CHAPTER IV

LABORATORY

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A. PURPOSE

The accurate measurement of components present in waste is imperative because of the limitations imposed on wastewater discharge to receiving streams. A comprehensive wastewater survey should:

i. Determine the quantity of discharge

ii. Locate major sources of waste within the plant

iii. Determine wastewater composition

iv. Analyze problems within a treatment unit or process and indicate methods for problem prevention

v. Establish the guidelines for treatment process control

vi. Evaluate effects on the receiving stream

vii. Provide an operating record for the treatment system

"Standard Methods for the Examination of Water and Wastewater " is recognized as standard by all state and national health departments, and by the courts for use in expert testimony. The text is designed and written to be used by trained chemists and technicians. For all careful and accurate work it should be followed explicitly because of the limitations and possible interferences associated with each test.

Because of detail in discussions and procedures within the text, the untrained treatment plant operator finds it difficult to follow "Standard Methods." This chapter of the Operation and Maintenance Manual has been prepared to offer a simplified discussion and procedure for the testing required at this wastewater treatment plant. The manual is not to be considered a substitute for "Standard Methods." It should be used with "Standard Methods" available for reference; and as the simplified techniques are mastered, the operator then should read the details as given in "Standard Methods" to be aware of possible pitfalls and interferences.

The results of laboratory analysis are of value as a record of plant operation. These data help the operator to know how efficiently his plant is operating and enable him to predict and prevent troubles that are developing in the processes. They are of value as a record of performance to the state, and often in damage suits; and to the designing engineer when plant expansions are necessary. For these reasons the laboratory tests should be made as carefully as possible. A poor test is worse than no test at all!

B. SAMPLING

1. Discussion

Laboratory analyses have little value or meaning if the material analyzed is not fairly representative of the condition or quality which actually prevails. With wastewater, obtaining this representative sample is the most difficult problem.

Sampling points must be where there is good mixing of the material to be sampled, uninfluenced by previous deposits and unrelated side effects. The conscientious operator, therefore, must study his facilities closely to find these points.

Even under the most favorable circumstances, errors or inaccuracies in sampling are usually much greater than those ascribed to laboratory methods. Moreover, costly equipment and careful work in the laboratory are wasted when samples are collected carelessly.

All samples which are not analyzed immediately should be preserved by refrigerating at 4°C (39°F). For certain tests preservatives are used which are discussed under procedures.

There are two types of samples that may be collected, depending on the time available, the tests to be made and the object of the tests. One is called a "grab" sample, which consists of a portion of wastewater all taken at one time. The other is a "composite" sample consisting of portions of wastewater of each portion being proportional to the wastewater flow at the time it is collected. All the portions are mixed to produce a final sample representative of the wastewater.

2. Grab sampling

Grab sampling will provide the operator with information which. may be invaluable for plant operational performance. Chlorine demand and chlorine residuals, in the domestic treatment plant particularly for disinfection and maintenance of residual within narrow limits, may require frequent adjustments of rate of dosage. Concentration and setteability at Aeration Tanks and Settling Tanks may dictate plant process adjustments.

Grab samples or single catch samples are taken when:

i. Frequent changes in characteristics and concentrations of certain constituents of the wastewater require concurrent changes in plant operational control.

ii. Unusual or undesirable constituents or concentrations are observed.

iii. A condition or operation is of short duration and quite uniform.

iv. A condition or quality remains relatively uniform for daily periods or longer.

v. The sample requires immediate analysis because of a high degree of instability of the constituent to be analyzed as for example dissolved oxygen.

3. Composite Sampling

Composite, or integrated, samples are collected when a measure of the average quality or condition in the plant or stream is sought, with sampling convering a period usually no longer than 24 hours. Ideally, a continuous sample should be taken with volumes at all times in proportion to rate of flow. Where this is not practical samples taken hourly and composited may give reasonably accurate results. Greater frequency may be required where sudden changes occur with wide variations in composition.

Where samples are collected during a period less than 24 hours, as in small plants, a relationship between the quality found during the shorter period with the daily average should be established. A factor representing this relationship should thereafter be applied to compute daily values.

4. Obtaining Samples for Laboratory Analysis

The procedure and locations in which the samples are derived will minimize errors in the laboratory analysis. The proper procedures and sampling points are defined in this portion of the operation and maintenance manual.

a. Sampling Procedures

Particles greater than 1/4" diameter should be excluded from the sample, or samples containing larger than normal floc.

No floating materials or growths should be included in the sample (especially for stream samples).

Influent and effluent samples should relate to the same waste. (Consideration of daily flow and detention time through the units will help to insure the proper relation.)

Collect enough sample in a suitable container. Error can result from attempting to collect small portions for a composite sample. The sample should be taken from a point in the treatment process where mixing has created a somewhat homogeneous condition. The nature of wastewater prevents the collection of a relatively small portion that represents the whole. This is particularly true of unsettled wastewater. A minimum sample should be at least 100 ml and a sample containing any unusual particle(s) should be rejected.

For general analyses, a 500 ml sample should be collected. For analyses of sludge volumes and settleable matter, a 1000 ml sample should be collected. For iron analyses, a 125 ml sample acidified with 15 drops of HCl or HNO_3 should be collected. In all instances, samples should be refrigerated if not analyzed immediately.

Always mix the sample before removing a portion. If this operation is neglected, the liquid removed will not represent the original. Mixing may be accomplished by shaking, stirring, or other means, depending on the analyses to be conducted and the judgment of the analyst.

b. Sampling Points

Wastewater should be sampled from areas in which it is well mixed. Generally samples should be taken from easily accessable areas. Included in this section of the operation and maintenance manual are suggested places for taking samples and some precautions to exercise.

(1) Deep Tanks or Pits

Care must be taken to prevent extraneous material in the tank from entering the sample.

(2) Pipes and Channels

Care should be taken to avoid skimming the surface (scum and greases), and dragging the bottom or sides. A sample collected from the middle third of the cross-section of flow is most desirable.

(3) Flumes and Troughs

Samples should be collected from the middle third (vertically) of the channel and the point of collection should be rotated across the channel, always taking care to avoid disturbance of the channel sides and to select a point where the velocity is sufficient to prevent settling.

(4) Raw Wastewater

Samples should be collected at the force main point of discharge.

(5) Below Weirs

Care should be taken in sampling below a weir since deposition of solids in the pool upstream from the weir and floating oils or grease just downstream can cause errors in sampling.

(6) Aeration Tank Mixture

Samples should be collected in locations that have as much turbulence as possible, insuring a well-mixed specimen.

(10) Settling Tanks

An effluent sample taken directly from the tank should be collected just ahead of the outlet weir and below any scum layer.

(11) Plant Effluent

Samples should be taken at the discharge of the effluent pipe, or in the effluent pipe itself, or in the final tank just ahead of the discharge weir. Preference would normally be in the order indicated.

(12) Chlorine Residual

Collect sample et point of discharge of domestic wastewater treatment plant (sewage treatment plant).

(13) Special Test Sampling Locations

Sometimes samples should be collected from several points in the same tank or channel. For example:

i. In aerators the maximum dissolved oxygen is likely to be near the outlet and the minimum near the inlet.

ii. In final settling tanks, the maximum setteable material probably will be near the inlet and the minimum near the outlet.

