settling tanks can be used, if flow-through time at 1/2 gpm is less than 4 hours. With open tanks a pump will be required to move the water through the filter.

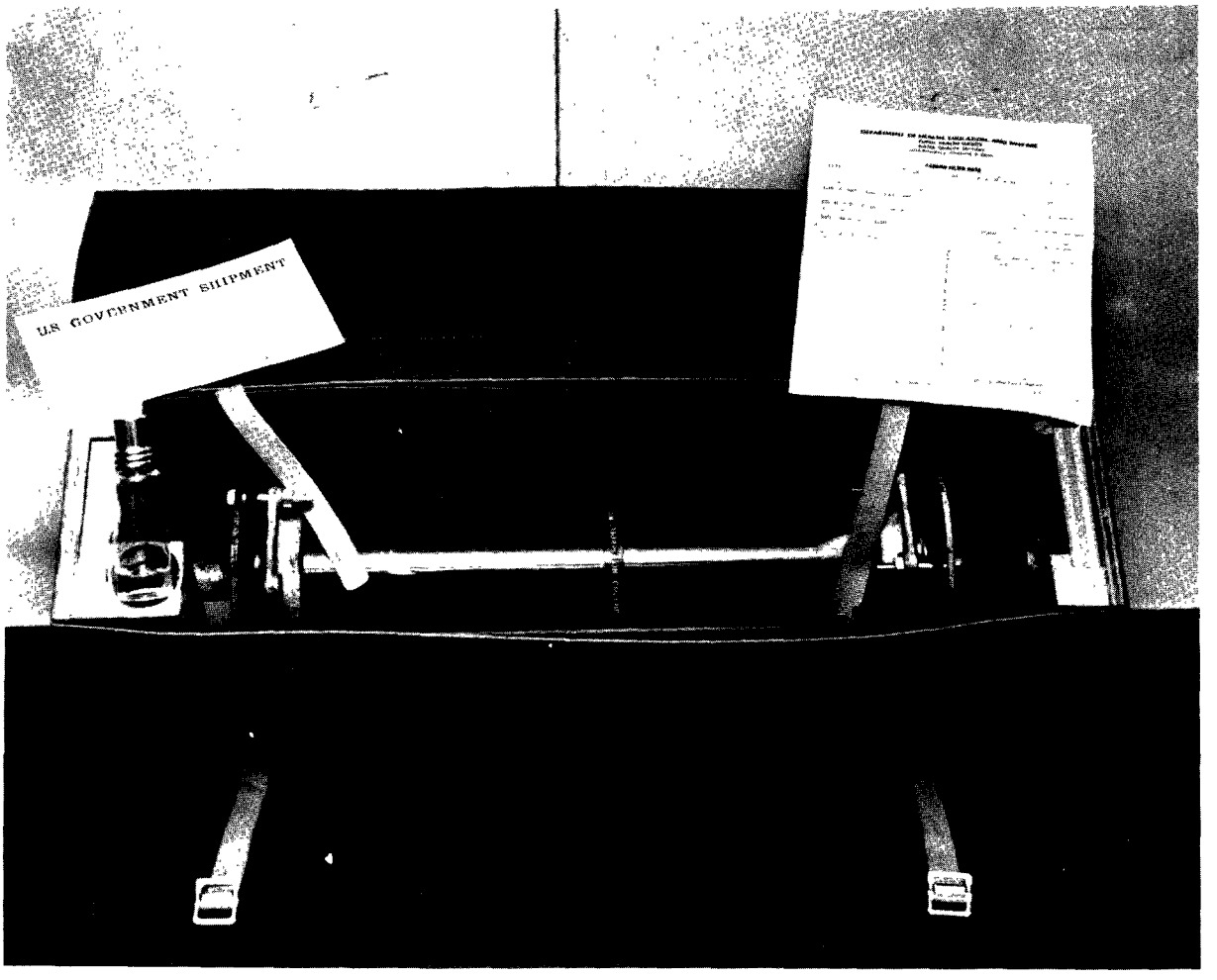


Figure 1 - Carbon Adsorption Column and Shipping Container. (Note COD Sample Bottle)

Sand Prefilter.

The sand prefilter provided by the Water Quality Section consists of a steel pipe 3 feet long and 3 inches in diameter, threaded at both ends, and equipped with 3 by 1-inch reducer couplings. Two discs of stainless steel screen are fitted to the inside diameter of the pipe. The space between the screens is packed with 6 inches of 1/8-inch gravel, 24 inches of 0.6 to 0.8 mm sand, and another 6 inches of 1/8-inch gravel. No free space is left in the pipe. The gravel is packed by jarring the pipe while filling. This arrangement provides a strainer, rather than a filter, with a movable bed. By such an arrangement backflushing can be done without disturbing the filter. The construction details are shown in Figure 2.

INSTALLATIONS WITH MANUAL BACKWASH

The presettling tank, the sand prefilter and the CAC should be installed at the most convenient source of raw water. If less than 15-psi pressure is available, it may be necessary to pump the water through the system. A drawing of a workable system is shown in Figure 3. Exact lengths of pipes, etc. are not given, since these will vary with the local situation. Both the sand and CAC are connected with unions at both ends for easy removal.

The raw water flows upward through the sand prefilter and the CAC. When the rate of flow through the system falls below 1/4 gpm, backwashing of the sand filter becomes necessary, with use of a high pressure source of water. A clean water hose is connected to the top of the sand filter, the valve to the CAC is closed, the drain valve on the sand filter is opened. The sand is backflushed until the water coming out is clear. The length of time between backwashings will vary. On the Missouri River, for example, it has been found that once every 8 hours is usually sufficient.

After backwashing connect the system as before and continue the sampling. To prevent a cross-connection, be sure to disconnect hose at top of sand filter after backwashing. A pressure gauge is inserted in the system to indicate when clogging is taking place in the carbon filter. Total pressure in the filter should not exceed 50 psi.

A water meter located at the end of the system is used to measure the volume of water sampled. A 5/8 by 3/4-inch, disc-type meter, or oscillating piston-type meter, registering in gallons and capable of measuring flows as low as 1/4 gallon per minute, may be used for this purpose. A valve following the meter throttles the flow, if necessary. A flow-regulating device may also be used for this purpose.

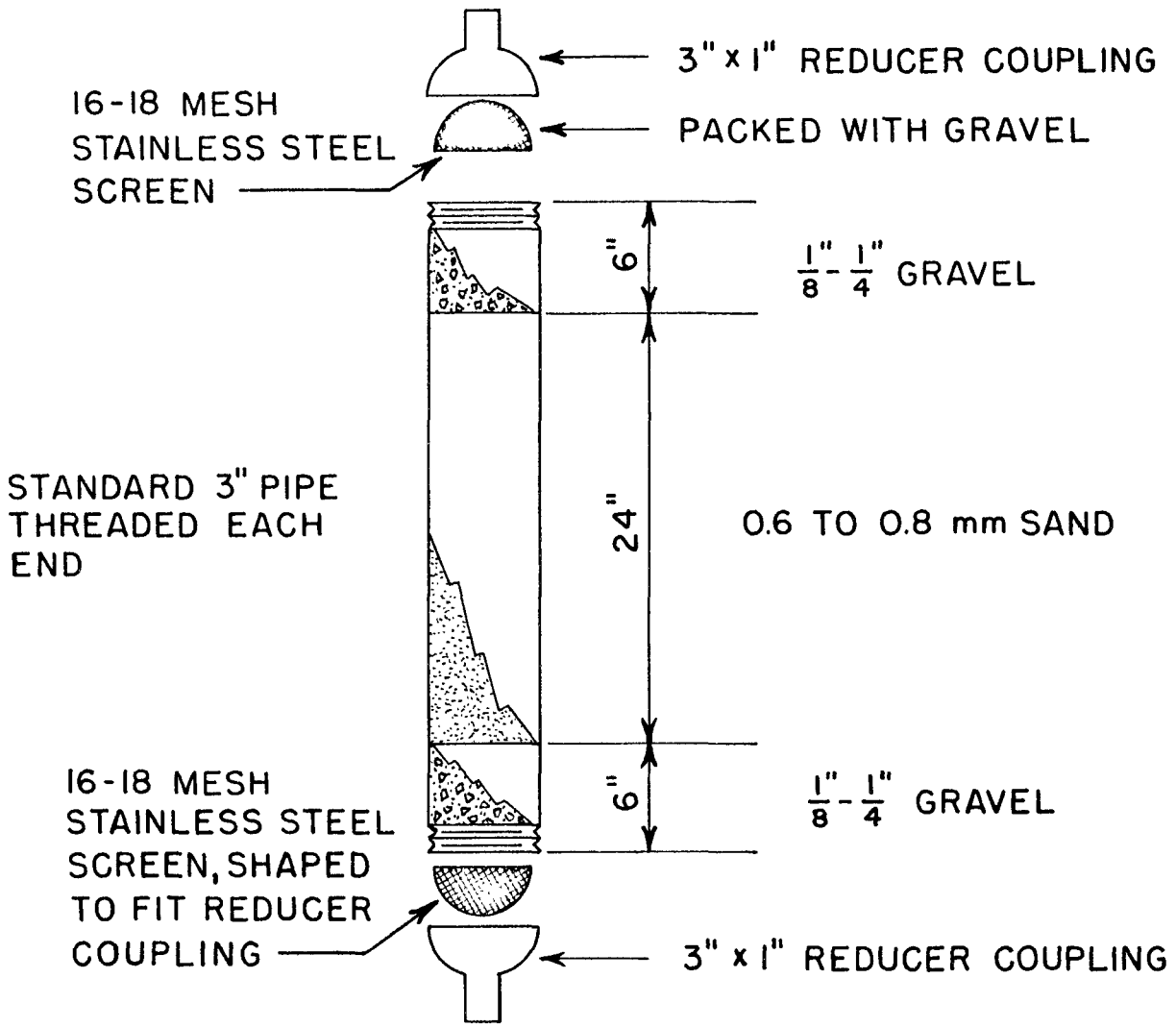


Figure 2 - Details of Sand Prefilter

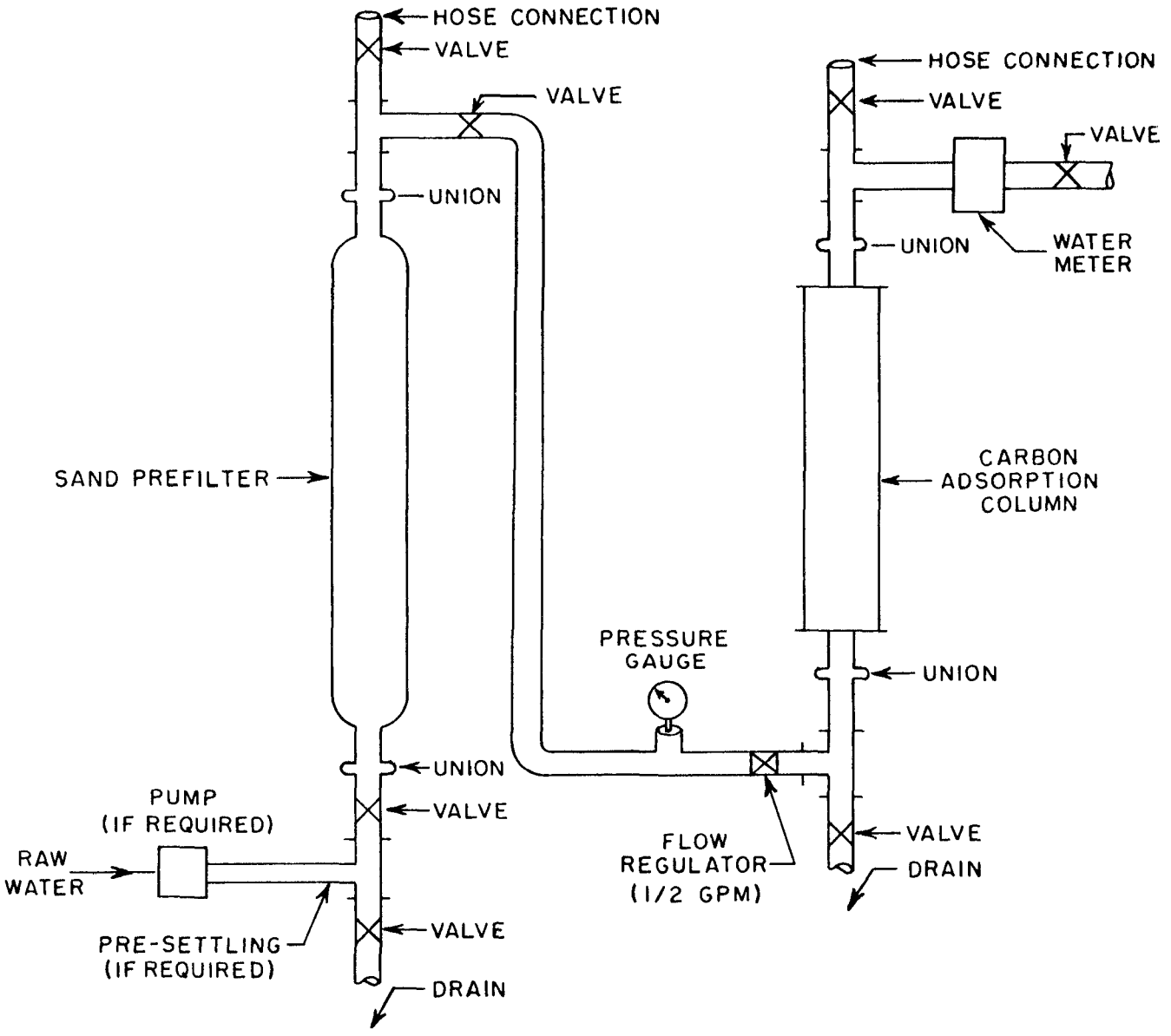


Figure 3 - Schematic Diagram of Piping Installation For Sand Prefilter and Carbon Filter

Fine carbon dust washes out of the CAC when it is first started. A few gallons of water should be passed through the top connection and through the CAC drain before the meter is cut in, to keep the meter free of the carbon.

The system outlined is not intended to remove all traces of turbidity from the water before it passes through the CAC. Its purpose is to take out gross materials, most large organisms, and permit the required volume of water to pass through the carbon.

Occasionally, some stations may experience clogging of the sand filter owing to high algae concentrations. These organisms tend to penetrate into the sand and are difficult to backwash. When this situation is anticipated, an increase in frequency of backwashing is indicated.

Backwashing every 2 hours is not uncommon under these circumstances. If, even after this precaution is taken, the sand filter becomes clogged, the only alternative is to replace the sand.

INSTALLATIONS WITH AUTOMATIC BACKWASH

Preassembled panel units with automatic backwash of the sand prefilter have been developed to ease installation and operation of the organics sampling apparatus. Figure 4 shows the Model H_2O-M1C panel unit designed for installation in water treatment plants and other buildings. This equipment has an electric timer and solenoid valves to backwash automatically the sand prefilter. The panel includes an electric disconnect switch of fuse plug type and grounding-type duplex outlet for pump. It also has three 3-way cocks, one to protect the water meter from fine carbon at the beginning of sampling, one to facilitate checking of the flow control valve and water meter, and one to check backwash performance.

For remote locations the sampling apparatus is installed in an insulated equipment shelter. An organics-sampling field unit, Model H_2O-M2C, containing preassembled panel apparatus, a 30-gallon presettling tank, electric space heater, and auxiliary equipment is shown in Figure 5. The pumping system will vary depending on the needs of the individual sampling station. A submersible pump was used for the field unit shown in Figure 6. The equipment shelter contains, however, sufficient space for a jet centrifugal-type pump, or other acceptable motor pump unit.

