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USGS TECHNICAL PROCEDURE HP-91, R0

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Collection and Field Analysis of Surface-Water Samples

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1.0 PURPOSE.

- 1.1 To assure the accuracy, validity, and applicability of the methods used to describe the collection and analysis of surface-water samples, this procedure provides a guide for USGS personnel and contractors to perform the described activity. From this procedure, the Department of Energy (DOE) and the Nuclear Regulatory Commission (NRC) can evaluate these activities for meeting requirements of the NNWSI Project, and competent, trained personnel can reproduce the work.
- 1.2 This procedure describes the components of the work, the principles of the methods used, and their limits. It also describes the detailed methods to be used for calibration, operation and performance verification of any equipment. In addition, it defines the requirements for data acceptance, documentation, and control; and it provides a means of data traceability.

2.0 SCOPE OF COMPLIANCE.

- 2.1 This procedure applies to all USGS personnel and their contractors who may perform work referred to in Para. 1.1, or use data obtained from this procedure if it is deemed to potentially affect public health and safety as related to a nuclear waste repository.
- 2.2 All data derived from this procedure that are presented to support licensing of the NNWSI Project repository, and any equipment calibrations or recalibrations that may be required shall be in accordance with this technical procedure. Variations are allowed only if and when this procedure is formally revised, or otherwise modified, as described in Section 8.

- 3.0 PERSONNEL RESPONSIBILITIES. The Principal Investigator (PI) is responsible for assuring full compliance with this procedure. Per QMP-2.02 and QMP-2.03, the PI shall require that all personnel assigned to work under this procedure shall have the necessary technical training, experience, and personal skills, to adequately perform this procedure; and they shall have a working knowledge of the USGS QA Manual. Responsibilities of others including the reviewer(s), contributing investigators, Branch/NHP Chief, QA Office and the Chief, Branch of NNWSI are as described in Para. 4.3, QMP-5.01.

4.0 DETAILED PROCEDURE.

The investigation of Yucca Mountain as a proposed high level radioactive waste repository involves all aspects of hydrology. Determination of the

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chemical constituents in surface water is important to many of these hydrologic investigations as an initial boundary condition. Infiltration of surface water is the initial stage in the development of groundwater. The tracability, chemical constituent development, isotopic origins, apparent age, and other characteristics are important in understanding how the present groundwater environment developed. The accurate measurement of our present hydrologic environment is one of the tools available for reading the past and preparing for the future.

4.1 Objective: To describe collection and analysis techniques for surface-water samples.

4.2 Methods Used: Some properties or constituents in surface water may change significantly within a few minutes or hours after sample collection. Immediate analysis in the field for certain of these constituents is required if dependable results are to be obtained.

Other constituents may be stabilized by preservative treatment. These treatments include refrigeration, the addition of metals such as mercury to minimize chemical changes due to biologic activity, or the addition of acid to prevent the precipitation of metal ions.

The development of sophisticated portable field equipment allows for accurate and precise analysis of water for many unstable constituents or properties at the collection site.

Each technique described herein will provide a summary of the principle and a step-wise description of the methods. Equipment needed for each method is summarized in para 4.4.

#### 4.2.1 Filtration -

##### 4.2.1.1 Summary of Filtration Method for Large-Volume Samples

1. Apply label tape to sample bottles or use permanent marker. Write sample identifier, sample-type designation, and filter-pore size on label and in field notes. (Use SIF as described in QMP-8.01 for each sample.)

If a backflush filter and peristaltic pump are to be used, the following procedure applies.

- a. Disassemble backflush filter.
- b. Place selected filter.
- c. Reassemble filter.
- d. Attach intake tubing to intake fitting on top plate using small tubing clamp. (Unit may be stored after use by unscrewing intake fitting rather than disconnecting intake tubing).
- e. Attach approximately 30 cm of pump tubing (medical grade

silicon) to exhaust fitting on bottom plate using small tubing clamp.

- f. Attach tripod legs to backflush filter.
- g. Insert intake tubing in pump head and connect the pump head to the pump as directed in manufacturer's instructions.
- h. Connect pump to power supply.
- i. Connect intake tubing to sample source or insert tubing in unfiltered sample if direct connection is unavailable.
- j. Turn on pump and discard the initial several hundred milliliters of filtrate.