5. Sampling Equipment

Some suggested equipment for wastewater sampling are listed herein to assist the operator in effective sampling procedures.

a. Dipper (Purchased Locally)

A dipper is a long-handled container of stainless steel or other corrosion resistant material. The dipper should be cylindrical in shape with a wide-mouth opening (minimum of two inches (five cm) and be large enough to contain largest portion to be collected. Calibrate handle.

b. Weighted Bottle (Shop Made)

A weighted bottle is a weighted device designed to hold a stoppered bottle while it is lowered to desired sampling depth. A cord or wire is attached to the stopper for removal of stopper at desired depth. Very little wastewater will be displaced from the bottle while it is being drawn to the surface.

c. Hand-Operated Pump (Purchased Locally)

A hand operated pump is a tube fixed to the suction of an ordinary "pitcher" pump. It may be lowered to a desired point from which a sample is to be collected.

d. Cross-Section Sampler

For stratified solutions, such as sludge in settling tanks or sludge holding tanks, a graduated glass or plastic tube or cylinder open at both ends and stopped may be used. The tube is lowered through the tank with both stoppers removed, cutting a "crosssection" sample. In sampling position, the stoppers are put in place by a lever arrangement.

C. LABORATORY REFERENCES

Reference guides which would be most helpful in the laboratory analysis of wastewater samples are listed below. These guides should be made available to persons responsible for laboratory work.

i. "Standard Methods for Examination of Water and Wastewater", 13th Edition, APHA, AWWA, WPCF.

ii. EPA publication "Methods for Chemical Analysis of Water and Waste" (GPD Stock No. 5501-0067).

iii. WPCF Publication No. 18, "Simplified Laboratory Procedures for Wastewater Examination.

iv. WPCF Manual of Practice No. 11, "Operation of Wastewater Treatment Plants."

v. "Manual of Wastewater Operations", Texas Water Utilities Association.

vi. Manual of Instruction for Sewage Treatment Operators", New York State Department of Health.

vii. Chemistry for Sanitary Engineers", Sawyer, McGraw-Hill.

D. TESTING

1. Temperature

a. Discussion

The temperature of any liquid can determine the chemical activity of various substances and the solubility of gases in the liquid. Temperature measurement is an important part of water quality monitoring, as some parameters, such as pH and dissolved oxygen, are temperature sensitive.

b. Sampling Procedure

Temperature measurement should be performed on-site at the time of sample collection. In addition, temperature checks should be made immediately prior to analysis for those parameters which are temperature sensitive. This will allow for correct calibration of laboratory instruments.

c. Sampling Points

i. Raw Water Influent Channel
ii. Settling Tank Influent
iii. Final Tank Effluent

d. Equipment Required

Thermometer, calibrated in centigrade scale

e. Reagents Required

None

f. Procedure

i. Immerse the thermometer bulb in the solution being tested for 2 minutes.

ii. While keeping the thermometer bulb immersed, read the temperature to the nearest 0.5°C and record.

q. Calculations

None. The thermometer is a direct reading device.

h. Possible Sources of Error

i. Insufficient immersion time or removal of the thermometer prior to reading will result in incorrect temperature measurement.

ii. Separations in the mercury column may result in erroneous readings. To reunite the column, carefully heat the thermometer bulb to raise the mercury column until all column sections are rejoined.

2. Dissolved Oxygen

a. Discussion

Dissolved oxygen is the oxygen in solution in a liquid. The solubility of oxygen in fresh waters ranges from 14.6 mg/l at 0°C to approximately 7 mg/l at 35°C. The solubility of oxygen is minimal at high temperatures. In wastewater testing, dissolved oxygen measurements are used to control oxidation treatment processes and to monitor oxygen content in receiving streams.

b. Sampling Procedure

Dissolved oxygen samples should be collected in 300 ml BOD bottles. Care must be taken to avoid entrapment of atmospheric air

in the sample bottle, continued contact with air, extreme agitation, or rapid or extreme changes in temperature or pressure, as all of these factors can significantly alter the gaseous content of the sample. The BOD bottle should be tightly stoppered and returned to the laboratory for immediate analysis, as a time delay between sampling and analysis can also cause errors in the determinations. Record the sample temperature at the time of collection.

c. Sampling Points

i. Flash Mixer Effluent
ii. Aeration Tank Effluent
iii. Final Tank Effluent

d. Equipment Required

i. BOD bottles, 300 ml, with stoppers (one for each determination)
ii. Thermometer, calibrated in centigrade scale
iii. Buret, automatic, 25 ml, for PAO solution
iv. Graduated cylinder, 250 ml
v. Erlenmeyer flask, 300 ml
vi. Pipet, volumetric, 1ml

e. Reagents Required

i. Manganous sulfate powder pillows
ii. Alkaline iodide-azide powder pillows
iii. Sulfamic acid powder pillows
iv. Starch indicator solution, stabilized
v. Standard PAO solution, 0.0250N

f. Procedure

i. Add the contents of one manganous sulfate powder pillow to the BOD bottle containing the sample.

ii. Add the contents of one alkaline iodidezide powder pillow to the BOD bottle.

iii. Stopper the bottle, taking care to exclude air bubbles.

iv. Shake the bottle to dissolve the powder and mix the floc that forms.

v. Allow the floc to settle about half way down the bottle.

vi. Remove the stopper, add the contents of one sulfamic acid powder pillow, restopper (again taking care to avoid entrapment of air), and shake to mix. If oxygen is present, the floc will dissolve and a yellow color will develop.

vii. Using a 250 ml graduated cylinder, transfer 200 ml of this sample solution into a 300 ml Erlenmeyer flask.

viii. Using the standard PAO solution, titrate the sample until it turns pale yellow. Swirl the flask during the titration to insure complete mixing of its contents.

ix. Add 2.0 ml starch indicator solution to the flask and mix well. A blue color will be formed.

x. Continue titrating the sample with standard PAO solution, while swirling the flask, until the blue color just disappears.

xi. Record the total mls of standard PAO solution required for the titration.

g. Calculations

ml standard PAO solution used = mg/l dissolved oxygen. Report final answer to the nearest 0.1 mg/l.

h. Possible Sources of Error

i. Accidental introduction of atmospheric air in the BOD bottle may cause erroneously high dissolved oxygen determinations. If difficulty is encountered when the bottle must be stoppered, the BOD bottle may be inclined somewhat and the stopper thrust in quickly. This will usually force the air bubbles out. If this procedure is unsuccessful, a few mls of distilled water may be slowly added to the bottle to raise the liquid level. It must be remembered, however, that the more distilled water added, the greater the experimental error being introduced.

ii. Occasionally, the test solution may begin to turn blue after it has become colorless at the end of the PAO titration. This color reaction should be ignored.

3. pH

a. Discussion

pH is a term used to express the intensity of the acidic or alkaline condition of a solution. The pH scale ranges from 0 to 14, with pH 7 being neutral. A ph below 7 indicates acid conditions, while a pH above 7 indicates alkaline conditions.

pH is usually measured potentiometrically by use of a calibrated pH meter.

b. Sampling Procedure

Samples should be collected in clean 500 ml polypropylene bottles and should be returned to the laboratory for immediate analysis.

c. Sampling Points

i. Raw Water Influent Channel
ii. Flash Mixer Effluent
iii. Aeration Tank Effluent
iv. Settling Tank Effluent
v. Final Tank Effluent

d. Equipment Required

i. pH meter, electrodes, and accessories
ii. Beakers, 100 ml (one for each determination plus one for each buffer solution)
iii. Graduated cylinder, 50 ml
iv. Wash bottle containing distilled water
v. Thermometer, calibrated in centigrade scale

e. Reagents Required

i. pH 4.00 buffer solution - prepare by mixing contents of two pH 4.00 buffer powder pillows in 50 ml distilled water.

ii. pH 7.00 buffer solution - prepare by mixing contents of two ph 7.00 buffer powder pillows in 50 ml distilled water.

iii. pH 9.00 buffer solution - prepare by mixing contents of two pH 9.00 buffer powder pillows in 50 ml distilled water.

f. Procedure

i. pH Meter Set-Up

(a) Assemble pH meter and probes according to manufacturer's instructions.