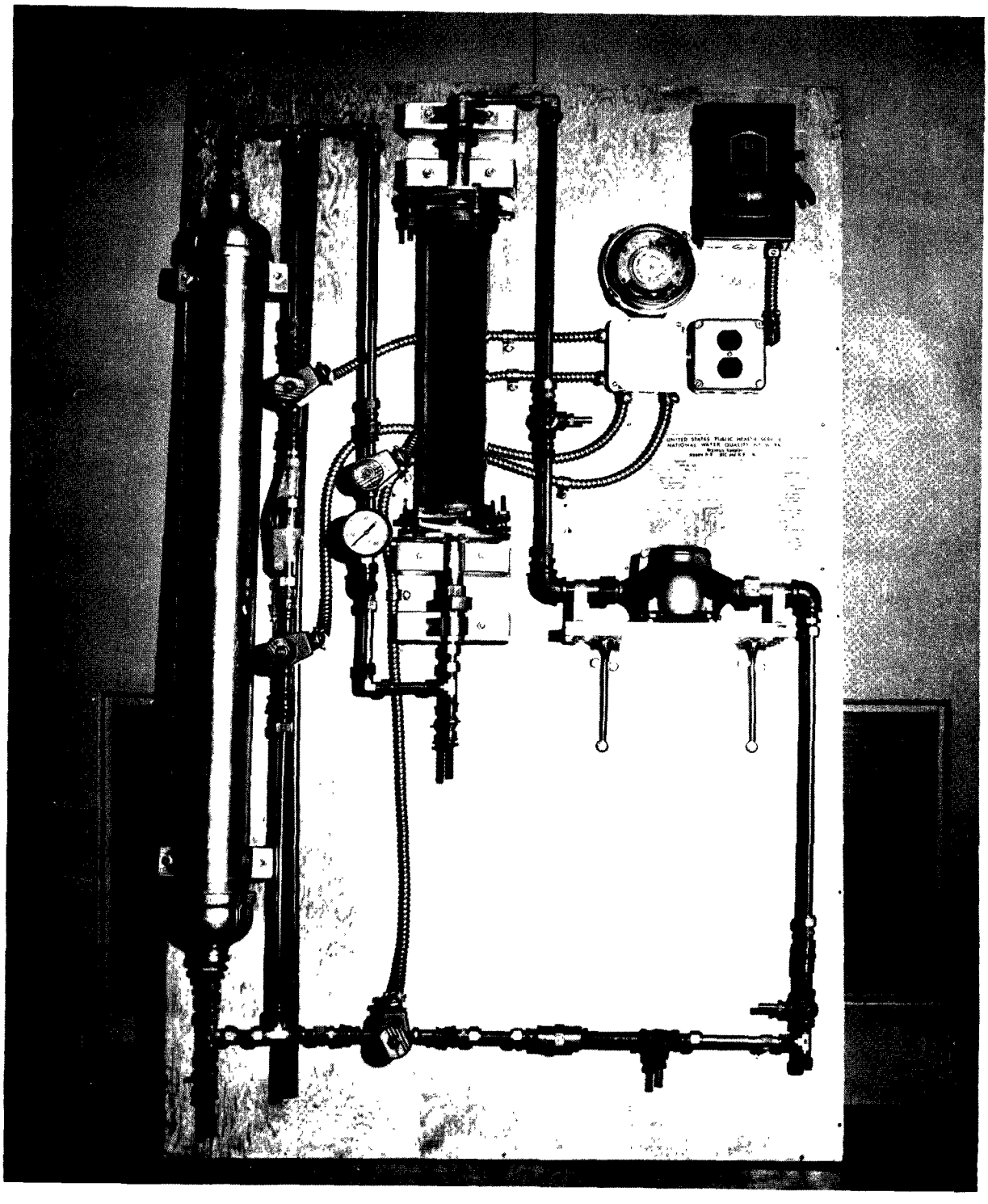


Figure 4 - Carbon Adsorption Unit Model H_2O-M1C with Pre-Sand Filter and Automatic Backwash.

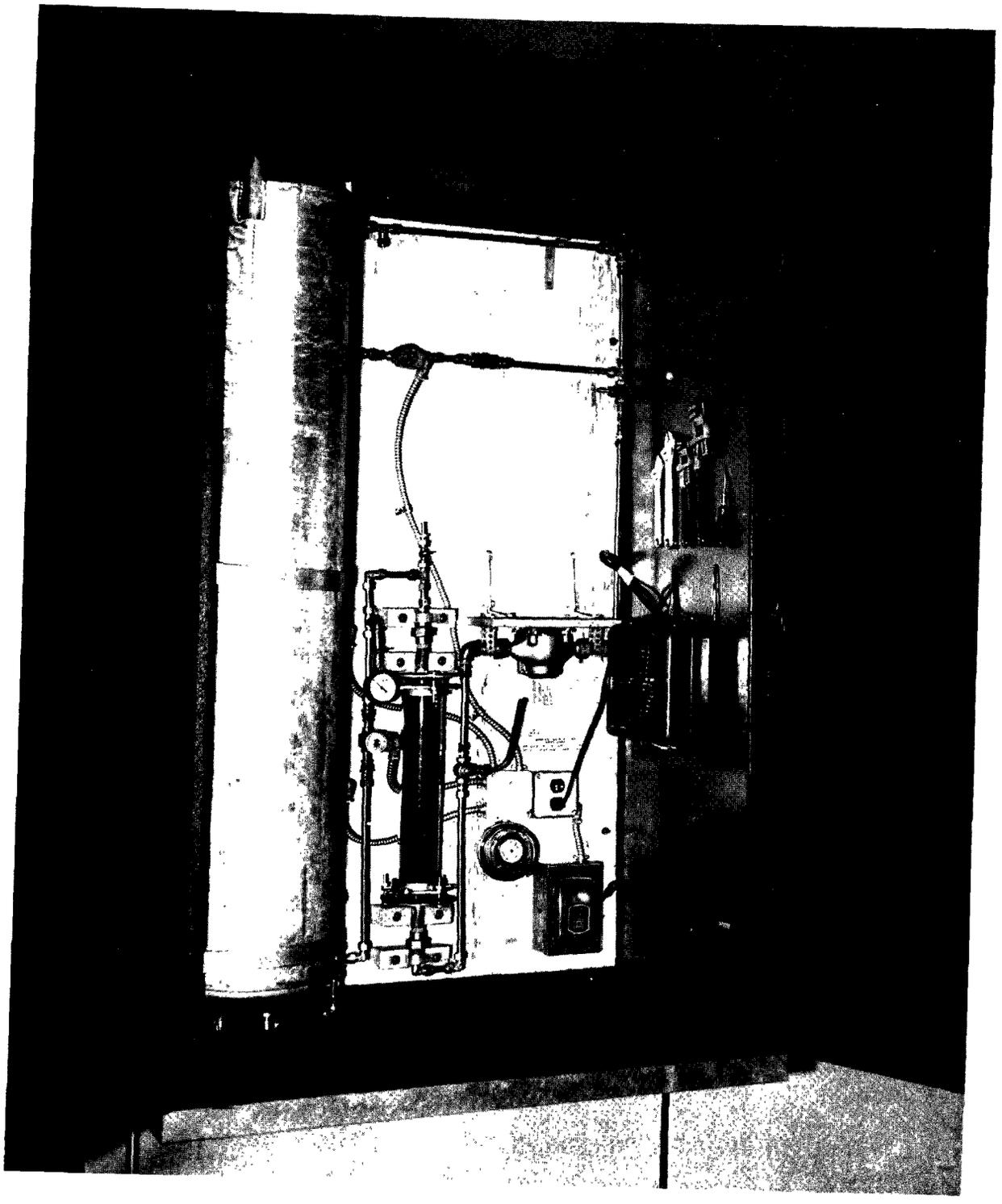


Figure 5 - Carbon Adsorption Unit, Model H_2O-M2C With Pre-settling Tank and Auxiliary Equipment in Shelter.

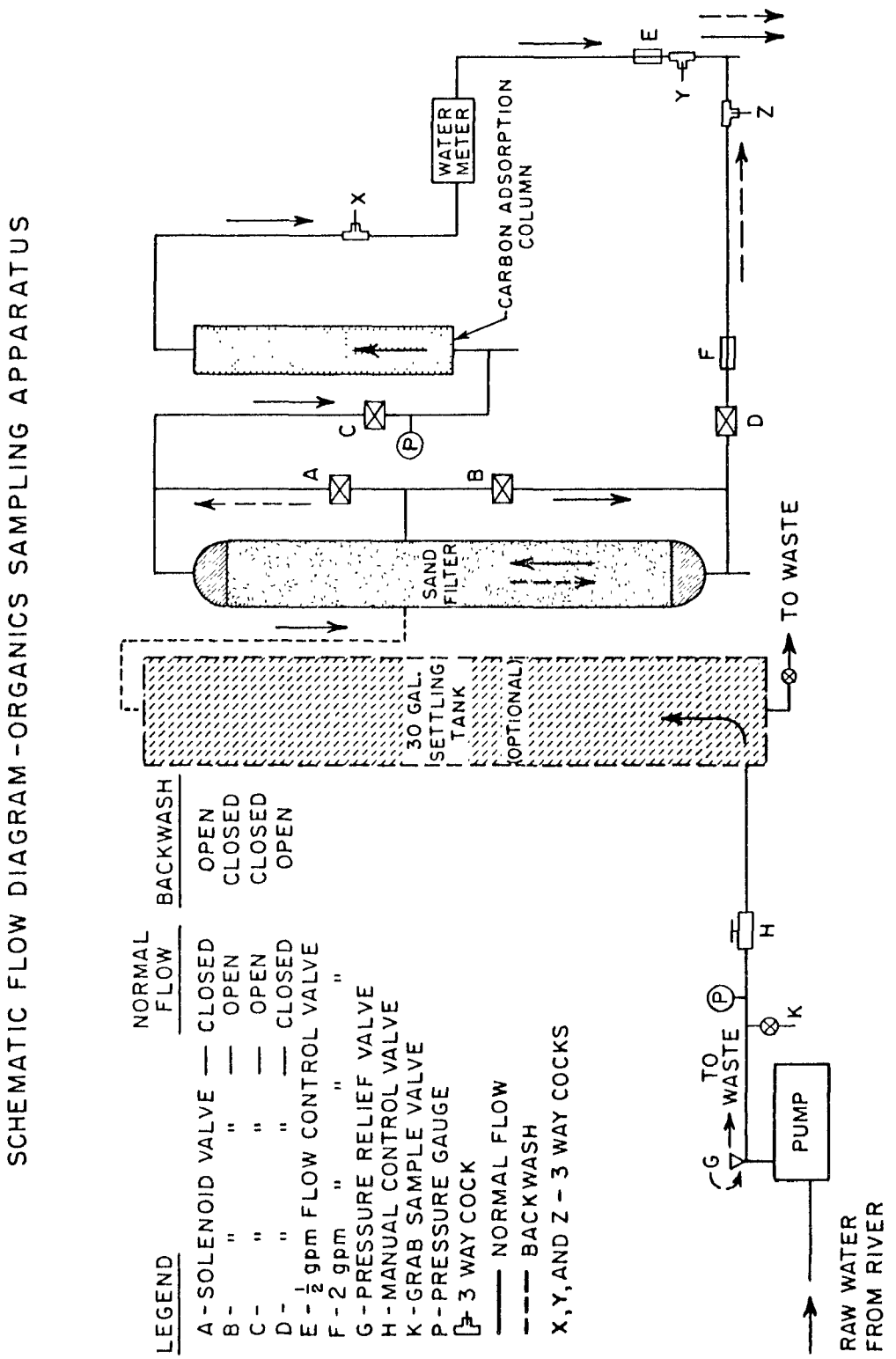


Figure 6 - Schematic Flow Diagram - Organics Sampling Apparatus.

PUMPING SYSTEMS

Pumps, piping, and accessories are selected to suit the specific conditions of each station. Shallow and deep well-type jet centrifugal pump systems are in use at many network installations to bring raw water from a representative sampling point to the sampling apparatus. Submersible pumps with helical screw rotors and synthetic rubber stators, rotary pumps with flexible impellers, and other pumping mechanisms may be installed to meet individual needs.

It is important that the pump used does not contaminate the sample through grease-type packing or other sources. The pump must have a greasless-type rotary shaft seal or special packing material to avoid contamination. New pumps are sometimes grease-coated and should be thoroughly cleaned before being put into service. Piping strainers, check valves, and all other accessories that come in contact with the raw water pumped to the CAC filter must also be cleaned (see Precautions, paragraph below.)

A prefabricated metal building can be provided, where required, to provide a permanent shelter for equipment and operating personnel. This type of building is usually installed on a reinforced concrete base. An organics-sampling panel unit (Model H_2O-M1C), a pumping system, and other sampling equipment may be installed in this type of facility.

A schematic flow diagram for the Organics sampler, Models H_2O-M1C and H_2O-M2C, is shown in Figure 6. Details of installation, operation, and maintenance of this equipment are contained in a separate manual, available on request.

PRECAUTIONS

The purpose of the CAC is to adsorb small amounts of organic impurities from the water in as great quantity as possible. It is important to avoid contamination of the carbon from other organic sources. Hence the following precautions should be observed:

a. New strainers, pipe fittings, and other accessories are usually coated with oil or grease. The oil should be removed by washing in kerosene (or chloroform) followed by a detergent wash before fittings are used for making connection to the CAC.

b. Ordinary organic pipe jointing compounds should not be used. Red lead (lead oxide) mixed to a paste with water can be used for this purpose. (A small supply of red lead is initially furnished for installation of the sampling system).

c. Plastic hose is to be avoided, and if rubber hose is used in any connections it should be flushed thoroughly before being connected to the CAC. Copper tubing is ideal for connections. NOTE: Polyethylene pipe and PVC (polyvinyl chloride) pipe meeting National Sanitation Foundation (NSF) standards for drinking water use are acceptable.

COLLECTION OF SAMPLE

Water should be passed through the CAC at a rate of 1/4 to 1/2 gallon per minute until up to 5,000 gallons have been sampled. With highly turbid waters, clogging may occur earlier. Although a suitable sample can sometimes be obtained with several hundred gallons, it is desirable to sample a minimum of 2,000 gallons, if at all possible. The sampling procedure is begun by installing the CAC and flushing with raw river water to remove carbon fines (through three-way cock "X" on panel units.) Make entries on data sheet as described under "Use of Carbon Column Data Sheet."

NOTE: If the filter clogs, turn filter end to end and/or backwash for 2 to 3 minutes once to obtain at least a 2,000 gallon sample.

If water meter does not register, measure rate of flow several times during run by timing flow to fill a 1-gallon container.

USE OF CARBON COLUMN DATA SHEET

Since the aim is to approach a quantitative evaluation of organics in water, it is important to have accurate flow measurements.

In Preparing the data sheet (see illustration 7):

1. Fill in all of the pertinent data at the top of the sheet. (i.e., state, station location, type of sample, collected by).

37

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE
WATER QUALITY SECTION
1014 Broadway, Cincinnati 2, Ohio

SAMPLE

CARBON FILTER DATA

STATE	STATION LOCATION (River Mileage) 518
OHIO	37 CINCINNATI - OHIO RIVER

TYPE OF SAMPLE (Raw, Finished, Other) RAW

COLLECTED BY: (Company or Agency) CINCINNATI WATER DEPARTMENT

DATE CARBON FILTER STARTED 3-25-63 STOPPED 4-2-63

TOTAL GALLONS FILTERED 5012

DATE	METER READING IN GALLONS	REMARKS	DATE	METER READING IN GALLONS	REMARKS
3-25	26150	10^{30} A.M. START			
3-26	26660	7^{30} A.M. GASKET	LEAK		
3-27	27230	7^{30} A.M.			
3-28	27940	9^{00} A.M. PUMP	REPAIR		
3-29	28520	7^{30} A.M REPLACE	FUSE		
3-30	29355	2^{00} P.M			
3-31	29745	7^{30} A.M			
4-1	30585	12 NOON			
4-2	31162	9^{10} AM STOP			
	→	NEED COUPLE	EXTRA	DATA SHEETS	

DISTRIBUTION: White Copy to Address Above; Pink Copy for Retention by Collecting Laboratory or Agency.

PHS-2845-7 (9-53) **WATER QUALITY BASIC DATA REPORT (CARBON FILTER)**

FORM APPROVED.
BUDGET BUREEAU NO. 68-R6 34

2. Insert the date the cartridge was placed in service.

3. On the first line of the table, again enter the date of starting and the meter reading at the time of start.

4. Keep a daily record of dates and meter readings throughout the sampling period, if possible.

5. When sampling is stopped make the last entry of date and meter reading in the table. Enter the final date again opposite "stopped".

6. Subtract the initial meter reading from the final meter reading and enter the difference opposite total gallons filtered.

(NOTE: If meter reads in cubic feet, cross out "gallons" and write in "cubic feet.")

7. Any pertinent observations related to difficulties with the equipment, weather problems, etc. may be entered under Remarks.

8. Place the white (top) copy of the data sheet in the box with the column for return to the Water Quality Section. The pink copy is retained by the cooperating agency.

