11.6 FIELD WATER CHEMISTRY

11.6.1 Water Temperature

A. EQUIPMENT

A thermometer of known immersion type marked in fractions of a degree calibrated against National Bureau of Standards (NBS) certified thermometer is desirable.

B. REAGENTS None

C. COLLECTION None

D. FILTRATION None

E. PROCEDURE

1. Immerse the thermometer to the correct depth. Total immersion thermometers are designed to be immersed to the top of the mercury column. In practice, keep the thermometer totally immersed until the temperature stabilizes, and partially immersed when reading the temperature.

76mm (3-inch) immersion thermometers are to be immersed exactly to that depth. Thermometers of this type usually have a line etched at that point.

2. Allow the thermometer to remain in the water until the temperature stabilizes.

3. Read the thermometer as accurately as possible. Estimate one decimal place more than the thermometer markings. Correct the reading and record on the data card.

F. PRESERVATION None

G. PRECAUTIONS

1. Since the water temperature in most streams is not constant from bank to bank, care must be exercised when measuring water temperature. Avoid shallow, slow moving sunlit areas. Select a location in the main flow of the stream, keeping the thermometer in the shade.

2. Lakes show vertical temperature gradients, so the temperature is measured at the same level the sample is taken. This depth is included in the site descrip tion on the sample card.

3. When using glass column alcohol thermometers, special care must be taken to prevent breakage. Mercury thermometers are not recommended because, when broken, sample and environmental contamination is a possibility.

H. QUALITY CONTROL

Thermometers must be standardized at a minimum of two temperatures (0 ^{o}C and 25 ^{o}C are preferable) by comparing readings with an ASTM or NBS standardized thermometer. Correction factors shall be recorded permanently on the thermometer. Restandardization may be desirable periodically.

I. SPECIAL INSTRUCTIONS

A second thermometer shall be carried into the field as a backup in case of breakage.

J. REFERENCES None

K. PROJECT

Clark Fork Basin Study, NPDES Compliance Monitoring, Intensive Surveys

11.6.2 pH

A. EQUIPMENT

1. Portable Mach One pH Meter, Model 43800-00

2. 50ml plastic beakers

B. REAGENTS

1. Buffers, pH 4.0, 7.0, and 9.0

2. DI water

C. COLLECTION

A sample can be placed in a 50ml plastic beaker for measurement away from the stream.

D. FILTRATION None

E. PROCEDURE

1. Turn the meter on (Press "0").

2. Press "pH".

3. Press "AUTO" manual. The "Auto" indicator shall light. The "S1" and "pH" indicators shall flash. Zeros shall appear on the display.

4. Place the electrode in the pH 4.0 buffer and press the Dispenser Button once. For best calibration, allow thirty seconds before pressing the key in step 5.

5. Press "STANDARD" and wait until the pH indicator stops flashing. The "S2" indicator now shall begin flashing. The actual pH value shall appear in the display. If the solution temperature deviates from 25°C, the display shall show the actual pH and not 4.01.

6. Rinse the electrode with deionized water. Place the electrode in the pH 7.0 buffer and press the Dispenser Button. Allow 30 seconds to elapse before performing step 7.

7. Press "STANDARD". "S2" shall stop flashing. Wait until the pH indicator stops flashing. The actual pH value shall appear in the display. If the solution temperature deviates from 25 °C, the display shall show the actual pH and not 7.00.

8. Pressing any other key than "pH" at this point

shall cause the meter to revert to its previous calibration, and the new calibration shall be lost.

9. Press "pH". Rinse the electrode with deionized water, place into the sample, and press the Dispenser Button.

10. Swirl the sample gently. The meter is now measuring the pH. Read the sample pH value in the display after the stability indicator stops flashing. Stability is usually reached in 20-30 seconds.

F. PRESERVATION None; analyze immediatel y

G. PRECAUTIONS

Read the instrument manual before use to become more familiar with key functions, one and two standard calibration procedures, maintenance, troubleshooting, error codes, etc.