(b) Connect meter to power source and turn mode switch to "standby".

(c) Immerse probes in distilled water and allow to soak over night before attempting to calibrate.

(d) When meter is not in use, keep mode switch on "standby" and store probes in distilled water. Do not allow probes to dry out.

(e) Periodically perform regular maintenance as prescribed by the manufacturer.

ii. pH Meter Calibration

The pH meter should be calibrated once every month using pH buffers of 4.00, 7.00, and 9.00. Calibration may be completed by following these steps

(a) Determine the temperature of the buffer solutions and adjust temperature control knob accordingly.

(b) Immerse the probes in approximately 50 ml of pH 7.00 buffer solution and turn mode selector to "pH". Allow meter to stabilize. If the meter does not read exactly 7.00, adjust the calibration control knob as required.

(c) Turn mode selector to "standby". Remove probes from pH 7.00 buffer and, using the distilled water wash bottle, rinse the probes thoroughly.

(d) Immerse the probes in 50 ml pH 4.00 buffer solution, turn mode selector switch to "pH", and allow meter to stabilize. Note meter reading; this reading should be 4.00 ± 0.10 pH unit. Record this reading to the nearest 0.05 unit.

(e) Turn mode selector switch to "standby", remove pH probes, and rinse thoroughly with distilled water.

(f) Immerse the probes in 50 ml pH 9.00 buffer solution, turn mode selector switch to "pH," and allow meter to stabilize. Note meter reading; this reading should be 9.00 ± 0.10 pH unit. Re cord this reading to the nearest 0.05 unit.

(g) If either of the 4.00 and 9.00 buffer readings differ more than ± 0.10 pH units, a calibration curve must be drawn and used for calculating all sample pH's. To construct the curve, use arithmetic graph paper. The horizontal scale will represent the actual (or buffer) pH, and the vertical scale will represent the experimental (or measured) pH. Plot actual versus experimental pH for the three determinations. (Example: locate 4.00 (actual) pH on horizontal scale and 3.85 (measured) pH on vertical scale. Make a point where the two lines, drawn perpendicular to the scales from these values, would intersect). Connect the three points from the three determinations with a smooth curved line.

iii. Sample Analysis

(a) Calibrate the pH meter using the pH 7.00 buffer solution as instructed in ii (a) thru (c).

(b) Pour approximately 50 ml sample into a clean, dry 100 ml beaker.

(c) Measure the temperature of each sample and adjust the temperature control knob on the pH meter accordingly.

(d) Immerse probes in sample, turn mode selector switch to "pH", allow meter to stabilize, and record sample pH to the nearest 0.05 pH unit.

(e) Turn meter to "standby" mode, remove and rinse probes thoroughly with distilled water.

(f) Repeat steps iii (b) thru (d) for each sample to be tested. If more than five samples are to be analyzed at one time, recalibrate the meter with pH 7.00 buffer after every fifth sample.

(g) When all samples have been analyzed," turn mode selector switch to "standby" and immerse probes in distilled water for storage.

g. Calculations

i. If the three measured pH points are within ± 0.10 pH unit of the actual pH's of the buffers used during the monthly calibration check, no calculation is necessary, and pH can be read directly from the meter scale. Report final results to the nearest 0.05 pH unit.

ii. If the monthly calibration check requires construction of the calibration curve as discussed in Section ii (g) above, a "corrected" pH reading must be recorded. To find the corrected pH, locate the measured pH value from each sample on the vertical scale of the calibration curve. Draw a horizontal line between this scale point and the plotted curved line. Draw a vertical line from the point where the horizontal line and the curved line intersect to the horizontal scale. Read the corrected (or actual) pH on the horizontal scale.

h. Possible Sources of Error

i. Incorrect temperature adjustment may cause significant error.

ii. Failure to standarize the meter before sample analysis or between every five samples may lead to incorrect readings.

iii. Failure to complete monthly calibration checks may cause significant longterm errors in pH analysis.

iv. Inadequate rinsing of probes between pH determinations may cause slow probe and meter response and possible premature acceptance of a meter reading.

4. Acidity - Total (Phenolphthalein)

a. Discussion

The occurence of acidity in water from natural sources is very unlikely; the presence of acidity usually indicates water pollution by acidic industrial wastes.

Total acidity includes free acidity (see paragraph 5, this section) plus weak acids such as carbon dioxide and organic acids.

b. Sampling Procedure

Samples should be collected in clean 500 ml polypropylene bottles and should be returned to the laboratory for immediate analysis.

c. Sampling Points
i. Raw Water Influent Channel
ii. Aeration Tank Effluent
iii. Final Tank Effluent

d. Equipment Required
i. Erlenmeyer flask, 250 ml
ii. Graduated cylinder, 50 ml
iii. Buret, automatic, 25 ml, for 0.020 NaOH
iv. Hot plate

e. Reagents Required
i. Phenolphthalein indicator solution
ii. Standard sodium hydroxide (NaOH), 0.020N
iii. Peroxide, 30% solution

f. Procedure
i. Measure a 50 ml sample and pour into the Erlenmeyer Flask. Care should be taken to prevent excessive agitation during pouring to prevent loss of carbon dioxide which is dissolved in the sample.
ii. Add 4 drops of phenolphthalein indicator solution and 6 drops of H_2O_2 and swirl to mix.
iii. Heat the sample to boiling and continue boiling for five minutes to allow for complete hydrolysis of metal salts. While heating, swirl the flask and titrate with 0.02 N Standard sodium hydroxide solution until the first appearance of a permanent pink color.

(Color should persist for 30 seconds to be considered permanent). Record the number of mls of soduim hydroxide used.

g. Calculations

Total acidity as mg/l calcium carbonate (CaCO3) = (mls 0.020N NaOH used) X 20. Report final answer to the nearest whole number.

Example:

5.25 ml soduim hydroxide x 20 = 105 mg/l
Total Acidity as $CaCO_3$

h. Possible Sources of Error

i. Excessive sample agitation and subsequent loss of dissolved carbon dioxide will result in erroneous test results.

ii. Under or overtitration will result in erroneous determinations. Carefull addition of the titrant in a dropwise fashion will aid in preventing this problem.

iii. On occasion, the pink color will appear before any titrant is added. If this is the case, report total acidity as 0 mg/l as $CaCO_3$.

iv. Soduim hydroxide solutions lose their strength over an extended time period. Use of a weakened solution will cause erroneously high results. To prevent such errors, standardize the soduim hydroxide solution against 0.020 N sulfuric acid (H_2SO_4) solution (used in total alkalinity test) weekly. This can be carried out by accurately measuring 20 ml. 0.020N H_2SO_4 in a 100 ml beaker. Add one drop phenolphthalein indicator solution and swirl to mix. Continue swirling and titrate with 0.020 N NaOH until a faint pink color persists for 30 seconds. Note the amount of NaOH used; if 20 mls NaOH were added, the NaOH solution is of proper concentration.