9. Upon receipt of the used CAC in Cincinnati, a new column will be returned to the station for the next run.

SHIPPING

When the sampling period is complete, disconnect the CAC and drain off the excess water. Cap both ends of the CAC. Place in the box with data sheet, and replace wooden chucking blocks, closing securely. Affix the address label to the top of the box. The box should be returned_____*. Pay no charges for shipment. If difficulties arise on this point, call the Chief, Water Quality Section, collect, 381-2200, Extension 2925.

*Carbon cartridges are returned from some National Water Quality Network stations by parcel post. The parcel post label marked "postage and fees paid, Dept. of HEW" is included for the use of these stations in returning the box.

Other National Water Quality Network stations must use Railway Express for return shipment. In boxes sent to these stations, Railway Express labels have been provided. These labels permit the box to be transported to Cincinnati (only) with the charges being paid in Cincinnati. Pay no charges!

SECTION IV

COLLECTION OF SAMPLES FOR RADIOACTIVITY MEASUREMENTS

A 1-liter grab sample of raw water is collected on a weekly basis for radioactivity measurements.

The sample should be collected at the same time that a portion is taken for the chemical analysis. It should be taken from the stream or from the raw water intake line, prior to any treatment whatever within the plant. This sample must reflect river quality. Therefore, it should be taken before there is any opportunity for sedimentation. Rinse the bottle with raw water before filling it to the bottle neck. Be sure to fill out the enclosed tag and attach it to the bottle. Sample bottles and shipping containers are shown in Figures 8 and 9.

Figure 8 Single Bottle and Shipping Container for Water Samples for Radioactivity.

Figure 9 Twinpak Bottles and Shipping Container Used When 1-liter Sample is Provided for Radioactivity and 1-liter Sample for Chemical Analysis at Cincinnati.

SECTION V

COLLECTION OF SAMPLES FOR PLANKTON ANALYSIS

Plankton samples are collected twice a month. The sample bottle is a 3-liter, polyethylene container mailed in a fibreboard container with a reversible label.

A single bottle in a shipping container is sent to each station several days before the sampling date. The 100 ml of preservative in the sample bottle has approximately 0.1 percent of Merthiolate (Thimerosal), sodium carbonate, and Lugol's solution.

The water sample should be taken from the stream or lake at a depth of 2 to 15 feet below the surface, if possible. The bottle should be filled to the line on the neck of the bottle. Care should be taken to prevent spillage of the preservative or dilution by overfilling. The preservative is effective for at least a month, but care should be taken to avoid exposure to excessive heat or sunlight, which will reduce its effectiveness.

Samples should represent the typical water of the stream or lake. Direct sampling from the water source is preferable, but in some cases water must be taken from a pipeline. Water that has passed through gravel or fine screens should be avoided because the plankton can be greatly reduced by the filtering action.

Each bottle is sent with a tape around the cap bearing suggested date of collection, and a tag containing a station number. The tape should be replaced on the bottle to insure its remaining tight during shipment, and the tag filled out with the requested station information and collection time.

Sample containers are sent to each station ten days prior to the sampling date. If, for any reason, a sample cannot be collected, the empty container should be returned to the Network Laboratory so that the preservative can be renewed.

The address label provided on the shipping container may be removed from the plastic frame. It is provided with the Water Quality Section address on one side and the station address on the other side. Ship the container by parcel post making sure that the label is turned to show the Water Quality Section address.

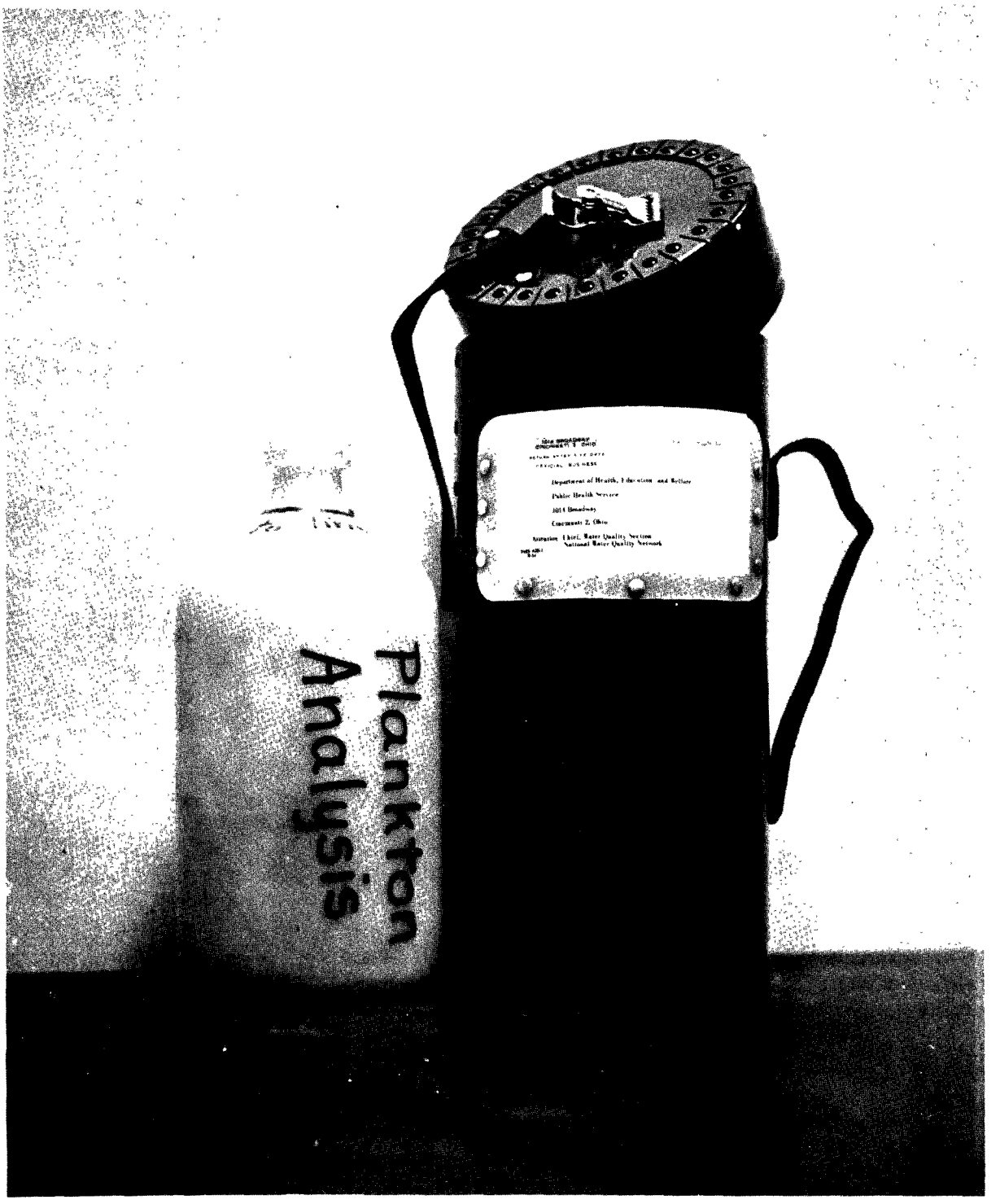


Figure No. 10. Plankton Sample Bottle and Shipping Container.

SECTION VI

MEMBRANE FILTER DELAYED INCUBATION PROCEDURE

Introduction

Stations of the National Water Quality Network conduct the initial steps in the delayed incubation membrane filter coliform test. These consist of:

1. Sample collection,
2. sample filtration,
3. placement of the inoculated membrane filter upon preservative medium, and
4. shipment to a National Water Quality Section Laboratory of the Water Quality Network.

Sampling and Sample Holding Considerations

The sample for the bacteriological examination is to be collected each week directly into a separate, clean, sterilized glass-stoppered bottle(1) at the time that the collections are made for the chemical and radiological samples. The bottle should not be filled beyond 1/2 to 3/4 full in order that the sample may be well shaken. Examinations will be made by the membrane filter delayed incubation technique. Because of the nature of bacterial organisms, it is very important that the sample be filtered immediately, and that the membrane be transferred to the holding medium and mailed to the Water Quality Section as quickly as possible. Membranes shipped long distances into a central laboratory after an undue delay has occurred do not represent a true picture of the bacterial populations present at the time of sample collection. Samples mailed on Monday, Tuesday or Wednesday are desired. Samples mailed on Thursday or Friday remain in shipment too long for satisfactory analysis.

SUPPLIES AND EQUIPMENT

The Water Quality Section will provide the necessary filtration equipment used for coliform density determinations to those cooperating laboratories which do not already have it on hand. All other related necessary supplies will also be provided by the Section. The filtration apparatus and shipping containers for the samples are shown in Figure 11 .

The Water Quality Section will also provide, at intervals, the supplies listed below for the membrane filter coliform test. When the current supply of most or all of the items is exhausted, return the shipping container with any unused materials to the Water Quality Section. Do not hesitate to notify the Water Quality Section when supplies are near depletion.

Each shipping container forwarded periodically to the cooperating laboratory will contain:

m-Endo Broth MF (dehydrated) ----------1/4 pound[2]

Denatured alcohol (25 ml)---------- 2 tubes

Sodium benzoate solution, 12% aqueous (25 ml)---------- 2 tubes

Sterile plastic membrane filter containers-------- 80

Sterile MF filters with absorbent pads (10/pack)---------- 8 packs

Phosphate buffer concentrate (20 ml)---------- 2 tubes

Mailing cartons---------- 26 each

Addressed franked labels for cartons---------- 26 each

Transmittal forms---------- 26 each

Preparation of Equipment and Reagents

The equipment for preparation of samples is listed below:

a. Filtration assembly unit consisting of metal funnel[3] and filter support base,

b. filter flask, 1000 ml capacity,

c. vacuum source (pump or aspirator),

d. sterile graduates or pipettes for measuring sample,

e. 99.0 ml sterilized phosphate-buffered distilled water blanks[4],

f. three sterile membranes with three absorbent pads for each sample to be examined,

g. three sterile plastic membrane filter containers,

h. forceps immersed in pure ethyl alcohol,

i. medium (see below).

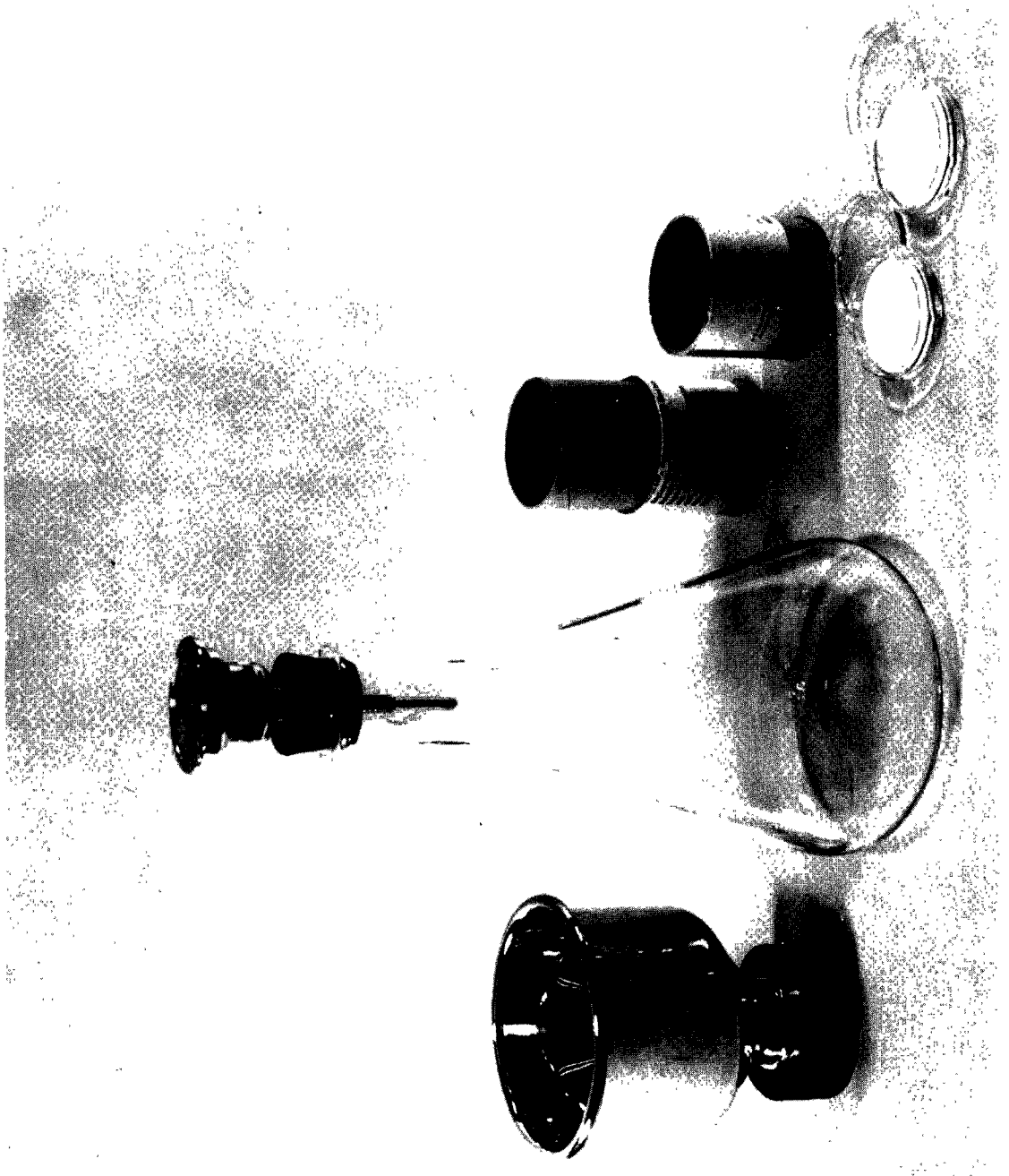


Figure 11. Filtration Apparatus and Shipping Containers for Coliform Samples.

Procedure for Sterilizing Equipment

a. Wrap funnel and filter base in kraft paper in separate packages and sterilize in autoclave for 15 minutes at 121° C (15 psi). Cool to room temperature before use. If an autoclave is not available, a bottle sterilizer or pressure cooker of sufficient size may be used. (For emergency use, in the absence of better sterilizing facilities, immerse funnel and filter support base in boiling water for five minutes. Remove the equipment, cool to room temperature and place the assembly on the filter flask and draw enough air through the porous support disc of the filter base to remove excess water.)

b. Membranes and absorbent pads are supplied by the Water Quality Section. Both the membranes and pads are supplied in sterilized packets in kraft paper and are ready for use in the procedure.

c. Sterilized plastic membrane filter containers are ready for use.

d. Pipettes, sample bottles, graduates, and other equipment should be properly protected by kraft paper and sterilized at 170° C in dry heat for two hours or by steam pressure (autoclave for 30 minutes at 121° C, 15 psi).

e. Sterilized, buffered, distilled water dilution blanks are prepared by the addition, with shaking, of 1.2 ml of phosphate buffer (supplied by Water Quality Section) to 1000 ml of distilled water(4). This is dispensed in 99.0 ml aliquots, plus or minus 2.0 ml. The bottles are autoclaved at 121° C/15 psi for 20-30 minutes. The sterilizer is slowly cooled and/or slowly exhausted. Caps or stoppers are loosened prior to sterilizing, and tightened when bottles have cooled. (Bottles may be filled with 90.0 ml, plus or minus 2.0 ml, if such is preferred; the use of 9.0 ml dilution blanks is not encouraged).(5)

Preparation of m-Endo Broth

a. m-Endo Broth-MF-Dehydrated (always use the latest shipment of medium(2).

b. Sodium benzoate solution, 12% aqueous (supplied as sterile stock solution in quantity to last six months).

c. Ethyl alcohol (ethanol or grain alcohol, U.S.P. grade, 95%).

d. Two sterile 1 ml pipettes.

e. Erlenmeyer flask, 125 or 250 ml.

Directions for preparation of m-Endo Preservative Medium:

a. Place 50 ml heated distilled water in a sterile and chemically clean 125 or 250 ml Erlenmeyer flask.

b. Add 1 ml ethyl alcohol.

c. Add with gentle agitation 2.4 grams dehydrated m-Endo Broth MF.

d. Place the flask containing the distilled water, alcohol and m-Endo MF medium in a beaker of boiling water until the medium is dissolved (6). Do not heat the flask over an open flame as this may cause some deterioration of the medium if the solution is overheated (see illustration, p. 36, figure 12.

e. Cool to room temperature.

f. Add 1.6 ml of sodium benzoate solution and mix gently. This is the finished medium and should be prepared fresh for each week's Basic Data test.(7)

SAMPLE VOLUME AND FILTRATION

Successful examination of untreated water for coliform density is dependent upon securing at least one membrane with between 20 and 60 coliform colonies and with not more than two or three hundred colonies of all types.