H. QUALITY CONTROL

Check the meter periodically using a pH 7.0 or 9.0 buffer. If drift has occurred, recalibrate.

I. SPECIAL INSTRUCTIONS

1. Calibration may be better if done with buffers that bracket the range of pHs being measured. If measuring lake and stream pHs, pH 7.0 and 9.0 buffers are more likely to bracket the expected pH values than pH 4.0 and 7.0 buffers.

2. If the screen displays a fluctuating reading or gives an E1 error code, air bubbles in the electrode solution tubing are causing trouble. Dispense more electrode solution with the Dispensing Button or by turning the Priming Knob counterclockwise to remove the air bubbles.

3. The probe indicator shall remain on if the calibration offset deviates from 0.0mV by 60 to 120mV and/or the slope deviates from the ideal slope of 59.2mV/pH unit by 15 to 30% (the expected slope may deviate from 59.2mV/pH unit by 5%; greater values indicate that the meter is unable to detect stable conditions). Use the "REVIEW" key to note the offset and slope. Correct a wrong offset by a one-buffer calibration. Correct a wrong slope and offset by a two-buffer calibration or return to the factory-set calibration by removing the battery from the meter for five seconds or longer.

J. REFERENCES

Manual for Portable Hach One pH Meter Model 43800-00

K. PROJECT

Clark Fork Basin Study, Intensive Surveys, Drinking Water

11.6.3 Dissolved Oxygen (Winkler Method)

A. EQUIPMENT

Field Kit including:

1. Two BOD bottles with glass stoppers
2. One filler tube and rubber stopper
3. One burette and 500ml reagent bottles
4. One 250ml erlenmeyer flask
5. One 200ml plastic volumetric flask
6. Nail clippers, knife, or razor blade
7. Small flashlight or penlight
8. One plastic 100ml beaker

B. REAGENTS

Manganous Sulfate Powder Pillows (Hach Catalog No. 1071)

Alkaline - Iodine - Azide Reagent Powder Pillows (Hach Catalog No. 1072)

Sulfamic Acid Powder Pillows (Hach Catalog No. 1073)

Phenylarsine Oxide (PAO) Standard Solution 0.025N (Hach Catalog No. 1070)

Starch Solution

C. COLLECTION

1. Rinse the BOD bottle three times with the sample water. Insert a filler tube-rubber stopper into the BOD bottle, and place bottle in water as shown below:

2. With a vented rubber stopper in place, hold the bottle vertically under water with a rubber vent tube above the water surface. Fill the bottle completely, making sure there are no trapped air bubbles.

D. FILTRATION None

E. PROCEDURE

1. Add one powder pillow of manganous sulfate and one powder pillow of alkaline-iodine- azide. Add the reagents slowly to avoid introducing air into the sample.

2. Stop with care to exclude air bubbles and mix by inverting the bottle at least 20 times.

3. Allow floc to settle below numbers on the bottle. Shake and allow to settle again.

4. Carefully add one powder pillow of sulfamic acid, re-stop, and mix by gentle inversion until floc dissolves. At this point, samples may be stored a few hours in the dark without changing the results.

5. Rinse the small volumetric flask several times with a small volume of an acidified sample. Insert the flask mouth into the BOD bottle and invert to fill the flask (for a 300ml sample bottle, 203ml volume is taken for titration).

6. Fill the burette with PAO solution using the squeeze bulb. Zero the initial reading by gently tapping the burette.

7. Rinse the erlenmeyer flask several times using the excess acidified sample from the BOD bottle. Pour the sample from volumetric flask into the erlenmeyer flask. Titrate with PAO, swirling the flask gently, to a pale straw color.

8. Add 12-15 drops of starch solution and continue titration to the first disappearance of the blue color. Refill the burette if more than 10ml of titrant is required.