If more or less than 20 mls NaOH were used, a correction factor must be used in calculating sample total acidities. To determine the correction factor, make the following calculation:

$$\frac{20}{\text{ml. NaOH used}} \times 20 = \text{correction factor}$$

Example:

$$\frac{20}{21.2 \text{ ml NaOH used}} \times 20 = 18.9$$

This correction factor, 18.9, replaces the multiplier of 20 in the calculations for sample total acidities.

The example calculation for sample total acidity cited in paragraph g, above then becomes:

5.25 ml NaOH x 18.9 = 99 mg/l Total Acidity as $CaCO_3$

5. Acidity - Free (Methyl Orange)

a. Discussion

Free acidity is the acidity of water which has been contributed by strong mineral acids such as hydrochloric and sulfuric acids. Excessive free acidity causes corrosive properties in water and can be detrimental to aquatic life in receiving streams.

b. Sampling Procedure

Samples should be collected in clean 500 ml polypropylene bottles and should be returned to the laboratory for immediate analysis.

c. Sampling Points
   i. Raw Water Influent Channel
   ii. Aeration Tank Effluent
   iii. Final Tank Effluent

d. Equipment Required
   i. Erlenmeyer flask, 250 ml
   ii. Graduated cylinder, 50 ml
   iii. Buret, automatic, 25 ml, for 0.020N NaOH

e. Reagents Required
   i. Brom cresol green - methyl red indicator solution
   ii. Standard soduim hydroxide (NaOH), 0.020N

f. Procedure

Procedure is the same as that used for total acidity (Paragraph 4, this section) except that 4 drops of brom cresol greenmethyl red indicator solution are used. Also no H_20_2 is added and the sample is not heated for the titration. The color change will be from red to a light pink grey with a bluish cast rather than from colorless to pink.

g. Calculations

Free acidity as mg/l calcium carbonate ($CaCO_3$) = (mls 0.020N NaOH used) x 20. Report final answer to the nearest whole number.

h. Possible Sources of Error

Possible sources of error noted for the total acidity analysis (Paragraph 4, this Section) also apply to the free acidity analysis with the exception of part iii.

If the sample solution exhibits the characteristic titration end point color (light pink grey with a bluish tinge) before addition of any NaOH titrant, report free acidity as 0 mg/l as $CaCO_3$.

Standardization checks of the 0.020N NaOH solution also apply to the free acidity analysis. It is very important that these checks be made and a correction factor be determined each week to prevent long term erroneously high acidity values.

6. Alkalinity - Phenolphthalein (Samples with pH above 8.3) & Total (Methyl Orange - Samples with pH values above 4.5)

a. Discussion

Alkalinity of water is a result of the presence of bicarbonates, carbonates and hydroxides of calcium, magnesium, sodium and other metals. The term alkalinity has little or no relation to pH of water; it refers to the acid neutralizing capacity of the water. In other words, alkalinity of water refers to the amount of various alkalies in the water which are capable of neutralizing acids.

The alkalinity is determined by titrating a sample of water with a standard solution of acid, with the use of pH indicators, one changing at a pH of 8.3 and another at 4.5 to 5.1. The titration to a pH of 8.3, with the use of Phenolphthalein Indicator, measures the hydroxide and gives half the amount of carbonate in the water. This is commonly referred to as Phenolphthalein Alkalinity.

Another titration with Methyl Orange or other suitable indicator that changes color at pH 4.5 to 5.1 (for example, bromcresol green-methyl red will give the total alkalinity, i.e., bicarbonate, carbonate, and hydroxide). This alkalinity is commonly referred to as Methyl Orange or Total Alkalinity. Alkalinities are expressed in mg/l as an equivalent amount of calcium carbonate ($CaCO_3$).

b. Sampling Procedure

Samples should be collected in clean 500 ml polypropylene bottles and should be returned to the laboratory for immediate analysis.

c. Sampling Points

i. Raw Water Influent Channel
ii. Aeration Tank Effluent
iii. Final Tank Effluent

d. Equipment Required

i. Erlenmeyer flasks, 250 ml (one for each sample and four for color comparisons)

ii. Buret, automatic, 25 ml, for 0.020N H_2SO_4

iii. Graduated cylinder, 50 ml.

e. Reagents Required

i. Phenolphthalein indicator solution
ii. Bromcresol green-methyl red indicator solution
iii. Standard sulfuric acid (H_2SO_4), 0.020N
iv. pH buffer powder pillows for the following pH's:

(a) pH 4.50
(b) pH 4.80
(c) pH 5.10
(d) pH 8.30

f. Procedure

i. Color Comparison Samples

The determination of the exact indicator shade of color at which to terminate both the phenolphthalein and total (methyl orange) titrations is somewhat difficult. Buffered samples at specific end point pH's to which the same amounts of indicator solutions have been added provide accurate color comparison samples to make these color comparison samples.

ii. Sample Analysis

(a) Phenolphthalein Alkalinity (sample pH above 8.3)

1. Measure a 50 ml sample and pour into a 250 ml Erlenmeyer flask.

2. Add 3 drops phenolphthalein indicator solution and swirl to mix. If a faint pink color is not produced, phenolphthalein alkalinity is 0 mg/l as $CaCO_3$.

3. If a pink color is produced, continue swirling flask and titrate sample with standard 0.02 N H_2SO_4 until the color just disappears, or to pH 8.3. Record the number of mls. of titrant used.

(b) Total Alkalinity by Methyl Orange Alkalinity Method (samples pH above 4.5)

1. Measure a 50 ml sample and pour into a 250 ml Erlenmeyer flask. Same sample as used for phenalphthalein alkalinity may be used after titration.)

2. Add 3 drops methyl orange indicator solution and swirl to mix.

3. While swirling the flask, continue titrating with 0.02N H_2SO_4 until an orange color is obtained (pH range 4.0 to 4.5). Record the total number of mls of H_2SO_4 used.

g. Calculations

i. Phenolphthalein Alkalinity

Phenolphthalein Alkalinity in mg/l as $CaCO_3$ = (mls. 0.020N H_2SO_4 used in phenolphthalein titration) x 20. Record final answer to nearest whole number.

ii. Total (Methyl Orange) Alkalinity

Total (Methyl Orange) Alkalinity in mg/l as CaCO3 = (Total mls. 0.02 N H_2SO_4 used in both titrations) x 20. Record final answer to nearest whole number. NOTE: If separate samples are used for the phenolphthalein alkalinity and methyl orange alkalinity, the mls. 0.02N H_2SO_4 used for the methyl orange alkalinity alone is used. Example:

Phenolphthalein Alkalinity: (3.25 ml. 0.020N H_2SO_4 used in phenolphthalein titration to pH 8.30 endpoint) x 20 = 65 mg/l Phenolphthalein Alkalinity as $CaCO_3$.