If nitrogen and a pressure filter system is to be used the following applies.

- a. Disassemble the filter assembly and install selected filter on support screen and reassemble filter assembly.
- b. Add sample to filter reservoir and secure filter top.
- c. Apply nitrogen pressure to sample reservoir and prepare to collect the filtrate. For most equipment maintain a nitrogen pressure under 40 p.s.i. If operator is unfamiliar with equipment or does not know the manufacturer recommendations, keep pressures under 20 p.s.i.
- d. Rinse sample bottle and cap three times with filter effluent and collect filtered sample from exhaust tube. Acidify or chill samples as required (see Table 1).
- e. Record porosity of filter used.
- f. After filtering is complete, unit should be disassembled and the filter removed, taking care that the lower screen is not contaminated by sediment caught on the membrane filter or upper screen.
- g. Thorough cleaning of the filter plate with deionized water is required after each sample.
- h. A clean membrane should be stored between the screens of the sandwich filter assembly to prevent contact of the soiled upper and clean lower screens. Interchange of upper and lower filter screens should be avoided. On pressure filters this procedure may not be necessary.

Note: This procedure is not exhaustive for valid filtration devices and procedures. The general steps for cleaning are similar for most filters although the assemblage may be different.

4.2.2 Sample Acidification - Ultra-pure nitric or hydrochloric acid is added to freshly collected samples in order to lower the pH to a value of 2.0 or less and thereby minimize oxidation, precipitation, and sorption of dissolved constituents. Acidification is required for samples to be analyzed for major cations and trace metals only (i.e. Ca, Mg, Na, K, Sr, Li, U, Fe, Mn, Al)(see Table 1).

#### 4.2.2.1 Summary of Sample Acidification Method

1. Collect several milliliters of filtered sample water before adding acid to sample.
2. Add approximately 2 ml of ultra-pure  $\text{HNO}_3$  or  $\text{HCl}$  for each liter of filtered sample collected to lower pH to 2.0 or less.
3. Label, store, and transport samples properly. Note information on label, field notes, and on SIF.

4.2.3 Hydrogen and Oxygen Isotopic Ratios - Different isotopic forms of water arising from the incorporation of naturally-formed deuterium ( $^2\text{H}$  or  $\text{D}$ ) and oxygen-18 into the  $\text{H}_2\text{O}$  molecule exhibit slightly different vapor pressures and freezing points. Because natural waters contain a mixture of isotopic forms ( $^1\text{H}_2$ ,  $^{16}\text{O}$ ,  $^1\text{H}^2\text{H}$ ,  $^{16}\text{O}$ ,  $^{16}\text{O}$ ,  $^1\text{H}^2\text{H}^{18}\text{O}$ ,  $^2\text{H}_2$ ,  $^{18}\text{O}$ , etc), the bulk of isotopic composition will change as a result of evaporation, condensation, freezing, melting, or chemical and biological reactions in a process known as isotopic fractionation. The effects of isotopic fractionation are such that strong regional trends are observed in the isotopic composition of natural precipitation. These regional isotopic trends can be correlated to latitude, altitude, distance inland, and season, so that the stable-oxygen and hydrogen-isotopic composition of shallow ground waters may be used to infer conditions at the time of recharge. In ground-water systems at higher temperatures, however, stable isotopic composition of water changes characteristically in response to exchange reactions with aquifer minerals, and no longer bears the isotopic ratio of the recharge water.

#### 4.2.3.1 Summary of Collection of Samples for Hydrogen/Oxygen Ratios

1. Apply label tape to 50-ml glass sample bottle, overlapping ends to ensure adhesion. Write sample identifier, sample-type designation and filter pore size (0.45 micron) on label, in field notes, and on SIF.
2. Filter sample and add  $^1\text{HqCl}_2$  tablet if laden with sediment or nutrients.
3. Rinse the sample bottle three times with sample water.
4. Fill the bottle to the shoulder with sample, leaving a small air space.