Development of colonies of non-coliform flora is generally restricted, to a great extent, by the indicator in the medium, but there are exceptions. A number of non-coliform colonies may be present on the membrane, particularly where the water sample is obtained from certain wells, lakes, and lagoons. Sewage, on the other hand, will show few non-coliform colonies via the m-Endo MF technique.

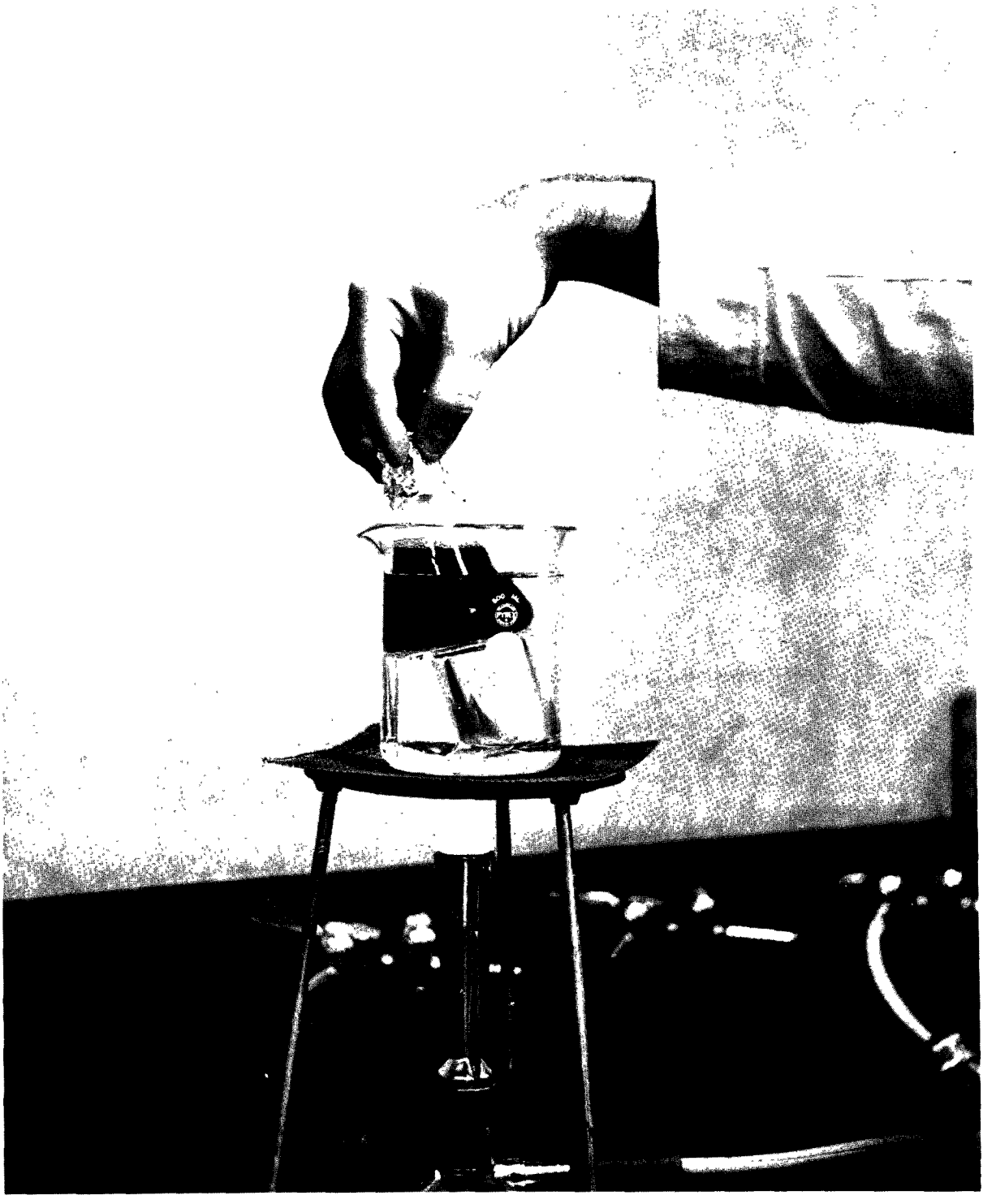


Figure 12. Preparation of m-Endo Broth

When there are no existing data on the coliform density of a water sample, the quantities to be used for routine sampling must be determined by a "trial and error" method. In this instance, begin sampling operations by using sample volumes of 0.01, 0.1, and 1.0 ml for the three dilutions.

In the delayed incubation membrane filter procedure, the local laboratory does not see the finished membranes to determine conformity with the above requirements. Therefore, the Water Quality Laboratory completing the test will immediately report to the local laboratory when any test is unsatisfactory due to excessive colony density or insufficient number of colonies, and when possible, recommend changes in quantities of water to be filtered for the test. If the sample is not subject to great weekly changes, the Public Health Service will then recommend volumes of approximately (1st membrane) 1/3 below and (3rd membrane)3.0 times above that volume (2nd membrane) which yields a total of 20 coliform colonies.

Filtration Procedure

The Delayed Incubation Membrane Filter Procedure (Tentative Test) for coliforms is described on Pages 513-515 of Standard Methods for the Examination of Water, Sewage and Industrial Wastes, 11th Edition, 1960. The delayed test has many procedures in common with the immediate test; Pages 508-513, and special reference is made to the illustration, "Fig. 20, Membrane Filter Assembly" and discussion of paragraph 1.6, page 510 (11th Ed.), for a typical assembly of membrane filtration equipment. The filtration of the sample after the equipment has been assembled is as follows:

a. Place absorbent pads in bottom of sterile plastic containers.

b. Saturate each pad with benzoated m-Endo MF broth and remove any excessive medium from pads by draining the plates gently.

c. Flame forceps and place sterile membrane (grid side up) in filter receptacle and seal funnel on membrane with care in order to avoid tearing or creasing the membrane.

d. Shake sample vigorously at least 25 times.

e. Measure water sample [8] in funnel with no vacuum on filter flask.

1. If volume of sample is 10 ml or more, transfer measured sample directly onto dry membrane.

2. If between 1.0 ml and 10 ml, pour about 20 ml of sterilized buffered distilled water into the funnel before transferring the measured sample onto the membrane. This facilitates good distribution of organisms.

3. If the volume of original water sample is less than 1.0 ml, prepare appropriate dilutions and proceed as in item 2.

Never pipette directly less than 1.0 ml; bacterial distribution is unsatisfactory if this is done!

4. Diluted samples should be filtered within 20 minutes of preparation because bacterial die-off is detectable after 30 minutes of holding at room temperature.

For required dilutions, the shaken sample should be added to the dilution bottle in the following amounts:

Dilution	Vol. Sample	Vol. Dilution Water
1:10	10.0 ml	90.0 ml in bottle
1:100	1.0 ml	99.0 ml in bottle
1:1,000	10.0 ml of 1:100	90.0 ml in bottle
1:10,000	1.0 ml of 1:100	99.0 ml in bottle

After the sample is added to the bottle, the bottle is then closed tightly and shaken vigorously at least 25 times.

f. Turn on vacuum and filter sample.

g. Rinse sides of funnel down twice with at least 20 ml of sterile buffered distilled water each time, keeping vacuum on.

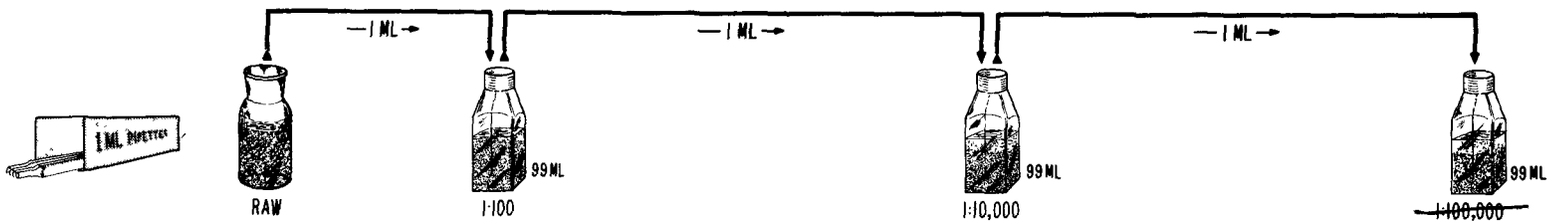
h. Remove funnel from receptacle and place on sterile paper.

NATIONAL WATER QUALITY NETWORK

DILUTION CHART FOR MEMBRANE FILTRATIONS

ALWAYS FILTER VOLUMES OF RAW OR DILUTED SAMPLE IN PORTIONS OF ONE MILLILITER OR MORE . ALL BOTTLES SHOULD BE SHAKEN RAPIDLY TWENTY-FIVE TIMES THROUGH AN APPROXIMATE ARC OF ONE FOOT BEFORE PIPETTING PORTION FOR FILTRATION.

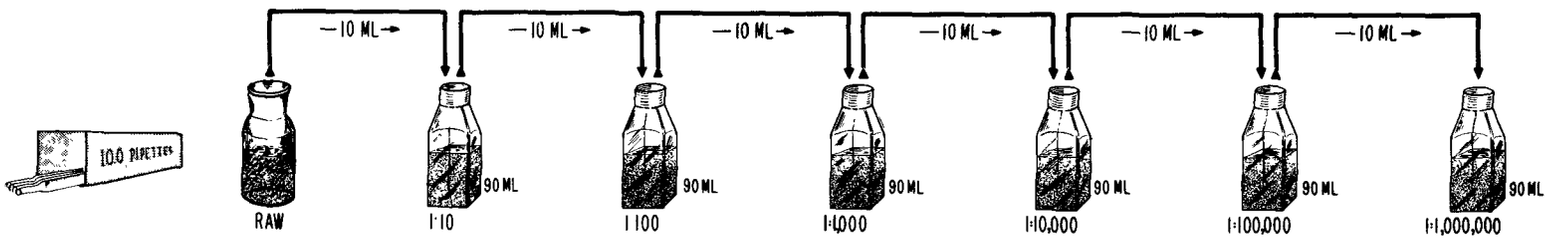
THE CHOICE OF THE DILUTION PROCEDURE DEPENDS UPON THE AVAILABILITY OF NEEDED GLASSWARE AND UPON PERSONAL PREFERENCE.



99.0 ML STERILIZED PHOSPHATE BUFFERED DISTILLED WATER DILUTION BLANKS

1 ML PIPETTES ARE USED EXCLUSIVELY IN THIS SERIES

1:1,000,000



90.0 ML STERILIZED PHOSPHATE BUFFERED DISTILLED WATER DILUTION BLANKS

10.0 ML PIPETTES ARE USED EXCLUSIVELY IN THIS SERIES

i. Flame the forceps. Using the forceps, remove the membrane from the filter base and lay it on the soaked absorbent pad in the plastic container, grid side up, with a rolling action at one edge, as shown in Figure 14. Use care to avoid trapping air bubbles under the membrane.

j. Place top of container gently over bottom and proceed with filtration of next volume of water. All three quantities in ascending order of volume can be filtered in same funnel apparatus with only the rinsing (described in "g") between dilutions. When using descending orders of volume, or when changing to samples of an unknown degree of pollution, the funnel must always be rinsed between filtrations.

k. Let membrane stand for about 5 minutes.

l. Inspect each transferred membrane for the presence of colorless spots under its surface; these indicate the presence of air bubbles.

m. If the membrane does not have a uniform pink color, remove with forceps and roll onto absorbent pad again.

n. Seal the plastic container by pressing top firmly on.

SHIPPING

a. Mark the top of each container with the station name or code number, the sample number and the volume of sample. A marking pen is provided for this purpose. The sample number should correspond to the appropriate number on the sample's transmittal sheet. The transmittal sheet should show clearly the volume sampled, or preferably, the dilution prepared and volume of that dilution which was used. (See sample forms on page 44. Do not mail membrane samples on Thursday or Friday since these samples are held by the Post Office over Saturday and Sunday before delivery to the Central Laboratory. A 72 hour delay causes unreliable results.

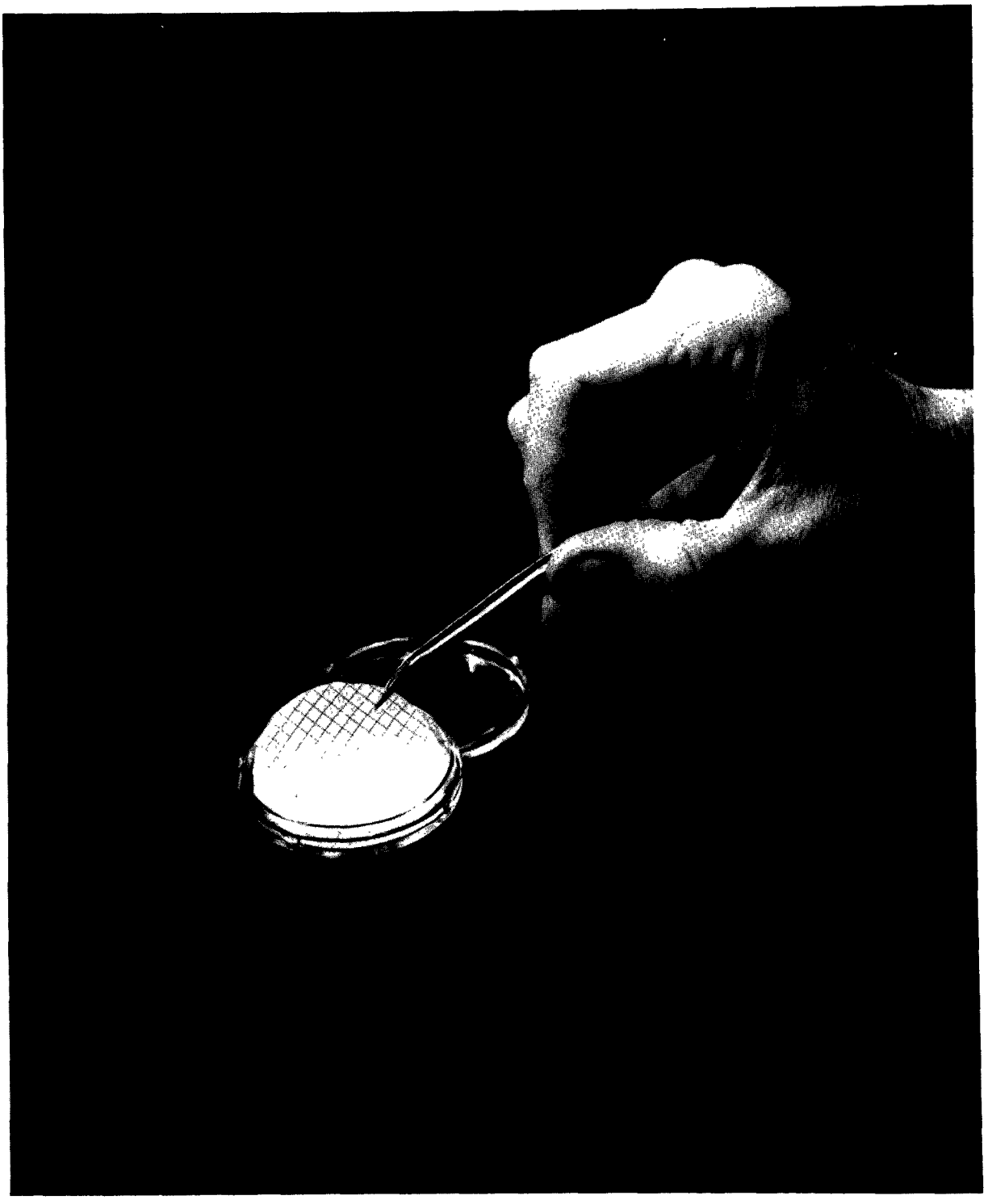


Figure 14. Placing Membrane on Pad Soaked with Preservative Medium.

NOTES

1. The sample of water should come into contact with no holding vessel other than the sterilized glass container; the raw sample is placed directly into the glass bottle.

2. The dehydrated medium will be supplied in quarter pound jars to those stations which have available a balance with sensitivity of ± 0.1 gram.

   If no balance is available, the medium can be supplied by the Public Health Service in small vials containing 2.4 grams each.