Total Alkalinity

(Total 6.0 ml 0.020N H_2SO_4 used in both titrations [3.25 ml for phenolphthalein titration plus 3.65 ml for bromcresol greenmethyl red titration] to pH 4.80 endpoint) x 20 = 138 mg/l Total (Methyl Orange) Alkalinity as $CaCO_3$.

h. Possible Sources of Error

i. Under or overtitration will result in erroneous determinations. Careful addition of titrant in a dropwise fashion will aid in preventing this problem.

ii. On occasion, phenolphthalein indicator addition to a sample will not produce a pink color and subsequent addition of bromcresol green-methyl red indicator will produce the characteristic endpoint color (greenish blue-grey) before the addition of 0.020N H_2SO_4 titrant. In such cases, report both the phenolphthalein and total (methyl orange) alkalinities as 0 mg /l as $CaCO_3$.

7. Alkalinity-Net

a. Discussion

Net alkalinity is the parameter which expresses the overall, or net, acidic or alkaline conditions of a water sample. Once total acidity (Paragraph 4) and total alkalinity (Paragraph 6) have been determined in the laboratory, net alkalinity can be calculated.

Net alkalinity is expressed in mg/l as $CaCO_3$.

b. Calculations

Net alkalinity (mg/l as $CaCO_3$) = Total Alkalinity Minus Total Acidity (mg/l as $CaCO_3$). Record final result to the nearest whole number.

Example:

138 mg/l (as $CaCO_3$) Total Alkalinity
-105 mg/l (as $CaCO_3$) Total Acidity
33 Mg/l (as $CaCO_3$) Net Alkalinity

If total acidity is greater than total alkalinity net alkalinity will be a negative value.

Example:

82 mg/l (as $CaCO_3$) Total Alkalinity
-105 mg/l (as $CaCO_3$) Total Acidity
=-23 mg/l (as $CaCO_3$) Net Alkalinity

8. Turbidity

a. Discussion

Turbidity in water is caused by the presence of suspended matter, such as clay, silt, finely divided organic and inorganic matter, plankton, and other microscopic organisms. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample.

It is important to note that turbidity and the weight concentration of suspended matter cannot be correlated because of the differing size, shape, and refractive properties of the suspended particulates.

Turbidity is measured directly: in Nephelometric Turbidity Units (N.T.U.'s) with the use of a nephelometer; in Formazin Turbidity Units (F.T.U.'s) with the use of a spectrophotometer.

b. Sampling Procedure

Turbidity samples should be collected in clean pyrex or polypropylene bottles and should be returned to the laboratory for analysis within 24 hours. If the sample cannot be analyzed immediately, it should be refrigerated at 4°C.

c. Sampling Points

i. Raw Water Influent Channel
ii. Final Tank Effluent

d. Equipment Required

i. Nephelometer, with sample cells
ii. Turbidity standard cells
iii. Lint-free paper wipers (Kimwipes)

e. Reagents Required

i. Distilled water

f. Procedure

i. Turn on nephelometer. Set scale adjust knob to 10.

ii. Fill a clean sample cell with distilled water. Wipe the outside of the cell with a lint-free wiper to remove dust, fingerprints, spots, etc. Insert the sample cell in the well in the nephelometer. Cover with sample cell cap.

iii. The meter scale should read zero. If it does not, adjust the zero control until the meter reads zero. Remove the sample cell.

iv. Wipe the 10 N.T.U. standard cell with a lintfree wiper to remove dust and fingerprints. (Note: DO NOT SHAKE THE STANDARDS) Insert the standard in the nephelometer well and cover with the cell cap.

v. The meter should read 10 N.T.U.'s on the 0-10 N.T.U. scale. If it does not, adjust to 10 N.T.U.'s with the calibration control. Remove the standard cell.

vi. Repeat zero and 10 N.T.U. calibrations until no further meter adjustments are necessary.

vii. Invert the sample bottle several times and pour approximately 30 ml of the sample into a clean dry sample cell. If air bubbles collect on the inside surface of the cell, tap the cell gently to dislodge them.

viii. Wipe the cell with a lint-free wiper to remove dust and fingerprints. Insert in the nephelometer well and cover with the cell cap.

ix. Read the turbidity of sample in N.T.U.'s directly from the 0-10 N.T.U. scale.

x. If sample turbidity is less than 1 N.T.U., turn scale adjust knob to 1 and repeat meter calibration using the 0.61 N.T.U. standard. Repeat the sample determination.

xi. If sample turbidity is more than 10 N.T.U.'s repeat meter calibration by turning the scale adjust knob to either 100 or 1000 and using either the 100 or 1000 N.T.U. standard as required. (NOTE: At these high turbidities, the cell riser included in the standards kit must be inserted in the nephelometer well before insertion of either the 100 or 1000 N.T.U. standards or the sample cell.

xii. When reading turbidities from the meter scale, report results as follows:

Turbidity Range N.T.U.	Record to the Nearest N.T.U.
0-1.0	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1000	50
>1000	100

The procedure for measuring turbidity by using a spectrophotometer and reporting the results in FTU's is as follows:

i. Measure a 25 ml sample and pour into a clean bottle.

ii. Measure 25 ml distilled water and pour into a second bottle. Insert turbidity scale in meter and adjust to proper wavelength setting.

iii. Insert distilled water into light cell and adjust light control for meter reading of zero FTU's.

iv. Insert sample into light cell and read turbidity on Spectrophometric scale.

v. If meter is off scale, determination must be repeated using a diluted sample.

g. Calculations

None. The nephelometer and the spectrophotometer are direct reading instruments.

h. Possible Sources of Error

i. Failure to wipe dust or fingerprints from the outside of the standard or sample cells may cause erroneous results. Likewise, dirt on the insides of the sample cells will cause errors.

ii. Badly worn and scratched sample and standard cells will also lead to errors in turbidity measurements. Should these cells become damaged, replace them immediately.

iii. Use of outdated standards will cause errors. These standards have a shelf life of approximately one year. New standards should be purchased each year and the old ones discarded.

iv. Switching of the scale control knob to make a turbidity reading without first recalibrating the nephelometer with the appropriate standard may cause errors in the determinations. Likewise, failure to use the cell riser in the 100 and 1000 N.T.U. ranges may lead to erroneous results.

9. Total Dissolved Solids (TDS)

a. Discussion

Total dissolved solids, is the measure of matter dissolved in water. High dissolved solids are undesirable in water as they affect palatability and the suitability of water for industrial applications. Water containing excessive dissolved solids may also be aesthetically unsatisfactory.

Dissolved solids give water the ability to conduct electricity. The degree of conductance of water is proportional to the total amount of mineral matter (TDS) present.

Conductance is measured with a conductivity meter which has been calibrated with sodium chloride solution. Sample conductivities are measured in ppm sodium chloride; this value can then be converted to micromhos, ohms, grains sodium chloride, or total dissolved solids as calcium carbonate with the use of the conversion table supplied with the conductivity meter.

b. Sampling Procedure

Samples should be collected in clean wide mouth polyprophylene bottles. Care should be taken to avoid excessive agitation and to protect the sample from atmospheric gases, as gases such as carbon dioxide and ammonia will dissolve in the sample and will rapidly alter the conductivity, particularly in those samples which have natural low conductivities. Samples should be returned to the laboratory to be analyzed as soon as possible and no later than 24 hours after collection.

c. Sampling Points

i. Raw Water Influent Channel
ii. Final Tank Effluent
iii. Waste Sludge Well

d. Equipment Required

i. Conductivity meter
ii. Thermometer
iii. Beakers, 300 ml

e. Reagents Required

i. Sodium chloride standard solution, 1000 mg/l (ppm); (1990 micromhos/CM.)
ii. Distilled water
iii. Gallic acid powder pillows (for highly alkaline samples)

f. Procedure

i. Prepare the conductivity meter for operation as directed in the instrument instruction manual and set the "range" switch to the highest range.