Table 1.--Summary of large-sample requirements

Determinations	Sample Size/ Container	Filter Pore Size	Preservation Procedure	Designation
Ca, Mg, Na, K, Li, Sr, Al, Fe, Mn, Si	500 ml/ polyethelene; polyseal cap	0.45, 0.10	Acid-rinsed sample bottle and cap; acidify with HNO <sub>3</sub>	filtered acidified
SO <sub>4</sub> <sup>4-</sup> , F, Cl, Br I, Si	500 ml/ polyethelene; polyseal cap	0.45, 0.10	---	filtered untreated
Alkalinity, pH	500 ml/ polyethelene; polyseal cap	unfiltered raw	---	Raw untreated
D/H, <sup>18</sup> O, <sup>16</sup> O	50 ml/glass; polyseal cap	0.45	HgCl <sub>2</sub> tablet; seecure cap w/ electrical tape or wax	DH, <sup>18</sup> O/ <sup>16</sup> O LC300/LC489
<sup>13</sup> C/ <sup>12</sup> C	1000 ml/glass; polyseal cap	filtered or unfiltered	Ammoniacal strontium chloride; secure cap w/ electrical tape or wax	<sup>13</sup> C/ <sup>12</sup> C, LC0440
<sup>3</sup> H	1000 ml/glass; polyseal cap	unfiltered	Secure cap w/ electrical tape or wax	LC0460 or LC1043
<sup>14</sup> C	55 gal/plastic- lined steel drum	unfiltered	Precipitate inorganic carbon; collect precipitate	<sup>14</sup> C, LC1199

5. Cap tightly with polyseal cap and wrap the top with electrical tape. If polyseal caps are unavailable, the cap may be sealed by wrapping with electrical tape and dipping the inverted bottle up to the shoulder in melted paraffin.
6. If the USGS Central Laboratory is to be used for sample analysis the following code numbers will be used to identify the analysis type.

Lab code numbers:  $^{18}\text{O}/^{16}\text{O}$  LC0489

D/H LC0300

4.2.4 Stable Carbon Isotopes - Water may contain a number of dissolved inorganic-carbon species including bicarbonate ( $\text{HCO}_3$ ), carbonate ( $\text{CO}_3$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), carbon dioxide ( $\text{CO}_2$ ), and others. Addition of ammoniacal strontium chloride reagent causes precipitation of the carbonate species, allowing for storage of the sample prior to analysis of the stable carbon isotopic composition of the sum of these species.

#### 4.2.4.1 Summary of Method for Stable Isotope Sample Collection

1. Apply label tape to sample bottle, overlapping ends to ensure adhesion. Write sample identifier and sample-type designation on label, in field notes, and on SIF.
2. Filter sample through a 0.45 micron filter as described in para 4.2.1 if the sample has a sign of sediment that contains carbonate.
3. Rinse each sample bottle and cap three times with sample water.
4. Fill each sample bottle to about 90% of capacity with sample water.
5. Rinse the 50-ml volumetric pipette with approximately 10 ml of ammoniacal strontium chloride solution and discard rinse.
6. Add 50-ml ammoniacal strontium chloride solution to each sample bottle.
7. Cap bottle tightly with polyseal cap. If polyseal caps are unavailable, the cap may be sealed by wrapping with electrical tape and dipping the inverted sample bottle up to the shoulder in melted paraffin.
8. Lab code number (see para 4.2.3.1 item 6) is LC0440.

4.2.5 Tritium Analysis - Prior to the advent of large atmospheric thermonuclear test in 1953, tritium ( $^3\text{H}$ ) was derived entirely from the natural process of nitrogen transmutation caused by the

bombardment of cosmic rays, resulting in concentrations on the order to 10 tritium units (TU; 1 TU = 1  $^3\text{H}$  atom in  $10^{18}$   $^1\text{H}$  atoms). Because tritium is a radioactive isotope with a half life of only 12.3 years, water recharged before 1953 should have tritium concentrations on the order to 2 to 4 TU. Waters recharged after 1953, however, can be expected to have tritium concentrations on the order of hundreds or thousands of TU. High tritium concentrations can therefore be used as an indicator of recently recharge modern water or as a tracer of mixing or leakage of such modern waters into older waters.