   The dehydrated medium will absorb moisture rapidly which results in caking and spoiling the powder. The jar containing the dehydrated stock medium must be sealed tightly each time after using to prevent absorption of atmospheric moisture.

3. Eventually, through use, the fixed nylon locking wheels of the metal funnel will develop localized flat areas. As a result, the filtration apparatus may leak. This can be relieved by using the small Allen wrench supplied with the filtration apparatus to loosen the set screw. The screw may then be loosened and the wheel rotated to an unused bearing surface. The screw again is tightened and the set screw drawn against it.

   Do not attempt to sterilize the metal funnel in a drying oven because the dry heat may damage the nylon locking wheels.

   The filtration apparatus should be cleaned by rinsing with tap water or with detergent and a brush, followed by a thorough rinse, and a final wipe with a clean, lint-free cloth. Never use scouring powder, steel wool, or an acid cleaning treatment.

   Following considerable use of the stainless filtration apparatus, areas of exposed copper may develop, particularly around the throat of the filtration apparatus. If exposed areas are visible, the filtration apparatus should be returned. A new one will be sent immediately to replace the old one.

4. If the distilled water used for dilutions and funnel rinsings come in <u>any</u> contact with copper or zinc, please notify us.

5. The dilution bottles holding the phosphate buffered distilled water should be of heat-resistant glass. Rubber stoppers and liners of screw caps should contain no toxic, heat-releasable component. Specialized-usage white liners and stoppers are preferred.

6. A small amount of grayish-black powder may remain in the bottom of the flask after the bulk of the m-Endo MF medium has gone into solution. This is a common occurrence and may be ignored.

7. For stations which desire to run the immediate MF test, the quantities can be doubled, medium divided into two 50 ml portions in step (5) and 1.6 ml of sodium benzoate solution added to one portion. The portion <u>without added</u> sodium benzoate can be used as a single step procedure for the immediate MF test. (Fifield, C.W. and C.P. Schaufus, JAWWA 1958: 50: 193-196.)

8. If water sample to be filtered is:

   Over 20 ml, use appropriate sterile graduate.
   Between 2-20 ml, use 10 ml or 20 ml sterile pipette.
   Between 1.0 - 2.0 ml, use 1 or 2 ml graduated sterile pipette.
   Less than 1.0 ml, make appropriate dilutions in sterilized buffered distilled water and use an appropriate sterilized pipette.

DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
PUBLIC HEALTH SERVICE
1014 Broadway, Cincinnati 2, Ohio

DELAYED INCUBATION TEST

STATION NO. 225

DATE COLLECTION JULY 1, 1965

TIME OF SAMPLE COLLECTION 0800 BY JOHN JONES

DATE FILTRATION JULY 7, 1965

TIME OF SAMPLE FILTRATION 0830 BY TOM WILSON

SAMPLE POINT LOCATION WINDING RIVER AT MILLVALE, OHIO

*RECEIVED W.Q.S. DATE _____ *TIME _____ *ELAPSED TIME _____ HOURS

LOCATION OF PLANT OR LABORATORY EASTERN MILLVALE SEWAGE TREATMENT PLANT

COLIFORM

MLS UNDILUTED	MLS IN 10 DILUTION	CONTAINER SERIES NO.	WQS *LABORATORY NUMBER	*COLIFORM COLONY COUNT	*COLIFORMS PER 100 ML.	REMARKS
———	2.0	1 *				
———	6.0	2				
2.0	———	3				
———	4.0 of 1:100	A **				
———	2.0 of 1:10	B				
1.0	———	C				

*FOR USE OF WATER QUALITY SECTION, CINCINNATI, OHIO DO NOT USE.

REMARKS

*A PROCEDURE FOR ENTERING ON THE TRANSMITTAL FORM SUCH EXAMPLE VOLUMES AS 0.2 ML, 0.6 ML, AND 2.0 ML.

**AN ALTERNATE PROCEDURE FOR ENTERING ON FORM SUCH EXAMPLE VOLUMES AS 0.04 ML, 0.2 ML AND 1.0 ML.

A REMINDER: FOR FILTRATION PROCEDURES, ONLY VOLUMES OF 1.0 ML, OR GREATER, SHOULD BE MEASURED DIRECTLY INTO THE FILTRATION APPARATUS.

PHS-2645-12 (REV. 8-62) NATIONAL WATER QUALITY NETWORK

FORM APPROVED BUDGET BUREAU NO 68 R6 34

SECTION VII

CHEMICAL AND PHYSICAL ANALYSES

PRELIMINARY REMARKS

Samples taken for chemical and physical analyses should be representative of the raw water in the river. A large enough sample should be collected to satisfy the requirements for the chemical analyses to be performed. A special sampling technique will be required for the dissolved oxygen (DO) and biochemical oxygen demand (BOD) determinations and will be described under these tests. The collected sample should be kept in a closed container except when portions are withdrawn for the various analyses. A 2-liter bottle of pyrex or polyethylene will be satisfactory for a container.

Detailed procedures are presented below for the chemical and physical analyses of the raw water sample. In most instances the methods described follow closely the procedures in Standard Methods for the Examination of Water, Sewage, and Industrial Wastes (10th Ed., 1955; 11th Ed., 1960). For the sake of uniformity, it is suggested that these procedures be used by all the cooperating laboratories in the National Water Quality Network. The laboratories have a free choice, however, in using any procedure found to be satisfactory, provided its precision and accuracy are within normally accepted limits. The Reference Samples, as sent out periodically by the Water Quality Section, will be one of the tools by which the precision and accuracy of the various analytical methods in use will be measured.

The procedures outlined in the following pages are in the same order as they appear on the Report Form (Form PHS 2845-1, Rev. 6-59). Those determinations numbered 1 through 8 should be performed as soon as possible after the sample is collected. This group includes: (1) Temperature, (2) dissolved oxygen (DO), (3) pH, (4) biochemical oxygen demand (BOD), (5) chemical oxygen demand (COD), (6) chlorine demand, 1 hour, (7) chlorine demand, 24 hours, and (8) ammonia nitrogen, NH_3/N. These tests should be performed, as far as possible, by the cooperating agency; the data cannot otherwise be obtained.

Since many of the cooperating agencies in the Network perform all the required determinations, the outlined procedures for tests 9 through 16 are also included. These tests

are specifically: (9) Chlorides, (10) alkalinity, (11) total hardness, (12) color, (13) turbidity, (14) sulfates, (15) phosphates, and (16) total dissolved solids, and are included for convenient reference. For those agencies with limited analytical facilities, arrangements can be made to have the 9 to 16 group performed in the Water Quality Section Laboratory. (See Section II, General Instructions, paragraphs a & b).

In general, in the procedures that follow, the standardization of reagents is not described. Many of these reagents are procurable as standard solutions from reliable supply houses. Those that cannot be easily obtained will be provided to participants, upon request, by the Water Quality Section.

TEMPERATURE (Standard Methods, 11th Ed., p. 270)

Accurate temperature readings are necessary for calculating dissolved oxygen saturation values, for correlation of biological activity, and for many other purposes.

The temperature to be reported should be representative of the temperature of the stream at the time the sample is collected. The temperature must, therefore, be taken at the sampling point. The thermometer should be immersed in the flowing stream, or in a large sample container filled with the sample, and held until the mercury is at rest. The temperature should then be read before removing the thermometer from the sample.

Record the temperature to the nearest fraction of a degree Centigrade, which can be estimated from the thermometer being used.

If Fahrenheit thermometer is used, convert readings to Centigrade as follows:

Subtract 32 from the Fahrenheit reading,
multiply the results by 10 and divide by 18.

If there is a doubt as to the accuracy of the thermometer being used, it may be sent to the Water Quality Section to be checked against a Bureau of Standards thermometer.

DISSOLVED OXYGEN (DO)

1. Collection of Sample. Whenever possible, samples should be taken from the stream. A sampling device should be used that provides for at least three volumes of water to pass through the DO sampling bottle without aeration by the atmosphere. The device may contain two bottles, in which case the second bottle may be incubated for the BOD. At least 1 liter of water, in a separate container, should be collected at the same time the DO samples are taken. It may be needed for the BOD test, if conditions for this test, listed under the BOD instructions, are violated. It can also be used for the other physical and chemical determinations. River temperature should be recorded at the time the DO sample is taken.

   If a source of raw river water, under pressure, is available, and it has been determined that there is no aeration from pumping, and that no treatment of the water has occurred ahead of the sampling point, then this source may be used as a satisfactory sampling point, but only if direct sampling from the stream is impractical.

2. Sampling Apparatus.

   2.1 Standard 300-ml BOD bottles.

   2.2 DO sampler (see p. 251, Standard Methods, 10th Ed., or p. 308, 11th Ed., for illustration). The Water Quality Section can provide this sampling device upon request.

3. Sampling Procedure.

   3.1 Sampling from the stream:

      a. Place 2 DO bottles in sampler.

      b. Immerse sampler in stream to the necessary depth (about one-half the depth at sample point) and hold until bubbling stops before lifting out.

      c. Carefully lift off the top, taking precautions to prevent contents of the bottle from coming in contact with air.

      d. Stopper the bottles carefully to avoid air entrapment under the stopper.

3.2 Sampling from raw water under pressure; this procedure may be used only if it is known that the raw water is not being aerated during the pumping, and no water treatment has occurred ahead of the point at which the sample is collected.

a. Place a rubber or glass tube from the raw water line into the bottom of a BOD bottle.

b. Run the water into the bottle until it is full and allow it to overflow two or three times its volume.

c. Slowly withdraw the sampling tube while the water is still running.

d. Carefully stopper the sample bottle, preventing any air from being entrapped.

e. Repeat with the second sample bottle.

4. Reagents.

4.1 Manganous sulfate solution. Use any one of the following compounds:

a. $MnSO_4 \cdot 4H_2O$, 480 g

b. $MnSO_4 \cdot 2H_2O$, 400 g

c. $MnSO_4 \cdot H_2O$, 364 g

Dissolve in distilled water and make up to 1 liter.

4.2 Alkaline iodide - azide solution.

Dissolve 500 g sodium hydroxide (NaOH),
135 g sodium iodide (NaI),
10 g sodium azide (NaN_3)

all together in distilled water. Make up to 1 liter.

4.3 Concentrated sulfuric acid - reagent grade.

4.4 Standard bi-iodate solution. Weigh out 0.8124 g of potassium bi-iodate and dissolve in 1 liter of water. This must be done carefully. The accuracy of the DO test depends on the care with which this solution is prepared.

4.5 Starch solution.

a. Make a paste of about 5 to 6 g potato, arrowroot, or soluble starch in a small quantity of water.

b. Add it to about 1 liter of boiling distilled water and boil a few minutes.

c. Cool, allow to stand overnight.

d. Pour off and save the clear solution.

e. Add a few drops of toluene as a preservative.

4.6 Standard thiosulfate solution.

a. Stock solution - 1.0N.

a.1 Dissolve 248 g $Na_2S_2O_3 \cdot 5H_2O$ (reagent grade) in freshly boiled and cooled distilled water. Dilute to 1 liter.

a.2 Add 5 ml chloroform or 1 g sodium hydroxide as a preservative.

b. Titrating solution - 0.025N.

Dilute 25.0 ml of the stock solution with distilled water to 1.0 liter. Add preservative as above.

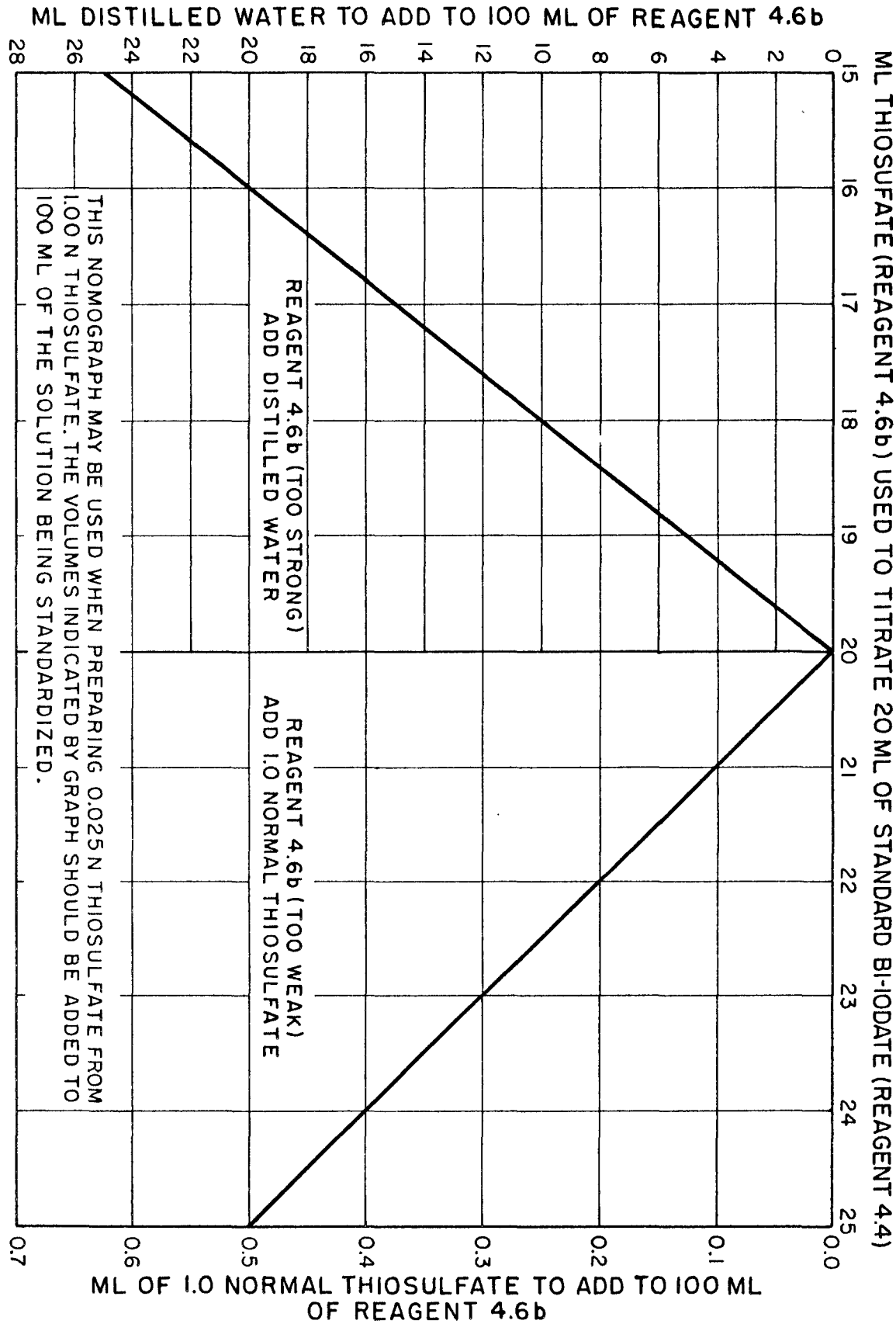
4.7 Standardization of titrating solution 4.6b.

a. Dissolve about 2 g sodium or potassium iodide in 100 to 150 ml distilled water.

b. Dilute 1 ml of concentrated sulfuric acid to 10 ml with distilled water and add this to the iodide solution.

c. Add <u>exactly</u> 20.0 ml of standard bi-iodate solution.

d. Dilute to 200 ml and titrate with .025N ~~sulfuric acid~~ thiosulfate solution until a pale yellow color is reached.


ML DISTILLED WATER TO ADD TO 100 ML OF REAGENT 4.6b
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
ML THIOSUFATE (REAGENT 4.6b) USED TO TITRATE 20 ML OF STANDARD BI-IODATE (REAGENT 4.4)
15 16 17 18 19 20 21 22 23 24 25
REAGENT 4.6b (TOO STRONG)
ADD DISTILLED WATER
REAGENT 4.6b (TOO WEAK)
ADD 1.0 NORMAL THIOSULFATE
THIS NOMOGRAPH MAY BE USED WHEN PREPARING 0.025 N THIOSULFATE FROM 1.00 N THIOSULFATE. THE VOLUMES INDICATED BY GRAPH SHOULD BE ADDED TO 100 ML OF THE SOLUTION BEING STANDARDIZED.
0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0
ML OF 1.0 NORMAL THIOSULFATE TO ADD TO 100 ML OF REAGENT 4.6b

e. Add starch solution and continue the titration carefully to the disappearance of the blue color. If the 0.025N ~~sulfuric acid~~ thiosulfate solution is of proper strength, it should take exactly 20.0 ml to reach the endpoint.

f. Adjust this reagent, either with 1.0N ~~sulfuric acid~~ or distilled water until its strength matches that of the 0.025N bi-iodate solution. thiosulfate solution

g. Recheck this solution once a week and adjust to proper strength.