ii. Immerse the probe in a beaker containing 1000 mg/l standard chloride solution. The depth of the solution must be sufficient to allow the probe to be immersed to the vent holes.

iii. If the conductivity meter is not designed for automatic temperature compensation, measure the temperature of the standard solution and adjust the instrument's temperature control accordingly.

iv. Select the appropriate range, beginning with the highest and working down. If the reading is in the lower 10 percent of the range, switch to the next lower range.

v. Read the mg/l sodium chloride. The reading should be 1000 mg/l. If it is not, adjust the instrument to read 1000 mg/l NaCl by using the standardization control.

vi. Remove the probe from the standard solution and rinse well with distilled water.

vii. Place the probe in a beaker containing the sample. Again, be sure the probe is adequately immersed.

viii. If necessary, measure the temperature of the sample and adjust the instrument accordingly.

ix. Select the proper range as instructed in Step iv above. If the mg/l NaCl of the sample exceeds the range of the instrument, the sample may be diluted in the following manner:

DILUTION	MLS. SAMPLE	DILUTED TO	DILUTION FACTOR
2:1	50	100 mls	2
5:1	20	100 mls	5
10:1	10	100 mls	10

x. Read the mg/l soduim chloride and record.

xi. Remove the probe from the sample and rinse well with distilled water.

xii. For additional samples, Repeat Steps vii thru xi.

g. Calculations

Using the conversion chart supplied with the instrument, convert mg/l NaCl to mg/l total dissolved solids (TDS) as calcuim carbonate for each sample.

If the sample was diluted, multiply the calculated TDS value by the appropriate dilution factor to obtain the final TDS value.

h. Possible Sources of Error

i. Water samples containing lime, gypsum and iron substances will coat the electrodes and affect the accuracy of the readings. Should this occur, the probe should be cleaned with a strong detergent solution or dipped in a one-to-four mixture of concentrated hydrochloric acid (HCl) and distilled water and then thoroughly rinsed with distilled water.

ii. Significant amounts of hydroxide in the sample may cause erroneously high readings. Neutralization of the sample with gallic acid (one power pillow per 50 ml sample) will prevent this problem. (One gallic acid powder pillow will neutralize approximately 1300 mg/l phenolphthalein alkalinity.)

10. Settleable Solids

a. Discussion

The term "settleable solids" is applied to solids in suspension which will settle, under undisturbed conditions, because of gravity. This test is an idication of the volume of solids removed by sedimentation, and results are measured and reported as milliliters per liter (ml/l) of settleable matter. Note that this is a volumetric test, as opposed to a weight test.

b. Sampling Procedure

Samples should be collected from points of thorough mixing in large, one liter or larger, polypropylene bottles. Care should be taken to collect a representative sample and to avoid entrapment of large particles or growths.

c. Sampling Points

i. Raw Water Influent Channel
ii. Flash Mixer Effluent
iii. Aeration Tank Effluent
iv Settling Tank Effluent
v. Final Tank Effluent
vi. Waste Sludge Well

d. Equipment Required

i. Imhoff cone
ii. Imhoff cone support

e. Reagents Required

None

f. Procedure

i. Place the Imhoff cone in the support stand.
ii. Thoroughly mix the sample by stirring or shaking.
iii. Immediatly fill the Imhoff cone to the 1 liter mark with the thoroughly mixed sample.
iv. Allow the sample to settle for 45 minutes.
v. Gently rotate the cone between the hands to loosen the solids which adhere to the inclined sides.
vi. Allow the sample to settle an additional 15 minutes.
vii. Read the milliliters of settleable matter from the scale at the bottom of the cone and record in milliliters per liter (ml/l)

g. Calculations

None - settleable matter volume can be read directly from the scale at the bottom of the cone.

h. Possible Sources of Error

i. Inadequate sample mixing may cause errors.
ii. Vibration of the support stand should be avoided, as this may cause abnormal compaction of the settled matter.

11. Chloride

a. Discussion

Chloride is one of the major inorganic anions in water and wastewater. Some potable waters containing 250 mg/l chloride may have a detectable salty taste if the cation present is soduim.

A high chloride content in waters harms metallic pipes and structures, as well as agricultural plants.

b. Sampling Procedure

Chloride samples should be collected in either polypropylene or borosilicate glass bottles. The samples may be held a maximum of 7 days before analysis.

c. Sampling Points

i. Raw Water Influent Channel
ii. Final Tank Effluent

d. Equipment Required

i. Graduated cylinder, 100 ml
ii. Buret, automatic, 25 ml, for 0.0141N $Hg(NO_3)_2$
iii. Erlenmeyer flask, 250 ml

e. Reagents Required

i. Standard mercuric nitrate ($Hg(NO_3)_2$), 0.0141N
ii. Diphenylcarbazone indicator - buffer powder pillows
iii. Sodium chloride standard solution, 1000 ppm

f. Procedure

i. Measure 100 ml sample in the graduated cylinder and pour it into a 250 ml flask.
ii. Add the contents of one diphenylcarbazone indicatorbuffer powder pillow. Swirl to mix.
iii. While swirling the flask, titrate with standard mercuric nitrate solution until a permanent light pink color develops. Record mls of titrant used.

g. Calculations

To determine the concentration of chloride in the sample, multiply the mls of titrant used by 5.

Example: 10.3 mls titrant used
mg/l chloride= 10.3 x 5 = 56.5 ppm

h. Possible Sources of Error

i. Chromate, ferric iron, and sulfite ions in excess of 10 mg/l in the sample may cause interference.
ii. Soiled or scratched colorimeter bottles may cause erroneous results.
iii. This method may be checked by using the sodium chloride standard solution in place of the sample.

12. Sulfates

a. Discussion

Sulfate (SO_4=) is widely distributed throughout the environment and may be present in natural waters in a wide range of concentrations. Mine drainage wastes are usually high in sulfates. Sulfates are generally stable in the environment and thus are often used as a method of tracing acid mine drainage.

b. Sampling Procedure

Samples should be collected in clean polyethylene bottles and may be stored up to 7 days at 4°C prior to analysis. (Note: Never collect samples in glass bottles, as sulfates will adhere to glass, causing low sulfate readings.)

c. Sampling Points

i. Raw Water Influent Channel
ii. Final Tank Effluent
iii. Waste Sludge Well
iv. Potable Water Supply

d. Equipment Required

i. Colorimeter
ii. Colorimeter bottles
iii. Graduated cylinder, 25 ml

e. Reagents Required

i. Sulfa Ver powder pillows

f. Procedure

i. Insert the sulfate meter scale and the 4445 color filter in the colorimeter.
ii. Fill a clean colorimeter bottle with distilled water, insert in the light cell, and adjust the light control for a meter reading of zero mg/l (ppm).
iii. If the sample is colored or turbid, filter so that the test solution is clear.
iv. Measure 25 mls of the sample solution and pour in a second clean colorimeter bottle.
v. Add the contents of one Sulfa Ver powder pillow to the sample colorimeter bottle. Allow the powder to lay on the surface of the sample for 30 seconds, and then swirl to mix.

vi. Allow sample to sit 5 minutes.

vii. Place the sample in the colorimeter light cell and read the sample sulfate concentration on the scale.