#### 4.2.5.1 Summary of Tritium Sample Collection

1. Apply label tape to sample bottles overlapping ends to ensure adhesion. Write sample identifier and sample-type designation on label, in field notes, and on the SIFs.
2. Allow sample to flow into bottle with as little disturbance as possible.
3. Rinse sample bottle and screw cap three times with unfiltered sample water.
4. Fill glass bottle to near top and note time, site, and date in the field book and on SIF.
5. Secure cap with electrical tape.
6. Lab code numbers (see para 4.2.3.1 item 6) are:

Lab code	Detection limit	Volume needed
452	20 pci	25 ml
460	2 pci	250 ml
881	15 pci	10 ml
1043	.2 pci	1000 ml

4.2.6 Carbon-14 - Prior to the advent of large thermonuclear tests in 1953,  $^{14}\text{C}$  in the global atmosphere was derived entirely from the natural process of nitrogen transmutation caused by bombardment of atmospheric nitrogen by cosmic rays. Oxidation of  $\text{CO}_2$  occurs quickly, followed by mixing with the atmospheric  $\text{CO}_2$  reservoir and incorporation in natural water systems as dissolved inorganic carbon. Because the radioactivity of  $^{14}\text{C}$  decreases characteristically with time, the apparent time that a ground water sample has been isolated from the atmosphere can be a readily calculated if the ground-water has not received carbon from other sources.

Collection of samples for radiocarbon analysis involves either the collection of a sample and the isolation from atmospheric  $\text{CO}_2$ , or the precipitation of the dissolved inorganic carbon present in a sample and subsequent collection of the precipitate with as little exposure to the atmosphere as possible.

#### 4.2.6.1 Summary of Method for Large-Volume Carbon-14 Sample

1. Before sampling, rinse drums thoroughly with tap water. Add approximately 20 gallons of tap water and 2 liters of 12N HCl to each drum. Remember, ALWAYS ADD ACID to water. Cap the drums and roll for several minutes to allow cleaning solution to contact all sides of the liner. Drain and properly dispose of the acid solution. Rinse drums with tap water for 10 minutes by inverting the drum and inserting a garden hose and spray head. If water pressure is not available, fill drums with approximately 20 gallons of tap water, roll, and drain; repeat this rinse three times. Drain tap water from barrels. Add 5 gallons of deionized water in each barrel, roll and drain.
2. Cap the large hole in drum securely. Insert open  $\text{N}_2$  gas line into the small hole and extend it to the bottom of the drum. Open the regulator to 20 psi and flush the drum with approximately 30 cubic feet of  $\text{N}_2$  (i.e. 270-psi change in tank pressure). Close regulator, remove  $\text{N}_2$  line and securely close drum.
3. Cover the end of the sampling-pump hose with a course cloth to eliminate sediment but still allow water to pass freely. Place suction end of the hose into the stream where the water is moving briskly. Extend discharge hose to the bottom of the drum to minimize aeration. Note time required to fill the drum and allow sample water to overflow the top of the drum for 1/2 that time. Remove hose and tightly cap the completely-filled drum. Repeat for the remaining drum.
4. Store drums indoors until the samples can be precipitated. If possible, begin precipitation within 24 hours.
5. Fill the precipitator with clean tap water. While stirring, add 12N HCl (reagent grade, concentrated HCl) until the pH of the solution drops below 2 when measured 5 minutes after the last addition of acid. Stir ten minutes more and drain.
6. Rinse precipitator thoroughly with tap water and allow to drain for 5 minutes. Repeat tap-water rinse.
7. Rinse a third time with 5 gallons of deionized water. Allow to drain for 5 minutes.