5. Procedure.

5.1 Add 2 ml of manganous sulfate followed by 2 ml of alkaline iodide to the DO sample. Take care to add these reagents with the tip of the pipette below the water surface. Carefully stopper and mix vigorously. Do not allow air to be entrapped below the stopper.

5.2 Let stand for 2 to 3 minutes and repeat the mixing, then let stand until the precipitate in the bottle has settled at least half way.

5.3 Add 2 ml of concentrated sulfuric acid and stopper carefully to prevent air bubbles from entering the bottle. Rinse the outside of the bottle with tap water; mix thoroughly as before.

5.4 Remove 204 ml of treated sample and transfer to a 500 ml Erlenmeyer flask.

5.5 Titrate with 0.025N sodium thiosulfate until a pale yellow color is reached.

5.6 Add approximately 5 ml of starch solution and carefully continue the titration to the disappearance of the blue color.

5.7 Record the titration.

5.8 Add 1 drop of 0.025N bi-iodate solution. This should bring back the blue color. If more than one drop is necessary, count the drops and subtract 0.05 ml from the titration for each drop in excess of one.

6. Calculation. If the 0.025N sodium thiosulfate is of proper strength, the volume added in the titration above gives the DO value directly in mg/l. Record to the first decimal.

HYDROGEN ION CONCENTRATION (pH) (Standard Methods, 11th Ed., p. 193)

pH can be measured either colorimetrically or with a pH meter. The later measurement is preferred, though colorimetric measurement is acceptable if a pH meter is not available.

1. Collection of Sample. Use the raw water sample collected for the mineral analyses.

2. Apparatus.

   a. Commercial pH meter, or

   b. commercial color comparator.

3. Reagents.

   3.1 Buffer, pH 4:

   Dissolve 10.2 g anhydrous potassium biphthalate in boiled and cooled distilled water. Dilute to 1 liter.

   3.2 Buffer, pH 7:

   Dissolve 1.361 g anhydrous potassium dihydrogen phosphate and 1.420 g anhydrous disodium hydrogen phosphate in boiled and cooled distilled water. Dilute to 1 liter.

   3.3 Buffer, pH 9:

   Dissolve 3.81 g sodium tetraborate decahydrate (borax) in boiled and cooled distilled water.

4. Procedure. Follow the recommended procedure of the instrument manufacturer.

5. Results. Report to the nearest 0.1 pH unit.

6. Precautions.

   6.1 pH meter.

   Be sure that electrodes are clean, the glass electrode is not cracked or scratched, the calomel electrode contains saturated potassium

chloride solution and its liquid junction (the tip) is not plugged. Remove the rubber stopper on the calomel electrode before use to permit flow of the electrolyte through the tip. When calibrating the instrument use the buffers which will bracket the pH value of the sample.

6.2 Commercial comparators.

Comparator tubes should be matched,both as to size and color of glass. Be sure that the light passing through the comparator tubes is of equal intensity. If pH reading of sample is at either extreme of the indicator range, check with the next indicator in the series available before reporting pH value. If indicator solution becomes turbid, replace with fresh indicator.

BIOCHEMICAL OXYGEN DEMAND (BOD)

1. Collection of Sample. Collect at least 1 liter of water at the same time the DO samples are collected. The water in the DO sampler may be saved for this purpose.

2. Procedure.

   2.1 Determine the DO on one of the samples collected for this purpose.

      a. If the DO value is between 9.2 and 6.9 mg/l, place the duplicate DO sample in the 20°C incubator and incubate for 5 days. Be careful to maintain the water seal on the sample during the incubation period, then proceed with 2.6 below.

      b. If the DO value is above 9.2 or below 6.9, discard the duplicate DO sample, and proceed with 2.2 below.

   2.2 Place about 1/2 gallon of the water collected at the time the DO sample was taken in a 1-gallon jug. Let it stand (or warm it) in the laboratory until it reaches room temperature.

   2.3 Stopper the jug and shake the sample vigorously to bring it to saturation with atmospheric oxygen. During the shaking, the stopper should be removed several times to allow the transfer of oxygen. Siphon it carefully into duplicate DO bottles.

   2.4 Determine the initial DO on one bottle.

   2.5 Incubate the other bottle for 5 days, as in 2.1a above.

   2.6 After 5 days of incubation determine the DO on the incubated sample.

3. Calculation. Calculate BOD as follows:

   Initial DO - Final DO = mg/l BOD

Note: In the event that the final DO is zero, the BOD reported should be indicated as "greater than". If zero DO in the incubated bottle recurs frequently, it will become necessary to set up dilutions of the original sample. Should this be necessary, follow the instructions in Standard Methods for the preparation of BOD dilutions.

CHEMICAL OXYGEN DEMAND (COD) (Reduced Strength Procedure for River Waters)

1. Collection of Sample. Use the raw water collected for BOD analyses (see Section II, page 8, paragraph f).

2. Apparatus. Every precaution should be taken to insure that the sample bottles and other equipment used in this test are clean and free from organic matter.

   2.1 Reflux condenser, Friedrichs (Corning #2600), with ground glass standard taper joint 24/40.

   2.2 Erlenmeyer flask, 500ml (Corning 5000) with ground glass neck to fit the condenser; standard taper 24/40.

3. Reagents

   3.1 Sulfuric acid, concentrated (reagent grade).

   3.2 Ferroin indicator solution.
   Dissolve 1.485 g of 1, 10-phenanthroline, with 0.695 g ferrous sulfate$\cdot 7H_2O$ in water and dilute to 100 ml.

   3.3 Standard potassium dichromate.

      a. Dissolve 12.2588 g of potassium dichromate ($K_2Cr_2C_7$), previously dried at 103°C for 2 hours, in distilled water and dilute to 1 liter. This is the stock solution 0.25 N.

      b. Carefully measure 100.0 ml of the stock solution into a 1-liter volumetric flask. Dilute to 1.0 liter with distilled water. This is the working solution - 0.025 N.

   3.4 Standard ferrous ammonium sulfate (referred to hereafter as FAS).

      a. Dissolve 98 g FAS$\cdot 6H_2O$ in distilled water. Add 20 ml concentrated sulfuric acid, reagent 3.1. Cool. Dilute to 1 liter. This is the stock solution.

b. Place 100 ml of the stock solution in a 1-liter volumetric flask. Carefully add 20 ml of concentrated sulfuric acid. Cool. Dilute to 1 liter. This is the working solution. It is approximately 0.025 N and must be standardized each time before use by the following procedure.

4. Standardization of FAS (Reagent 3.4b).

4.1 Take 25.0 ml of 0.025 N potassium dichromate and add to about 300 ml of distilled water in a flask.

4.2 Add 50.0 ml of concentrated sulfuric acid carefully. Allow to cool.

4.3 Add 8 to 10 drops of ferroin indicator.

4.4 Titrate with FAS (reagent 3.4b) to a deep red color. This is a sharp end point if the sample has been cooled properly before adding the indicator.

5. Calculating the Normality of FAS:

$$\text{Normality} = \frac{\text{ml potassium dichromate X } 0.025}{\text{ml FAS}}$$

6. Procedure for COD.

6.1 Take 50.0 ml of the well-mixed sample and add it to the sample flask.

6.2 Add exactly 25.0 ml of 0.025 N potassium dichromate.

6.3 Carefully and with thorough mixing, add 75 ml of concentrated sulfuric acid.

6.4 Add 8 to 10 clean glass beads or porcelain chips. Attach the flask to the condenser, place over the burner or hot plate and maintain at gently boiling temperature for 2 hours.

CAUTION: Before applying heat, be sure that the acid has been thoroughly mixed in the flat-bottom flask and that the condenser water has been turned on.

6.5 Cool. Wash down the condenser with about 25 ml of distilled water, then transfer, with thorough rinsing, to the titration flask. Dilute to about 350 ml with distilled water.

6.6 Add 8 to 10 drops of ferroin indicator to the cooled sample.

6.7 Titrate with FAS (reagent 3.4b) to the red end point.

6.8 If no dichromate remains, as indicated by an immediate red color that occurs when ferroin indicator is added, the test must be rerun with a lesser quantity of sample. Repeat the test with 25.0 ml of sample plus 25.0 ml of distilled water.

7. Calculation of COD.

7.1 Dichromate consumed by digestion:

$$25.0 - \left(\frac{\text{ml FAS X normality of FAS}}{0.025}\right)$$

= ml dichromate consumed.

7.2 $\frac{\text{ml dichromate consumed}}{\text{ml sample}}$ X 200 = Gross Demand.

7.3 Correction for chloride:

mg/l chloride in sample X 0.23 = chloride correction

7.4 Subtract result in 7.3 from Gross Demand and report as COD to the nearest mg/l.

8. COD Samples for WQS. Space has been provided in the carbon filter shipping container to simplify forwarding of this sample, as shown in Figure 1, page 14. It will be necessary, therefore, to schedule the collection of this sample for the second week of the month. This is necessary to avoid errors owing to prolonged storage of COD samples. Add 50 ml of the sample collected for the weekly mineral analyses to the sample bottle in the carbon filter box. Fill out the attached tag and replace in the carbon filter shipping container. This bottle already contains acid. Do not rinse out or spill any of it. Do not send this sample separately by mail.

CHLORINE DEMAND (Standard Methods, 10th Ed., p. 63, 11th Ed. p. 83)

The results of the chlorine demand test are dependent to a considerable degree on the procedures and techniques used. Although there are a number of methods used for the evaluation of chlorine demand of water, a uniform procedure must be used when comparisons among several stations are desired. To demonstrate changes within a river basin, each laboratory must, therefore, use the identical test procedure. For this reason, the procedure described below is the only one that should be used in reporting chlorine demand results to the Network.

1. Collection of Sample. Use raw water collected for the mineral analyses. You may need several liters; be sure to collect enough water for all the tests.

2. Apparatus. About 6 to 10 clean, quart-size bottles or flasks.

3. Reagents.

   3.1 Sulfuric acid (reagent grade) 20 ml per liter. Add 20 ml of concentrated sulfuric acid to approximately 750 ml distilled water. Dilute to 1 liter.

   3.2 Potassium iodide, (crystals) reagent grade.

   3.3 Starch solution (see DO instructions, page 50).

   3.4 Sodium thiosulfate - 0.025 N (see DO instructions, use reagent4.6b,page 50).

   3.5 Chlorine solution (500 mg/l).

      a. Stock solution - a bottle of clorox contains approximately 5 percent chlorine (50,000 mg/l).

      b. Working solution (500 mg/l).

         Take 10 ml of (a) and dilute to 1 liter.

4. Standardizing the Chlorine Solution (Reagent 3.5b).

   4.1 Add about 500 ml of distilled water to a titrating flask or bottle.

4.2 Add 3 to 4 crystals of potassium iodide.

4.3 Add 10 ml sulfuric acid.

4.4 Measure accurately 25.0 ml of chlorine working solution (reagent 3.5b) and add to the flask, swirling rapidly during the addition.

4.5 Titrate with sodium thiosulfate to a pale yellow.

4.6 Add 5 to 10 ml of starch solution.

4.7 Titrate carefully to the disappearance of the blue color, adding the reagent dropwise.

5. Calculating the Strength of Chlorine Working Solution (Reagent 3.5b):

$$\text{mg } Cl_2 \text{ per ml of working solution} = \frac{\text{ml of thiosulfate X } 0.025 \text{ X } 35.5}{\text{ml of working solution taken}}$$

6. Procedure for Chlorine Demand.

6.1 Measure out 500 ml of sample into each of 6 to 10 flasks or bottles.

6.2 Add 1, 2, 3, 4, etc. ml of working solution to the respective samples. These should now contain approximately 1, 2, 3, 4, etc. mg/l chlorine.

6.3 Set aside at room temperature in the dark for 1 hour.

6.4 After 1 hour, take the first flask and add three or four crystals of potassium iodide.

6.5 Add 10 ml sulfuric acid solution.

6.6 Add 5 to 10 ml of starch solution.

If blue color is observed, titrate with sodium thiosulfate carefully to the end point. If no blue color is observed, repeat with the second flask, etc.

7. Calculation of Chlorine Residual.

7.1 Calculate the chlorine residual in the first flask showing a blue color as follows:

$$\text{mg/l } Cl_2 \text{ residual} = \frac{\text{ml of thiosulfate X } 0.025 \text{ X } 35.5 \text{ X } 1000}{\text{ml of sample}}$$

When the normality of the thiosulfate is exactly 0.025 and the sample size is 500 ml, this is simplified to:

$$\text{mg/l } Cl_2 \text{ residual} = \text{ml thiosulfate X } 1.78$$

7.2 If chlorine residual is less than 1 mg/l, repeat the titration with the next sample in the series. Continue until you find the first one having a residual greater than 1.0 mg/l.

7.3 Hold the remaining samples 24 hours, then repeat the titration on all of the remaining samples.

8. Calculation of Chlorine Demand.

8.1 One-hour demand.

a. Calculate the chlorine added to the first sample that showed a residual greater than 1 mg/l as follows:

$$\text{ml chlorine working solution added X mg } Cl_2\text{/ml X } 2 = \text{mg/l } Cl_2 \text{ added}$$

b. Subtract the chlorine residual that was determined for this sample. The result is the 1-hour demand.

8.2 Twenty-four hour demand.

a. Following the titration in paragraph 7.3 calculate the chlorine residual for each of the remaining flasks, as in paragraph 7.1.

b. If your water has a breakpoint you will notice that the chlorine residuals will rise, then fall, then rise again as the remaining samples are titrated. For calculating the 24-hour demand, use the first sample having a residual above 1 ppm after the second rise (breakpoint).

c. If your water has no breakpoint, calculate the demand on the first sample having a residual above 1 ppm.

AMMONIA NITROGEN (Standard Methods, 11th Ed., p. 167)

The distillation procedure is most accurate when interferences are known to be present, and should be used if equipment is available. In the absence of distillation apparatus, the direct procedure can be used and should be satisfactory for most surface waters of the Network. It is described below.

1. Sample Collection. Use the raw water collected for the mineral analyses.

2. Apparatus.

   2.1 Spectrophotometer or filter photometer, or

   2.2 a Nessler tube series of permanent color standards as specified on p. 146, Standard Methods, 10th Ed., or p. 172, 11th Ed., or

   2.3 permanent standards for ammonia nitrogen, as provided with commercial comparators.

3. Reagents.

   3.1 Ammonia-free water.

      a. Treat distilled water by storage in a "Quickpure" demineralizer for about 20 minutes (distributed by E. H. Sargent & Co., Cat. #S-27810).

      b. Pass distilled water through a column of mixed resin such as Amberlite Mb-1, or

      c. add about 10 g of Folin's ammonia permutit to 1 gallon of distilled water and shake.

   3.2 Nessler reagent.

      a. Dissolve 100 g anhydrous mercuric iodide and 70 g anhydrous potassium iodide in about 50 to 100 ml of ammonia-free water.

      b. Prepare a solution of 160 g sodium hydroxide in 500 ml water. Cool.

      Add the first solution (a) to (b) slowly with stirring. Dilute to 1 liter with ammonia-free water and store, well stoppered, in pyrex.

3.3 Standard ammonium chloride solution.

a. Prepare a stock solution by dissolving 3.819 g anhydrous ammonium chloride in ammonia free water, dilute to 1 liter. One ml of this solution is equivalent to 1.00 mg of ammonia nitrogen.

b. Dilute 10.0 ml of (a) to 1 liter with ammonia-free water. One ml of this solution is equivalent to 0.01 mg of ammonia nitrogen.

3.4 Rochelle salt solution.

Dissolve 500 g of potassium sodium tartrate in 1 liter distilled water. Boil off about 200 ml. Cool. Dilute to 1 liter with ammonia-free water.

3.5 Zinc sulfate solution.

Dissolve 100 g zinc sulfate in ammonia-free water. Dilute to 1 liter.

3.6 Sodium hydroxide.

Dissolve about 250 g sodium hydroxide in ammonia-free water and dilute to 1 liter.

4. Procedure.

4.1 Take 100 ml of raw water sample. Add 1 ml of zinc sulfate solution, and mix.

4.2 Add about 0.5 ml of sodium hydroxide solution. The pH should be about 10.5 by test. Mix thoroughly and allow the floc to settle.