9. Final burette reading equals mg/L of dissolved oxygen. Record to nearest 0.05mg/L.

F. PRESERVATION None; sample may be stored temporarily (refer to Procedure step 4).

G. PRECAUTIONS

1. Certain oxidizing agents cause positive interferences; certain reducing agents cause negative interferences ; certain organic compounds partially obscure the titration endpoint. Higher concentrations of ferrous or ferric iron also reduce accuracy.

2. Starch solution shall be as "fresh" as possible. Old starch solution may make the endpoint difficult to observe.

3. Keep fixed samples out of direct sunlight.

4. Using PAO of a different normality shall require a conversion of the final reading.

H. QUALITY CONTROL

A duplicate shall be analyzed near the beginning of a survey to assess analytical technique.

I. SPECIAL INSTRUCTIONS None

J. REFERENCES

Standard Methods, 15th Edition, pp 388-393.

K. PROJECTS

Clark Fork Basin Study, Intensive Surveys

11.6.4 Dissolved Oxygen(DO Meter Method)

A. EQUIPMENT

YSI Model 54A Oxygen Meter with probe and acces sories (membran es, KCl probe solution, o-ring, razor blade)

B. REAGENTS None

C. COLLECTION

Samples for the measurement of dissolved oxygen shall be collected very carefully so that atmospheric oxygen is not introduced into the sample. Avoid aeration, turbulence, or any other kind of agitation that could introduce air into a sample.

D. FILTRATION None

E. PROCEDURE

1. Calibration

a) Switch the instrument to "OFF" and adjust the meter to mechanical zero.
b) Switch to "RED LINE" and adjust to zero.
c) Plug the probe into the instrument, and wait 10 to 15 minutes for the probe to polarize. Keep the probe in a high humidity environment (i.e., a calibration chamber).
d) Switch to "ZERO" and adjust to "0" on the PPM scale.
e) Switch to "TEMP" and read on °C scale.
f) Use the probe temperature and true local atmospheric pressure (or elevation above sea level) to determine the calibration values from Tables I and II on the back of the meter.
g) The correct calibration value is calculated by multiplying the DO concentration at the probe temperature by the factor for the station elevation.
h) Switch to 0-10 or 0-20ppm DO range and adjust the meter with "CAL" control to the calibration value determined in step g.

2. Measurement

a) Place probe in sample and stir.
b) Allow sufficient time for probe to stabilize to the sample temperature and dissolved oxygen concentration.
c) Read the dissolved oxygen on the approp riate range.

F. PRESERVATIONS

None; measure dissolved oxygen immediately

G. PRECAUTIONS

1. Before using the probe, check the membrane for wrinkling or for bubbles in the solution underneath the membrane. If either condition exists, refill the probe with KCl solution and replace the membrane.

2. Avoid agitation of the sample (see step C).

H. QUALITY CONTROL

When possible, a Winkler titration shall be performed on a sample to check the meter's performance.

I. SPECIAL INSTRUCTIONS

1. Sluggish or erratic meter performance could indicate that the probe solution or membrane needs replacing.

2. The instrument shall be left on "ZERO" between measurements to avoid having to repolarize the probe.

J. REFERENCES

Instructions for YSI Model 54 Oxygen Meter

K. PROJECTS Intensive Surveys

11.6.5 Specific Conductance

A. SCOPE AND APPLICATION

This method is applicable to ground, surface, and saline waters, in addition to domestic and industrial wastes.

B. SUMMARY OF METHOD

- The specific conductance of a sample is measured by the use of a self-contained conductivity meter, Whetstone bridge-type, or equivalent.

- Samples are p referably analyzed at 25 °C. If not, temperature corrections must be made and the results reported at 25 °C.

C. TEST PROCEDURE

1. Follow instructions manual for the specific field conductivity meter used.

2. Check the meter with two standard solutions of approximate specific conductances of 100 and 1,000umhos/cm, or standards that bracket the expected sample conductance. If the meter does not read within one percent of the standards, determine what the problem is and correct it before proceeding. Most field instruments read conductivity directly; with those instruments, follow the manufacturer's instructions. Report the results to the nearest ten units for readings less than 1,000umhos/cm and the nearest 100 units for readings more than 1,000umhos/cm.