8. Firmly screw an empty Mason jar into the bottom of the precipitator and fully open the butterfly valve.
9. Close all top ports, leaving only the lower sample spigot open slightly. Allow approximately 40 cubic feet of  $N_2$  to enter the precipitator through the quick-connect fitting (40 cu. ft. = 360 psi change in pressure). Close the sample spigot after  $N_2$  flushing.
10. Remove bungs from one barrel of sample water and replace with garden hose and pressure line fittings. The garden hose should not extend to the bottom. This eliminates the removal of any sediment that has settled. Connect pressure line to  $N_2$  regulator and garden hose to the top of the precipitator. Set  $N_2$  regulator to 10 psi to fill precipitator with sample. When sample has been removed from the drum, disconnect the hose at the precipitator and plug the hose fitting on the precipitator. Close the  $N_2$  regulator.
11. Disconnect the  $N_2$  line from the drum and connect to the top of the precipitator. Open the regulator and adjust to minimum flow. Turn on the precipitator stirrer.
12. Add 2 liters of  $BaCl_2/LaCl_3$  reagent.
13. Turn on heater.
14. Add NaOH reagent in 5-ml increments 10 minutes apart through a separatory funnel until the pH of the sample reaches 10. Measure pH using a pH meter calibrated with pH 7 and pH 10 buffers. Draw a 100- to 200-ml sample aliquot from the spigot and the bottom of the precipitator and discard. Collect 50-ml of sample water from the spigot for pH measurement between additions of NaOH reagent.
15. Allow approximately four hours for the precipitator temperature to reach  $70-80^{\circ}C$ . The precipitator will automatically maintain this temperature once reached.
16. Turn off the stirrer, allowing precipitate to settle for approximately one hour. Tap the sides of the precipitator with a mallet or hand to release any clinging precipitate.
17. Turn on the stirrer for no more than 3 seconds and allow precipitate to settle for an additional half hour.
18. Close the butterfly valve. Remove the collection jar, cap tightly, and label with sample identifier and sample-type designation. Complete a SIF for each sample. Lab code: LC1199.
19. Drain precipitator and repeat steps 8-18 for second barrel of sample water.

20. Clean precipitator and return it to its storage area. Store and maintain in clean condition.

#### 4.2.7 Temperature Analyses

4.2.7.1 Summary of Method - Immerse thermometer or thermocouple in the flow (to the immersion-depth mark if applicable) and read directly after time for equilibration. Record time and temperature in field notes after each reading. Continue measurements until 2 consecutive readings are identical ( $\pm 0.5^{\circ}\text{C}$ ).

Calibration is done by comparison to a NBS thermometer as required by NNWSI-USGS-QMP-12.5.3. The field instrument shall agree with the NBS calibrated thermometer within  $\pm 0.25^{\circ}\text{C}$ . The instrument is compared at two different temperatures which bracket the temperature range normally measured in the field. Calibration should be done annually or before if the instrument is suspected of misuse, damage, erratic or erroneous readings.

4.2.8 Specific Conductance - The specific conductance of a water sample is a measure of its ability to carry an electrical current, and is an indication of the concentration of dissolved solids in the water.

The ability of a solution to conduct an electrical current is a function of the concentration and charge of the ions in solution and of the rate at which the ions can move under the influence of an electrical potential. As the number of ions per unit volume of solution increases, the rate at which individual ions can move decreases because of inter-ionic attraction and other effects. A graph of total ion concentration versus specific conductance, even for solutions of a single salt, is a straight line only for values below 1,000 micromhos/cm. As specific conductance increases to above 5,000 micromhos/cm, the specific conductance may be only an approximate index of ion concentration. The temperature of the electrolyte also affects the ionic velocities and, consequently, the specific conductance.

Specific-conductance meters used in the field should be battery operated, properly calibrated, equipped with temperature compensator for at least one of the scales, and should read directly in microsiemens/cm<sup>2</sup> or micromhos/cm<sup>2</sup> at 25°C when possible. The direct-reading meter is recommended to save time in converting resistance values to specific conductance and to ensure that the value is read in the field. This procedure is meant to supplement the manufacturer's instructions for the Tab-line Lectro Mko-Meter which is the commonly used meter at present.

##### 4.2.8.1 Summary of Specific Conductance Method

###### 1. Calibration

- a. To check the calibration and operation of this instrument, turn the range selector to "test". Note

that a balance occurs precisely at central scale division 1.0 when the "Press" button is depressed. With the cell disconnected and range selector on any measuring scale, check to see that the balance indicator shows full-scale deflection when the "Press" button is depressed. Partial deflection or indecisive balance indicates that the battery should be replaced. Use only an "EverReady" type 266, 9-volt Battery, or equivalent.

- b. To check the linearity of the conductance cell, use two standards that bracket the anticipated sample conductivity. Measure each standard as described in step 2a below. If the measured conductance of the standards are within 5% of the known value proceed with sample measurement. For variance greater than 5%, recalibrate, loosen the allen screw in the center scale and adjust to the correct value.
- c. Calibration and linearity are very stable for the Tab-line Lectro Mho-meter. The procedures mentioned in steps a above are necessary at the beginning of a field trip or laboratory session. Step b should be checked every 6 months.