viii. If the meter is off-scale, the determination must be repeated using a diluted sample. Dilutions can be made in the following way:

DILUTION	MLS. SAMPLE	DILUTED TO	DILUTION FACTOR
2:1	50	100 mls	2
5:1	20	100 mls	5
10:1	10	100 mls	10

(Note: This method is applicable in the range of 0-300 ppm. A 2: 1 dilution will allow determination of sulfates up to 600 ppm; a 5: 1 dilution up to 1500 ppm; etc.)

g. Calculations

i. Undiluted Samples

None. Sulfate concentration may be read directly from the meter.

ii. Diluted Samples

ppm $SO_4^=$ = meter reading x dilution factor

Example: For a 5:1 dilution, the meter reading is 265 ppm $SO_4^=$

265 mg/l x 5 = 1325 mg/l $SO_4=$
(Meter reading) (dilution factor)

h. Possible Sources of Error

i. Soiled colorimeter bottles will lead to erroneously high readings. It is extremely important that colorimeter bottles used for sulfates determinations be scrubbed thoroughly with soap and a brush, as the precipitate (barium sulfate) formed during the test will coat the bottle interiors with a white film.

ii. Some interferences may result in colored ions present in acid mine drainage. If interferences result, first exchange the sample with cation exchange resin to remove this interference.

13. Aluminum

a. Discussion

Aluminum, like manganese, may be present in natural waters in low concentrations. Significant levels of aluminum, however, may result from water flowing over and through aluminum-bearing strata. Elevated aluminum concentrations are not uncommon in areas of mine-related activity.

b. Sampling Procedure

Samples should be collected in the same manner as manganese samples. If desired, both the aluminum and manganese determinations can be made on samples from the same bottle. See paragraph 18 page IV-36 for manganese testing discussion.

c. Sampling Points

i. Raw Water Influent Channel
ii. Final Tank Effluent

d. Equipment Required

i. Colorimeter or Spectrophotometer
ii. Colorimeter bottles
iii. Graduated cylinder, 50 ml
iv. Erlenmeyer flask, 250 ml

e. Reagents Required

i. Nitric acid, concentrated
ii. Alu Ver power pillows
iii. Bleaching powder pillows
iv. Distilled water
v. Aluminum standard solution, 1 ppm
vi. Sodium hydroxide solution, 1 normal

f. Procedure

i. Measure 50 ml sample in the graduated cylinder and pour into the Erlenmeyer flask.

ii. Add the contents of one Alu Ver powder pillow and swirl to dissolve the powder. If aluminum is present, a pink color will develop.

iii. Immediately divide the sample into two 25 ml portions by filling two clean colorimeter bottles.

iv. To one of the colorimeter bottles, add the contents of the Bleaching powder pillow. Swirl the bottle to dissolve the powder. This solution should be light orange.

v. Allow 30 minutes for color development.

vi. Insert the colorimeter bottle containing the bleaching powder in the colorimeter light cell. Insert the Aluminum (Alu Ver Powder Method) meter scale in the meter and use the 4445 color filter.

vii. Adjust the light control for a meter reading of 0 mg/l (ppm).

viii. Place the other colorimeter bottle (sample without bleaching powder) in the light cell and read the mg/l aluminum in the sample.

ix. If the meter is off-scale, repeat the analysis using a diluted sample.

g. Calculations

i. Undiluted Samples

No calculation is necessary. Aluminum concentration in mg/l may be read directly from the meter scale.

ii. Diluted Samples

Multiply the meter scale reading by the appropriate dilution factor to obtain the final mg/l aluminum.

h. Possible Sources of Error

i. This method is subject to a slight interference from iron. Approximately 10 mg/l iron, regardless of form, will give the equivalent of 1 mg/l aluminum.

ii. The Alu Ver reagent used in this test will deposit on the colorimeter bottle surfaces and may contain some of the bleaching material which could interfere with subsequent aluminum tests. To prevent this problem, the colorimeter bottles should be cleaned with a brush and a solution of soduim hydroxide (30-40 grams/liter; CAUTION: This solution is caustic).

iii. Otherwise soiled or scratched colorimeter bottles will result in erroneous determinations.

14. Iron-Total And Dissolved

a. Discussion

Iron found in natural ground and surface waters generally does not exceed 1 mg/l. In some cases, however, some ground waters and acid surface draining waters, particularly acid mine drainage from coal mines and coal refuse areas, contain considerably more iron. Iron is not desirable in drinking waters as it may cause staining of laundry and porcelain and may impart a bittersweet astrigent taste to the water. Elevated iron concentrations are also undersirable in surface waters because of the detrimental effects to the aesthetics of these waters. Iron may be both dissolved and suspended. Laboratory procedures are the same for both, but sample collection methods differ.

b. Sampling Procedure

i. Total Iron

"Fix" a polypropylene bottle with concentrated hydrochloric or nitric acid (2.5 ml HNO_3/500 ml bottle). Collect the sample without rinsing the bottle.

ii. Dissolved Iron

"Fix" a polypropylene bottle with HNO_3 or HCl as directed above. Using a polypropylene funnel and Whatman No. 2 filter paper, filter the sample into the bottle. Acid-fixed samples are stable for six months. CAUTION: Both hydrochloric and nitric acid are extremely corrosive and may cause serious chemical burns. When collecting the sample, take care not to splash the acid on skin or clothing. In case of contact, flush immediately with water and, if necessary, seek medical attention. Hydrochloric and nitric acid will also fume when it comes in contact with the sample. Avoid inhaling these fumes, as they may injure the respiratory tract.)

c. Sampling Points

i. Raw Water Influent Channel
ii. Final Tank Effluent
iii. Waste Sludge Well
iv. Potable Water Supply

d. Equipment Required

i. Funnel
ii. Whatman No. 2 filter paper
iii. Colorimeter or Spectrophotometer
iv. Colorimeter bottles
v. Graduated cylinder, 25 ml

e. Reagents Required

i. Nitric acid, (concentrated) or Hydrochloric Acid.
ii. Ferro Ver powder pillows

f. Procedure (for both total and dissolved iron)

i. Fill a clean colorimeter bottle with distilled water and place it in the colorimeter light cell.

ii. Insert the Iron (Ferro Ver Method) meter scale in the meter and use the 4445 color filter, or suggested wavelength setting.

iii. Adjust the light control for a reading of 0 mg/l (ppm).

iv. Fill the graduated cylinder with 25 ml sample and pour into a clean colorimeter bottle.

v. Add the contents of one Ferro Ver powder pillow to the sample and swirl to mix. Let the sample stand for at least 2 minutes but no longer than 10 minutes).

vi. Place the sample in the light cell and read the mg/l iron. This method is accurate for the range of 0-3 mg/l iron. If the sample iron concentration is above 3 mg/l, repeat the test using a diluted sample diluted in the following way:

DILUTION	MLS. SAMPLE	DILUTED TO	DILUTION FACTOR
50:1	50	100 mls	2
20:1	20	100 mls	5
10:1	10	100 mls	10

g. Calculations

i. Undiluted Samples

No calculation is necessary for undiluted sample. Concentration may be read directly from the meter scale.

ii. Diluted Samples

For diluted samples, multiply the meter scale value by the appropriate dilution factor for the final concentration.

h. Possible Sources of Error

i. Soiled or scratched colorimeter bottles may lead to erroneously high results.