4.3 Decant about 25 ml of supernatant through filter paper and discard.

Collect the next 50 ml of filtrate (or aliquot diluted with ammonia-free water) in 50 ml Nessler tubes and add 1 to 2 drops of Rochelle salt solution.

4.4 Add 1.0 ml Nessler reagent and mix by inverting the tube. Allow to stand 10 minutes.

4.5 Compare with standards or read in spectrophotometer set at 400 to 425 wave length.

a. Calibration curve and control test.

Prepare a calibration curve using increasing quantities of standard ammonium chloride solution, into 50 ml of ammonia-free water, and carry out the Nesslerization as in steps 4.1 through 4.4. Run a known ammonia sample concurrently with the raw river water whenever the quality of the Nessler reagent is under suspicion.

5. Calculation.

Determine the concentration of ammonia nitrogen from the spectrophotometer curve, or by comparison with standards. Multiply by the dilution factor, if a dilution was made, and report as mg/l ammonia nitrogen, to the nearest tenth.

CHLORIDES (Standard Methods, 11th Ed., p. 79)

Three satisfactory methods are described in Standard Methods. The mercuric nitrate method, detailed below, is the one currently used by many laboratories.

1. Collection of Sample. Use raw sample for the mineral analyses.

2. Apparatus. Conventional titrating equipment.

3. Reagents.

3.1 Standard sodium chloride solution, 0.0141 N.

Dissolve 8.243 g NaCl in approximately 250 ml of distilled water and dilute to exactly 500 ml. Dilute 50.0 ml to 1.00 liter. Each ml contains 0.500 mg Cl.

3.2 Standard mercuric nitrate solution, 0.0141 N.

Dissolve 2.3 g of $Hg(NO_3)_2 \cdot 2H_2O$ in 100 ml of distilled water containing 0.25 ml of concentrated HNO_3. Dilute to just under 1 liter and standardize against the 0.0141N sodium chloride solution using the procedure described below for samples. Adjust the mercuric nitrate solution to exactly 0.0141 N and perform a final standardization. Store away from the light in a dark bottle. Standard mercuric nitrate, 0.0141 N is equivalent to 0.500 mg Cl per 1.00 ml.

3.3 Mixed indicator solution: Dissolve 0.5 g of diphenylcarbazone and 0.05 g of bromphenol blue in 100 ml of 95 percent ethyl alcohol. Store in a brown bottle.

3.4 Nitric acid solution; 0.2 N. Dilute 12.9 ml of concentrated HNO_3 to 1 liter.

4. Procedure.

4.1 Use a 100 ml sample, or an aliquot diluted to 100 ml containing less than 10 mg of chloride.

4.2 Add 10 drops of the mixed indicator solution to the sample.

4.3 Add 0.2 N nitric acid dropwise to the sample until the color becomes a definite yellow (approximately pH 3.6). Add 5 drops more.

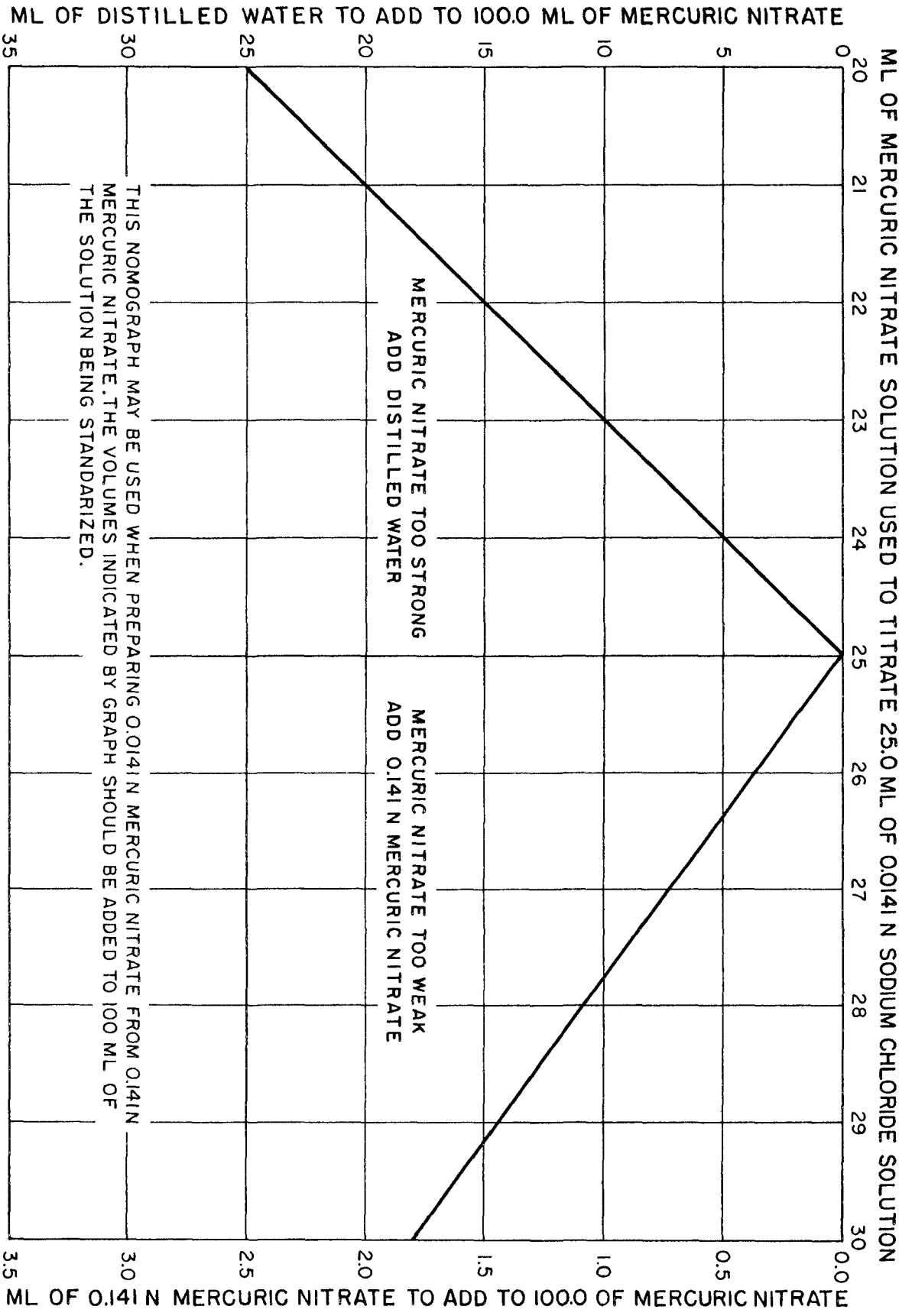
4.4 Titrate with 0.0141 N mercuric nitrate solution to the first permanent tinge of violet.

5. Calculation:

$$\text{mg/l chloride} = \frac{\text{ml of mercuric nitrate} \times \text{N of mercuric nitrate} \times 35.46 \times 1000}{\text{ml of sample}}$$

Note: If mercuric nitrate is exactly 0.0141 N, and if a 100-ml sample is used, this formula becomes:

mg/l chloride = ml of mercuric nitrate X 5.


ML OF DISTILLED WATER TO ADD TO 100.0 ML OF MERCURIC NITRATE
35
30
25
20
15
10
5
0
ML OF MERCURIC NITRATE SOLUTION USED TO TITRATE 25.0 ML OF 0.0141 N SODIUM CHLORIDE SOLUTION
20
21
22
23
24
25
26
27
28
29
30
MERCURIC NITRATE TOO STRONG
ADD DISTILLED WATER
MERCURIC NITRATE TOO WEAK
ADD 0.141 N MERCURIC NITRATE
THIS NOMOGRAPH MAY BE USED WHEN PREPARING 0.0141 N MERCURIC NITRATE FROM 0.141 N MERCURIC NITRATE. THE VOLUMES INDICATED BY GRAPH SHOULD BE ADDED TO 100 ML OF THE SOLUTION BEING STANDARIZED.
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ML OF 0.141 N MERCURIC NITRATE TO ADD TO 100.0 OF MERCURIC NITRATE

TOTAL ALKALINITY (Standard Methods, 11th Ed., p. 44)

1. Collection of Sample. Use the raw water sample collected from the mineral analyses.

2. Apparatus. Conventional titration equipment.

3. Reagents.

   3.1 Standard sulfuric acid, 0.0200 N.

   3.2 Indicator solution.

   a. Methyl purple - obtainable from Fleisher Chemical Co., Ben Franklin Station, Washington 4, D. C.

   b. If a pH meter is available with extended leads it can be used as the indicator, with endpoint taken at pH 4.6.

4. Procedure.

   4.1 Place 50 to 100 ml sample into an Erlenmeyer flask or porcelain dish.

   4.2 Add 2 to 4 drops indicator.

   4.3 Titrate with 0.0200 N sulfuric acid to the endpoint.

5. Calculation: (Total alkalinity as calcium carbonate, mg/l)

$$\text{mg/l Alkalinity (as } CaCO_3\text{)} = \frac{\text{ml standard acid X 1000}}{\text{ml sample}}$$

Note: Other indicators are available but methyl purple is recommended for clarity of its color change.

TOTAL HARDNESS (Standard Methods, 11th Ed., p. 132)

Universal acceptance of the complexometric (EDTA) procedure for hardness has practically eliminated the soap procedure for this test. Standard Methods described several alternative methods. The procedure outlined below has been found to be the most used, but the others described are equally useful and may be substituted if desired.

1. Collection of Sample. Use the raw water collected for the mineral analyses.

2. Apparatus. Standard titration equipment.

3. Reagents.

3.1 Eriochrome Black T - dry mixture.

Weigh out 1 gram of indicator and thoroughly mix with 250 g of dry sodium chloride crystals. Keep dry and well stoppered.

3.2 Buffer solution.

Take 150 ml of concentrated ammonium hydroxide,
add 17 g ammonium chloride,
dilute to 250 ml
keep well stoppered

3.3 Inhibitor solution.

If an endpoint is not readily obtainable, it may be due to interference from heavy metals. (See p. 115 of Standard Methods, 10th Ed., or p. 134, 11th Ed., for the preparation of inhibitor solution to overcome this interference).

3.4 Standard calcium solution.

Dry several grams of pure calcium carbonate at 105°C. Weigh out 1.00 g into a 500-milliliter Erlenmeyer flask. Add dilute hydrochloric acid dropwise until the calcium carbonate has dissolved. Add 200 ml H_2O and boil to remove carbon dioxide. Cool. Add methyl red indicator and adjust to orange color with dilute ammonium hydroxide. Transfer completely to a 1-liter volumetric flask and dilute to the mark with distilled water. One ml of this standard contains 1.00 mg of calcium, as calcium carbonate.

3.5 EDTA titrant.

Dissolve 4.0 g disodium dihydrogen ethylene diamine tetraacetate dihydrate (EDTA) and 0.1 g $MgCl_2 \cdot 6H_2O$ in 800 ml water.

Standardize against standard calcium solution as follows:

Put 5.0 ml of standard calcium into about 50 ml distilled water. Add 2.0 ml buffer solution and mix. Add a small scoop of indicator (about .3 to .5 g). Titrate with EDTA to the endpoint - red to blue. The titration should take between 4.0 and 5.0 ml of titrant. Adjust the EDTA with distilled water so that 1.0 ml equals 1.0 mg hardness as calcium carbonate.

Repeat the titration. If the standard EDTA was correctly adjusted, exactly 5.0 ml of titrant should be used for this titration.

Store in pyrex or polyethylene only.

4. Procedure.

4.1 Select sample size so that no more than 5.0 ml of titrant is used, and dilute to 50 ml with distilled water.

4.2 Add 1.0 ml buffer solution, and a scoop of indicator powder; mix by swirling.

4.3 Titrate with EDTA, to blue endpoint.

5. Calculation:

$$\text{mg/l hardness, as } CaCO_3 = \frac{\text{ml EDTA} \times 1000}{\text{ml sample}}$$

Note: If the endpoint from red to blue is not sharp and clear, the use of an inhibitor solution may be necessary. See Standard Methods, 11th Edition, p. 135

COLOR (Standard Methods, 11th Ed., p. 111)

For this test to be significant, all turbidity must be removed prior to analysis. The method for removal of turbidity is critical since filtration through filter paper will also remove some of the color.

Turbidity can be removed by: (a) Centrifuging, and (b) by filtration through a membrane filter (centrifuging is preferred).

1. Collection of Sample. Use raw water sample collected for the mineral analyses.

2. Apparatus.

   2.1 A series of Nessler tubes containing chloroplatinate color standards, or

   2.2 permanent standards for color as provided with the Hellige aqua tester, the Taylor analyser or similar equipment.

3. Reagents. None

4. Procedure.

   4.1 Take 100 ml of raw sample and remove turbidity by centrifuge or through a membrane filter. If the membrane filter is used, allow turbidity to settle for 1 hour, then gently pour the supernatant through the membrane without disturbing the settled matter. This technique will insure a volume of about 50 ml which is necessary for comparison with standards.

   4.2 Transfer the clear sample to the comparator and match with the appropriate standard.

   4.3 Record to the nearest color unit.

   4.4 If color is too high, prepare a dilution using distilled water. Multiply the color value obtained by the dilution factor.

The Water Quality Section will provide color standards for this test, if requested. Either the permanent standards used with comparators or the Nessler tube series can be provided, as desired.

TURBIDITY. (Standard Methods, 10th Ed., p. 207, 11th Ed., p. 261).

Turbidity is the expression used to describe the presence of particulate matter such as silt, clay, organic debris, algae, or any suspended particles that obstruct the passage of light through water. It is not directly related to the weight of matter in suspension. The Jackson Candle Turbidimeter is the recognized instrument. Other instruments must be calibrated in Jackson units before they can be used in reporting turbidity. Unless turbidity results are reported in Jackson units, they cannot be used by the Network.

1. Collection of the Sample. Use the raw water collected for the mineral analyses.

2. Apparatus.

   2.1 Jackson Candle Turbidimeter, or

   2.2 commercial turbidimeter, calibrated in Jackson units.

3. Reagents. None

4. Procedure.

   4.1 For turbidities between 25 and 1,000 units:

   a. Shake the sample vigorously and add 1 to 5 ml to the turbidimeter.

   b. Light the candle. (Do not light the candle while the tube is empty!)

   c. Shake sample again. Add small increments to the turbidimeter until the image of the candle flame is no longer distinguishable. As the sample is added to the tube, the flame outline will gradually fade until it can no longer be distinguished, only diffused light being observed. This is the preliminary reading.

   d. Note the preliminary reading and remove the sample from the tube. Rinse the tube with distilled water.

e. Shake sample again. Add sufficient sample to the tube to give about 80 percent of the preliminary reading, then add small increments until the flame disappears again. Record this value.

f. Repeat this operation twice. Record the average of the three readings.

4.2 For turbidities greater than 1,000 units:

a. Make a dilution of the sample such that the turbidity falls near 500 units.

b. Carry out the steps outlined in procedure 4.1.

c. Multiply the average turbidity reading by the dilution factor and record.

4.3 For turbidities below 25 units:

a. Compare the sample with a series of standard turbidities prepared at 5-unit intervals. To prepare the turbidity standards first determine turbidity of a sample of water that falls within the range of the Jackson Candle.

b. Using this water, prepare dilutions with distilled water to give turbidities in the range 0 to 25 units.

c. Transfer these, including the samples, to a series of bottles of identical size, shape, and type.

d. Match the sample to the nearest standard.

SULFATE (Standard Methods, 11th Ed., p. 237)

The gravimetric procedure is the most accurate for samples containing more than 10 mg/l. It is also very time consuming.

The turbidimetric procedure is less accurate than the gravimetric but is much shorter, and is the preferred method for samples up to 60 mg/l. Other methods for sulfate are available and can be used if their accuracy is comparable to the Standard procedures. The turbidimetric method is described in detail below.

1. Collection of Sample. Use the raw water sample collected for the mineral analyses.

2. Apparatus. Commercial photometer or spectrophotometer. Wave length, approximately 420 millimicrons.

3. Reagents.

   3.1 Conditioning solution:

   Dissolve 75 g of sodium chloride in 300 ml of distilled water and add 30 ml of concentrated HCl, 50 ml of glycerine and 100 ml of 95 percent ethyl alcohol or isopropyl alcohol.

   3.2 Barium chloride crystals:

   Obtain crystalline $BaCl_2$, 20 to 30 mesh.