## 2. Measurements

- a. Rinse the measuring cell three times with the water to be measured. Fill the measuring cell with fresh sample or standard and plug cable into the "measuring cell" socket. Allow the temperature to stabilize and then set the temperature dial to the temperature of the sample if using the temperature-compensated scale. Record the sample temperature and remove the thermometer from the measuring cell. Set the meter temperature dial to the sample temperature. Remember only the  $10^3$  scale is temperature compensated. Hold the "Press" button down and rotate the measuring dial until the balance indicator moves to center scale. Read the dial setting and multiply by the range factor and cell constant. The result is the specific conductance of the sample in microsiemens/cm<sup>2</sup> at 25°C only if the temperature compensated scale ( $10^3$ ) is used.
- b. Record temperature, time, date, cell constant, range factor, and location.

4.2.9 pH - The pH of a solution is a measure of hydrogen-ion activity or moles accurately, and is the negative logarithm of the hydrogen-ion activity in moles per liter:

$$\text{pH} = -\log [a^{\text{H}^+}]$$

In aqueous solutions, pH is controlled by reactions that produce or consume H<sup>+</sup>, including practically all dissolution and hydrolysis

reactions. The primary control over pH in most potable natural water is the carbonate ion, although other dissolved species, such as hydrogen sulfide and ammonia, can also affect the pH.

The pH is determined with a glass hydrogen-ion membrane electrode compared against a reference electrode of known potential by means of pH meter or other potential-measuring device with a very high input impedance. Because pH is exponentially related to concentration, great care must be exercised in making a measurement.

A high sodium content will give an anomalous pH reading, which must be corrected according to the recommendation of the manufacturer of the pH electrode. Measurement of pH is temperature sensitive, so the standard buffers should be within  $\pm 2.5^{\circ}\text{C}$  of the sample solution for precise determinations.

#### 4.2.9.1 Summary of the pH Method

##### 1. Calibration

- a. Check and fill the combination electrode with internal filling solution recommended by the manufacturer. Be sure the cover for the filling hole is off during measurements and returned after measurement.
- b. Select two buffer solutions bracketing the expected pH of the water sample. Adjust the buffer solutions to near the sample temperature.
- c. Set up and level the pH meter and check to insure that the needle is properly adjusted to 7.00 when in stand by.
- d. Rinse electrode surface with deionized water.
- e. Place the near 7.0 pH buffer in a beaker and place the electrode into the buffer. Set the temperature dial to the temperature of the buffer and set the slope bezel at 100%.
- f. Turn the meter to "pH" and adjust the calibration knob so that the meter reads the pH value of the buffer. The pH of the buffer solution varies with temperature, so it is necessary to refer to the temperature-pH curve supplied with the buffer in order to determine the actual pH at the operating temperature. Record the theoretical pH of the buffers used, in field notes. If the electrode has not been used recently, or has been allowed to dry for several days, it may take 10-20 minutes or longer for the reading to stabilize. (Electrodes should always be hydrated for at least 24 hours before use. If the electrode will not stabilize, use a new pH electrode. To keep the electrode from drying and ready for use, the electrode tip should be

immersed in a rubber or plastic sack in which a few milliliters of deionized water with a few drops of filling solution and pH 6.86 buffer have been added).

- g. Turn the meter to the standby position and remove the electrode from the lower-pH buffer. Remember to always have the meter on standby when the probe is out of fluid, otherwise the electrode can be easily polarized.
- h. Rinse the electrode thoroughly with deionized water.
- i. Place the electrode into the 4 or 10 pH buffer, bracketing the expected pH of the sample.
- j. Switch on the meter and allow several minutes for stabilization before making the final adjustments.
- k. Make any final adjustments necessary by turning the temperature (slope) knob, then turn slope bezel so that the temperature now indicates the actual temperature of the buffer.
- l. Turn the meter to the standby position.
- m. Check the adherence of the response of the electrode to the theoretical Nernst slope. On the Orion meter this is the percent slope value read off the slope bezel. To check the response on other meters you must measure the potential of each buffer and calculate the actual slope using the Nernst equation.
- n. If the observed percent slope value is less than 90% on the slope bezel, the electrode may be defective. Any measurement problems should be noted and the electrode replaced as soon as possible.
- o. Rinse the electrode with distilled water and then with the 7-pH buffer solution. Recheck the value of the 7-pH buffer by placing the electrode in the buffer solution and switching on the meter. If drift from the original setting has occurred, repeat steps d-o.