3. Record the actual sample temperature when the measurement is made. The meter reading shall be converted to specific conductance at 25 °C using the information in the manufacturer's instruction manual.

D. APPARATUS SECTION

- Beckman SoluBridge ® Model RB-5/RB-6
- YSI Model 3530 Flow Through Cell
- Hydrolab Corporation Surveyor II

E. PRECISION AND ACCURACY

These conductivity meters have an accuracy of ± 2% of reading. With satisfactory equipment, results within 1% of the true value shall be obtained.

F. REFERENCES

Standard Methods for the Examination of Water and Wastewater, 16th Edition, p. 76, Method 205 (1985).

Annual Book of ASTM Standards, Part 31, "Water," Standard D1125-64, P. 120.

Methods for Chemical Analysis of Water and Wastes, US-EPA, 120.1 (1983).

Instruction Manual, SoluBridge ® RB-5/RB-6, Beckman Instruments, Inc., Rev. January 1982.

Surveyor II Operating Manual, Hydrolab Corporation, Rev. A February 1985.

YSI Model 3560 Water Quality Monitoring System Instructions, July, 1988.

11.6.6 Free and Total Chlorine(Colorimetric Method)

A. EQUIPMENT

Hach Free and Total Chlorine Test Kit, Model CN-70

B. REAGENTS

1. DPD Total Chlorine Reagent Powder Pillows for 25ml Sample, Catalog No. 14064

2. DPD Free Chlorine Reagent Powder Pillows for 25ml Sample, Catalog No. 14070

C. COLLECTION

No special instructions are required for the collection of the samples.

D. FILTRATION None

E. PROCEDURE

1. Rinse the square mixing bottle thoroughly with the sample water. Fill the bottle to the 25ml mark.

2. Add the DPD free chlorine or DPD total chlorine powder pillow to the bottle. Swirl the bottle until most of the reagent has dissolved.

3. Fill one viewing tube to the 5ml mark with the prepared sample.

4. Hold the color comparator with the front facing you (Hach logo is visible). Insert the tube of the prepared sample into the top right opening of the comparator.

5. Fill the second viewing tube with an untreated water sample. Insert this tube into the top left opening.

6. Hold the comparator up to a light (sky, window, lamp) and view through the openings in the front. Rotate the disc to obtain a color match.

7. Read the mg/L free chlorine through the scale window within one minute of the addition of the powder.

F. PRESERVATION None

G. PRECAUTIONS

1. High concentrations of monochloramine shall interfere with the results of the free chlorine test. The free chlorine concentration must be read within one minute of adding the reagent.

2. This method is only acceptable for potable water. The spectrophotometric method needs to be used for wastewater or ambient samples due to the increase accuracy of this instrument. Regulation 40 CFR 136 (NPDES) does not allow the colorimetric method for regulatory purposes.

H. QUALITY CONTROL

Check the method against a laboratory spectrophotometer, or test laboratory-prepared chlorine standards.

I. SPECIAL INSTRUCTIONS

This procedure is applicable for free or total chlorine concentrations of 0 to 3.5mg/L. If a more accurate measurement of low concentrations (0.0-0.7mg/L) is desired, the following modifications to the procedure must be made:

1. Fill the viewing tubes (steps E3 and E5) to within 1/16 inch of the top. The tubes must be stoppered carefully to exclude air bubbles.

2. The lengthwise viewing adapter and tubes must be inserted as shown in the diagram below:

3. Divide the value read from the scale windows by 5 to obtain the mg/L free or total chlorine

J. REFERENCES

Instructions for Hach Free and Total Chlorine Test Kit, Model CN-70

K. PROJECTS Drinking Wat er