15. Iron - Ferrous

a. Discussion

Sometimes iron is present, particularly in some ground waters and acid waters, in the unoxidized state. This form of iron is referred to as ferrous iron. The ferrous iron determination does not register ferric (or oxidized) iron.

b. Sampling Procedure

Collect ferrous iron samples in polypropylene bottles fixed with concentrated hydrochloric or nitric acid (2.5 ml HNO_3 in a 500 ml bottle). Return samples to the laboratory for immediate analysis, as ferrous iron is very unstable and will oxidize to the ferric state readily.

c. Sampling Points

i. Raw Water Influent Channel
ii. Final Tank Effluent
iii. Waste Sludge Well
iv. Potable Water Supply

d. Equipment Required

i. Colorimeter or Spectrophotometer
ii. Colorimeter bottles
iii. Graduated cylinder, 25 ml.

e. Reagents Required

i. Ferrous iron powder pillows
ii. Nitric acid or Hydrochloric Acid
iii. Distilled Water

f. Procedure

i. Fill a clean colorimeter bottle with distilled water and place it in the colorimeter light cell.

ii. Insert the Iron (Ferro Ver Method) Meter Scale and use the 4445 color filter, or wavelength setting.

iii. Adjust the light control for a reading of 0 mg/l (ppm).

iv. Measure 25 mls of sample in the graduated cylinder and pour into a clean colorimeter bottle.

v. Add the contents of one ferrous iron powder pillow and swirl to mix. Allow 2 minutes for color development.

vi. Place the sample in the light cell and read mg/l ferrous iron . If the meter is off-scale, repeat the test using a diluted sample

g. Calculations

i. Undiluted Samples

For undiluted samples, no calculation is necessary. Ferrous iron concentration may be read directly from the meter scale.

ii. Diluted Samples

For diluted samples, multiply the meter reading by the appropriate dilution factor to obtain the final ferrous iron concentration.

h. Possible Sources of Error

i. Soiled or scratched colorimeter bottles will cause erroneously high results.

ii. Time delays between sample collection and analysis may lead to erroneously low results.

16. Iron - Ferric

To determine ferric iron concentration, subtract the ferrous iron concentration from the total iron concentration.

Example:

Total Iron	3.2 mg/l
-Ferrous Iron	-1.6 mg/l
Ferric Iron	1.6 mg/l

17. Manganese

a. Discussion

Manganese is commonly found in low levels in many ground and surface waters. Manganese may exceed natural levels, however, if water flows through or over disturbed strata containing manganous materials. Elevated manganese concentrations are quite common is waters generated by mining activity.

b. Sampling Procedure

Samples should be collected in polypropylene bottles which have been fixed with concentrated nitric acid (2.5 ml HNO_3/500 ml bottle). Manganese samples preserved in this manner are stable for six months.

c. Sampling Points

i. Raw Water Influent Channel
ii. Final Tank Effluent

d. Equipment Required

i. Colorimeter
ii. Colorimeter bottles
iii. Graduated cylinder, 25 ml
iv. Erlenmeyer flask, 250 ml
v. Hot plate

e. Reagents Required

i. Nitric acid, concentrated
ii. Manganese II powder pillows
iii. Distilled water
iv. Manganese standard solution, 5 ppm

f. Procedure

i. Measure 25 ml of sample in the graduated cylinder and pour into the Erlenmeyer flask.

ii. Add the contents of one Manganese II powder pillow to the flask.

iii. Place the flask on the hot plate and bring the solution to a gentle boil. Allow the sample to boil for 30 seconds.

iv. Remove the flask from the hot plate and allow it to cool in air for at least 5 minutes.

v. While the sample solution is cooling, fill a clean colorimeter bottle with distilled water and place it in the colorimeter light cell. Insert the Manganese (Persulfate, Periodate, and Silver Peroxide Methods) meter scale in the meter and use the 4445 color filter.

vi. Adjust the light control for a meter reading of 0 mg/l (ppm).

vii. After the sample solution has air-cooled at least 5 minutes, return it to the graduated cylinder. If the volume is less than 25 ml, add distilled water to return the volume to 25 ml. Pour the solution into a clean colorimeter bottle.

viii. Place the sample colorimeter bottle in the light cell and read the mg/l manganese. (This method has a range of 0.2 to 10 mg/l manganese.)

g. Calculations

No calculation is necessary, as the concentration of manganese in the sample may be read directly from the meter scale.

h. Possible Sources of Error

i. It is necessary to boil the sample for 30 seconds and then allow it to cool in air for a full 5 minutes to obtain full color development. Failure to boil for 30 seconds and/or cooling more quickly will result in incomplete color development and low test results. To check on this technique, a standard test may be completed by testing the 5ppm manganese standard solution.

ii. Soiled or scratched colorimeter bottles may lead to errors.

18. Chlorine - Total Available

a. Discussion

Total available chlorine is the chlorine remaining at the end of a specified contact period. This analysis is used to determine if desired chlorination (disinfection) objectives are being met. Total available chlorine is reported in mg/l.

b. Sampling Procedure

Because chlorine in aqueous solution is not stable, determinations should be made on-site. If this is not practical, samples may be collected in polypropylene or amber glass bottles and returned to the laboratory for immediate analysis. A sample holding period of not more than 10 minutes is suggested. Care should be taken to avoid exposure of the sample to heat, sunlight, strong artificial light, and excessive agitation, as this will cause rapid deterioration of chlorine.

c. Sampling Points

i. Final Tank (Effluent from Domestic Sewage Treatment Plant)

d. Equipment Required

i. Colorimeter

ii. Colorimeter bottles

iii. Pipet, 1 ml

iv. Graduated cylinder, 25 ml

e. Reagents Required

i. O - Toli Ver solution

f. Procedure

i. Add 1 ml O-Toli Ver solution to a clean, empty colorimeter bottle.

ii. Measure 25 ml of sample in the graduated cylinder and pour into the bottle containing O-Toli Ver. Swirl to mix. If chlorine is present, a yellow color will develop.

iii. If the temperature of the sample is below 20°C, bring it to this temperature by holding the colorimeter bottle under a hot water tap, or by some other suitable means.

iv. Allow 1 to 5 minutes for color development.

v. While waiting for color development in the prepared sample, fill a second clean colorimeter bottle with sample and place it in the light cell. Insert the chlorine meter scale and use the 5543 color filter.

vi. Adjust the light control for a meter reading of 0 mg/l (ppm).

vii. Place the prepared sample in the light cell and read the mg/l chlorine.

viii. If the meter reads above 1 mg/l on the meter scale, the test must be repeated as follows:

(a) Measure 20 ml distilled water in the graduated cylinder and pour into a clean colorimeter bottle.

(b) Add 1.0 ml O-Toli Ver solution and swirl to mix.

(c) Pipet 5.0 mls of sample into the colorimeter bottle and swirl to mix.

(d) Continue analysis as in Steps iii thru vii above.

g. Calculations

i. Undiluted Samples

No calculation is necessary. Total available chlorine (in mg/l) may be read directly from the meter scale.

ii. Diluted Samples

Multiply the meter scale reading by 5 to determine the final total available chlorine concentration in mg/l.

h. Possible Sources of Error

i. Excessive sample agitation, exposure to light, exposure to heat, or extended periods between sample collection and analysis may lead to erroneously low results.

ii. Soiled or scratched colorimeter bottles may also cause errors in chlorine determinations.

iii. Failure to raise sample temperature to 20°C may inhibit color development and cause low results.