   3.3 Standard sulfuric acid solution 0.02 N:

   (Use alkalinity reagent 3.1, p. 71).

4. Procedure.

   4.1 Measure out 50 ml of filtered sample (or aliquot diluted to 50 ml if sulfate is above 60 mg/l) into a 125 ml Erlenmeyer flask.

   4.2 Add exactly 10 ml of conditioning solution and mix.

   4.3 Add approximately 0.4 to 0.5 g barium chloride crystals, using a small spoon for uniform measurement, and immediately upon addition of the crystals begin stirring at a constant rate for 1 minute. A magnetic stirrer is very useful for this operation.

4.4 Let stand 4 minutes.

4.5 Transfer the suspension to the photometer cell and read immediately. (Prepare a blank by using 50 ml of filtered water to which 10 ml of conditioning solution has been added. Use this to zero the photometer.

5. Preparation of Standard Curve.

5.1 (Use the 0.020 N sulfuric acid used for the alkalinity test). Pipette 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 ml of 0.020 N sulfuric acid into 125 ml Erlenmeyer flasks. Dilute each portion to 50 ml with distilled water. These standards are respectively 0.0, 9.6, 19.2, 28.8, 38.4, 57.6, and 76.8 mg/l of SO_4.

5.2 To each flask in the series, carry out procedural steps 4.2 through 4.5 before proceeding with the next flask. Use the zero standard to zero the photometer.

5.3 Prepare a calibration curve, plotting photometer reading vs concentration of sulfate.

6. Calculation of Results. Read the sulfate concentration of the sample from the calibration curve, multiply by the dilution factor, if any, and report as mg/l sulfate.

Note: The limit of usable concentration for this test is approximately 60 mg/l. Somewhere between the 57.6 and 76.8 mg/l standards (paragraph 5.1) the standard curve will begin to skew from a straight line.

DETERMINATION OF PHOSPHATES (Ortho plus Poly)

Phosphate can be determined as three separate entities in the water environment, as ortho, poly and organic. To do this would require considerable laboratory time, as the organic phosphate procedure is long and tedious, and separate tests are necessary to differentiate ortho from poly. To collect the information of greatest value to the Network, and to reduce laboratory time to a minimum, it is felt that a single determination combining ortho plus poly phosphate will fulfill the needs of the Network without imposing an excessive burden on the participating laboratory.

1. Collection of Sample. Use the raw water collected for the mineral analyses.

2. Apparatus.

   2.1 Spectrophotometer or filter photometer, for use at 690 millimicrons, or

   2.2 Nessler tubes, 50 ml.

3. Reagents.

   3.1 Phenolphthalein indicator: Dissolve 2.5 gms. of phenolphthalein powder in 250 ml of ethyl alcohol, add 250 ml of distilled water, then add 0.020 N NaOH dropwise to a faint pink color.

   3.2 Sulfuric acid: Add 310 ml of concentrated H_2SO_4 slowly to about 600 ml of distilled water. Cool to room temperature and dilute to 1.0 liter.

   3.3 a. Stock standard phosphate solution (0.50 mg PO_4 per ml). Dry a portion of reagent grade potassium dihydrogen phosphate overnight at 103° before use. Dissolve 0.7164 gm of the KH_2PO_4 in distilled water and make up to 1.0 liter.

   b. Working standard phosphate solution (0.005 mg/PO_4 per ml): Dilute 10.0 ml of the stock standard phosphate to 1.0 liter with distilled water. Protect this solution from the light and make up fresh each month.

   3.4 Ammonium molybdate solution: Dissolve 25.0 gms of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 175 ml of distilled water. Add 155 ml of concentrated H_2SO_4 slowly to 400 ml of distilled water, and cool.

Add the molybdate solution to the sulfuric acid solution (never in reverse) and dilute to 1.0 liter.

3.5 Stannous chloride solution: Dissolve 2.5 g of a fresh supply of $SnCl_2 \cdot 2H_2O$ in 100 ml of reagent grade glycerine. Heating in a water bath and stirring with a glass rod are recommended to hasten solution. This reagent is STABLE, requiring neither the addition of preservatives nor special storage.

4. Procedure.

Preliminary Cleaning of Glassware. Because laboratory detergents contain phosphate, which cannot be easily rinsed off, a preliminary treatment with phosphate reagents is necessary to remove that adsorbed on the glass surfaces. After the glassware has been properly cleaned it should be reserved for this test only.

4.1 Clean and thoroughly rinse all glassware in the usual manner.

4.2 Before use, treat each container that will come in contact with the sample as follows:

a. Fill each container with distilled water and add 2.0 ml of ammonium molybdate solution and mix.

b. Add 1 ml of sulfuric acid solution and 5 drops of stannous chloride solution; mix thoroughly and allow to stand for 10 to 15 minutes. Make certain that all internal surfaces of the containing vessels come in contact with the reaction mixture. Discard the reaction mixture and rinse each container with distilled water.

Once this cleaning procedure has been performed the glassware can be reused without repeating the treatment, unless it has been cleaned with detergent.

4.3 Preparation of standards (photometric procedure).

Observe room temperature. Standards and samples must be run at same temperature, $\pm$ 2°C, for reproducible results.

a. Add increasing volumes of working standard phosphate solution to several vessels (previously cleaned according to paragraph 4.2). Add 1.0 ml of sulfuric acid. Make up to 50.0 ml with distilled water.

The following table is suggested as a convenient series for use with a photometer.

ml of phosphate standard (Reagent 3.3b)	mg PO_4/50 ml	PO_4, mg/l
0 (Blank)	0	0 (Blank)
0.5	.0025	.050
1.0	.0050	0.10
2.0	.0100	0.20
5.0	.0250	0.50
10.0	.0500	1.00

b. Add 2.0 ml of ammonium molybdate, and mix.

c. Add 5 drops (0.25 ml) of stannous chloride solution. Mix and allow to stand for 20 ($\pm$ 5) minutes.

d. Read in spectrophotometer at 690 millimicrons or in a filter photometer at 600 to 700 millimicrons. Use the blank to zero the instrument.

e. Prepare calibration curve.

4.4 Raw water sample (photometric procedure).

a. Filter at least 100 ml of the sample to remove turbidity.

b. Place 100 ml of the filtered sample containing not more than 0.050 mg PO_4 or an aliquot diluted to 100 ml in a beaker or an Erlenmeyer flask. Carry a blank of 100 ml distilled water along with the sample.

c. Omit this step if the pH is below 8.2. Otherwise:

c.1 Add two drops of phenolphthalein.
c.2 Add sulfuric acid solution, dropwise, to discharge the pink color.

d. Add exactly 2.0 ml of sulfuric acid and boil gently for one-half hour. Add a small amount of distilled water if volume drops below 25 ml during the boiling period.

e. Cool, make up to 100 ml with distilled water and adjust to temperature of standard curve.

f. Take 50 ml of the treated sample and add 2.0 ml of ammonium molybdate solution and mix.

g. Add 5 drops (0.25 ml) of stannous chloride, mix, and allow to stand for 20 (± 5) minutes for color development.

h. Read in the spectrophotometer, using the distilled water blank to zero the instrument.

4.5 Calculation:

$$\text{mg/l } PO_4 = \text{mg } PO_4 \text{ (from standard curve) } X \frac{1000}{\text{ml sample}}$$

Report to the nearest 0.1 mg/l.

4.6 Procedure for Nessler tubes: Follow steps (a) through (e) under photometric procedure 4.4.

f. Cool, transfer 50 ml to a Nessler tube.

g. Add increasing volumes of working standard, reagent 3.3b, to a series of 50 ml Nessler tubes (previously cleaned according to paragraph 4.2). Add 1.0 ml of sulfuric acid, reagent 3.2. Dilute to 50 ml with distilled water. The following table is suggested as convenient for use in Nessler tubes.

ml of Phosphate Standard (Reagent 3.3b)	mg PO_4/50 ml	PO_4, mg/l
0	0	0
0.5	0.0025	0.05
1.0	0.005	0.10
3.0	0.015	0.30
5.0	0.025	0.50

h. Add 2.0 ml of ammonium molybdate to each standard and sample and mix.

i. Add 5 drops (0.25 ml) of stannous chloride, mix, and let stand for 20 (± 5) minutes for color development.

j. Match the color in the sample with the closest standard.

4.7 Calculation:

$$\text{mg/l } PO_4 = \text{mg } PO_4 \text{ in closest matching standard} \times \frac{1000}{\text{ml sample}}$$

Report to the nearest 0.1 mg/l.

5. Notes.

5.1 The concentration of acid in the sample and standards has a direct effect on the amount of color produced. It is important, therefore, that addition of the sulfuric acid solution be performed accurately.

5.2 The phosphomolybdate blue produced by the reaction is not stable and tends to fade gradually after about 20 minutes. Most accurate results are obtained when time requirements are observed.

5.3 Temperature is another variable that affects the color formation. Samples and standards may be adjusted to room temperature after boiling by allowing to stand for several hours before addition of reagents 3.4 and 3.5.

5.4 If the phosphate concentration in the sample is completely unknown, several dilutions of the sample may be run simultaneously and that aliquot used for final reading, which falls near the middle of the standard series.

5.5 Scrupulous care should be observed in cleaning the glassware prior to use. If color appears in the blank, or if a particular standard appears out of line, phosphate contamination is probably responsible.

5.6 When using the photometric procedure, only one blank is necessary if the standards and sample are run at the same time.

5.7 The working standard phosphate solution (reagent 3.3b,) should be kept in the dark to prevent reduction of phosphate concentration through algal growth.

5.8 In preparation of the ammonium molybdate solution (reagent 3.4), the molybdate must be added to the sulfuric acid, never the reverse. Reversing the addition precipitates some of the molybdate, which is then very difficult to dissolve.

TOTAL DISSOLVED SOLIDS (Standard Methods, 11th Ed., p. 215)

For this test all turbidity must be removed prior to analysis. Turbidity can be removed as in the Color Test, page 74, or by filtration. To obtain satisfactory accuracy the sample size selected should be large enough to produce at least 25 mg of residue following the drying operation.

1. Collection of Sample. Use the raw water sample collected for the mineral analyses.

2. Apparatus.

   2.1 Analytical balance, capable of accurate weighing to ± 1 mg.

   2.2 Drying oven controlled at 103°to 105°C.

3. Reagents. None

4. Procedure.

   4.1 Clean an evaporating dish (about 3 to 4 inches diameter) thoroughly and dry in oven overnight at 103°to 105°C.

   4.2 Cool and weigh to ± 1.0 mg.

   4.3 Set the evaporating dish in the drying oven or on a steam bath. Measure out a volume of filtered sample that will give at least 25 mg of residue. Add this to the evaporating dish in increments until the total volume selected has been added.

   4.4 Evaporate to dryness and hold for 1 hour at 103° to 105°C.

   4.5 Transfer to dessicator and cool.

   4.6 Weigh to ± 1.0 mg.

5. Calculation:

$$\text{mg/l total dissolved solids} = \frac{(\text{Wt of dish + sample - wt of dish}) \times 1000}{\text{ml of sample}}$$

SECTION VIII

HANDLING OF ANALYTICAL DATA

Reporting of Results

Each participating agency is furnished a supply of Form PHS 2845-1 (Rev. 6-59) National Water Quality Network Report (Field), for reporting the results of the determinations performed by its laboratory. These are provided as multiple copy "snapout" forms with interleaved carbons to simplify reporting of results. The forms consist of a white page, a blue page, and a pink page. The white and blue copies are sent to the Water Quality Section at Cincinnati and the pink copy is retained by the cooperating agency for its files. Franked, return-addressed envelopes are provided for mailing purposes.

The forms have been designed for easy transcription to permanent records, because the data are to be entered later on machine-sorted punch cards. A fixed code has been established that cannot accommodate variations in reporting practice. To avoid errors in the compilation of the data, each laboratory is requested to observe the following procedures in tabulating the analysis on the forms provided.

State: Insert the State in which the sampling point is located.

Station location: Insert the name of the river being sampled, the city or other geographical "landmark" identifying the location, and the river mileage from the mouth to the station, if available.

Laboratory: Insert the names of the laboratory and the person completing the report.

In reporting data, round out the values to the nearest unit shown on the report form. For example, a chloride value of 20.6 mg/l should be reported as 0021 mg/l. The form may be completed with a hard pencil or ballpoint pen, or by typing. Whatever the method used, care should be taken to make each copy legible. A sample completed report form is shown on the following page.

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
DIVISION OF WATER SUPPLY AND POLLUTION CONTROL

PROVISIONAL DATA—SUBJECT TO REVISION

#40

FOR WASHINGTON USE ONLY						
1-2	3-4	5-6	7-8	9-12		
CHECKED BY:				DATE		

STATE	STATION LOCATION
Maryland (D.C.)	Potomac River, Great Falls, Maryland

LABORATORY	DATE SAMPLE TAKEN
Dalecarlia Washington, D.C., G.E.Harrington	24 September 1962

TEST RESULTS

INSTRUCTIONS: All boxes should contain a figure or preceeding zeros. If test is not made, put "X's" in every box
EXAMPLE: If D O is 10.5 mg/l(ppm) enter as follows [1 | 0 . 5]
If Turbidity is 50 units, enter as follows [0 | 0 | 5 | 0]

1. TEMPERATURE	[1 | 8 . 3] (13 – 15)	*Degrees C. to tenths*
2. DISSOLVED OXYGEN (DO)	[0 | 7 . 0] (16 – 18)	*mg/l to tenths*
3. pH	[0 | 8 . 2] (19 – 21)	*To tenths*
4. BIOCHEMICAL OXYGEN DEMAND (BOD)	[0 | 1 . 2] (22 – 24)	*mg/l to tenths*
5. CHEMICAL OXYGEN DEMAND (COD)	[0 | 1 | 8] (25 – 27)	*mg/l in units*
6. CHLORINE DEMAND - 1 HOUR	[0 | 1 . 4] (28 – 30)	*mg/l to tenths*
7. CHLORINE DEMAND - 24 HOURS	[0 | 4 . 0] (31 – 33)	*mg/l to tenths*
8. AMMONIA NITROGEN (NH_3-N)	[0 | 0 . 1] (34 – 36)	*mg/l to tenths*
9. CHLORIDES	[0 0 | 1 | 8] (37 – 40)	*mg/l in units*
10. ALKALINITY (*as* $CaCO_3$)	[0 | 9 | 3] (41 – 43)	*mg/l in units*
11. TOTAL HARDNESS (*as* $CaCO_3$)	[0 1 | 3 | 0] (44 – 47)	*mg/l in units*
12. COLOR	[0 | 0 | 5] (48 – 50)	*In scale units*
13. TURBIDITY	[0 0 | 1 | 5] (51 – 54)	*In scale units*
14. SULFATES	[0 0 | 5 | 1] (55 – 58)	*mg/l in units*
15. PHOSPHATES	[0 | 0 . 1] (59 – 61)	*mg/l to tenths*
16. TOTAL DISSOLVED SOLIDS (TDS)	[0 2 | 2 | 7] (62 – 65)	*mg/l in units*

DISTRIBUTION: RETAIN PINK COPY IN PARTICIPATING LABORATORY. FORWARD ORIGINAL (WHITE) AND BLUE COPY TO WATER QUALITY SECTION, CINCINNATI, OHIO.

PHS-2845-1 REV. 6-59 NATIONAL WATER QUALITY NETWORK REPORT (FIELD)

FORM APPROVED
BUDGET BUREAU NO 68-R8 34-1

Presentation of Results

The data are processed and printed by the Basic Data Branch of the Water Supply and Pollution Control Division in Washington, D. C. The data are transferred from the original sheets forwarded by the Water Quality Section to Washington D. C. to machine-punched cards for listing in chronological order of testing in such manner that the determinations performed by the cooperating laboratories and by the Water Quality Section will be coordinated. Four times a year the data will be summarized and reported back to each agency in printout form. Each quarterly report will include the chemical, radiological, bacteriological, biological, and organic data collected for that portion of the year in which the summary is prepared, plus the summaries of the preceding quarters. A complete national compilation containing the data from every station is printed on an annual basis, copies of which are supplied to each participating agency.

Interim reports can be prepared with data listed by geographical area, such as by state or by major and/or minor river basins. The machine tabulation operation is also capable of carrying out statistical analyses of the data such as the development of means, medians, and frequency distributions. Requests for special analyses of the data and for tabulations covering a particular area should be made to the Public Health Service Regional Office concerned.