## 2. Measurement

- a. If sufficient sample is available, rinse the electrode with sample water and place it in a fresh sample aliquot that has been collected in a beaker. Be sure the nylon junction tip or the ground glass junction port is below the water level in the flask.
- b. Turn on the meter.

- c. Allow one minute for equilibration without stirring. Record the time and record the pH value to the nearest 0.02 unit.
- d. Turn meter to standby position.
- e. Thoroughly rinse electrode system with deionized water.

### 3. Check for Electrode Drift

- a. Immediately after completing the sample measurements, rinse the electrode with the 7-pH buffer, insert the electrode into the temperature-equilibrated buffer, and wait for equilibration as described in step 2c. Record the value. Thoroughly rinse the electrode with deionized water, then with a small amount of the second buffer.
- b. Place the electrode in the second buffer, turn on the meter, wait for equilibrium, and record the value.
- c. If the buffers are reading more than  $\pm 0.10$  pH units different from the value the manufacturer's temperature curve, drift has occurred during the measurement. If the cause of the drift can be identified in the system, it should be rectified (for example, replace the electrode if it will not yield a stable buffer reading), and the measurement repeated. If the cause can not be pinpointed (for example, external temperature fluctuation causing different electronic response) the measurement can be corrected for the amount of drift that has occurred. The corrected reading is simply the measurement reading changed proportionately to reflect the drift of the two buffer readings and weighted to reflect the nearness of the measurement reading to both of the standardization points.

If during readings, a static charge builds on the plastic pH-meter face causing erratic meter movement, antistatic spray may be sprayed on the meter face to minimize interference. Keep the meter protected from extreme temperature change during measurements, as this will affect the stability of the electronic system and consequently the accuracy of the measurement.

**4.2.10 Carbonate and Bicarbonate Alkalinity** - For chemical-equilibrium calculations related to carbonate minerals it is essential to have an accurate value for pH, carbonate, and bicarbonate concentrations.

The carbonate ( $\text{CO}_3$ ) and bicarbonate ( $\text{HCO}_3$ ) concentrations are determined by potentiometric titration of the water sample with a standard solution of sulfuric acid.

The reactions involved are:

1.  $\text{CO}_3^{-2} + \text{H}^+ = \text{HCO}_3^-$  (This reaction is complete near pH 8.3).
2.  $\text{HCO}_3^- + \text{H}^+ = \text{H}_2\text{CO}_3$  (This reaction is complete near pH 4.5).

The end point of the bicarbonate titration process is graphically determined from either a plot of pH versus titrant volume, where the end point corresponds to an inflection point of the curve (Figure 1a), or a plot of the rate of change in pH per unit volume between two successive values (i.e. pH/ml of titrant, Figure 1b). The end point is the value at which the maximum rate of change of pH per volume of titrant added occurs. The latter approach is less subjective and permits a consistent choice of the end point, but requires exacting analytical procedures. The assurance of complete equilibrium of pH after each increment of acid added is required for both methods.

Salts of weak organic and inorganic acids, such as silica, may yield erroneous results when present in large amounts. In addition, oils, greases, and colloidal material if present, may tend to foul the pH electrode and prevent its proper operation.

#### 4.2.10.1 Alkalinity Method Summary

1. Let sample temperature stabilize with surrounding air temperature. Note if outgassing is occurring.
2. Calibrate pH electrode in 7.41 and 4.01 buffer solutions as specified in para 4.2.9.1 (pH determination). Buffers should be at sample temperature.
3. Rinse electrodes with sample water if sufficient sample is available.
4. Insert the clean, dry stirring bar and adjust the stirrer to slow speed.
5. Insert the pH electrode into the sample in the 100-ml beaker as per para 4.2.9.1 (pH determinations).

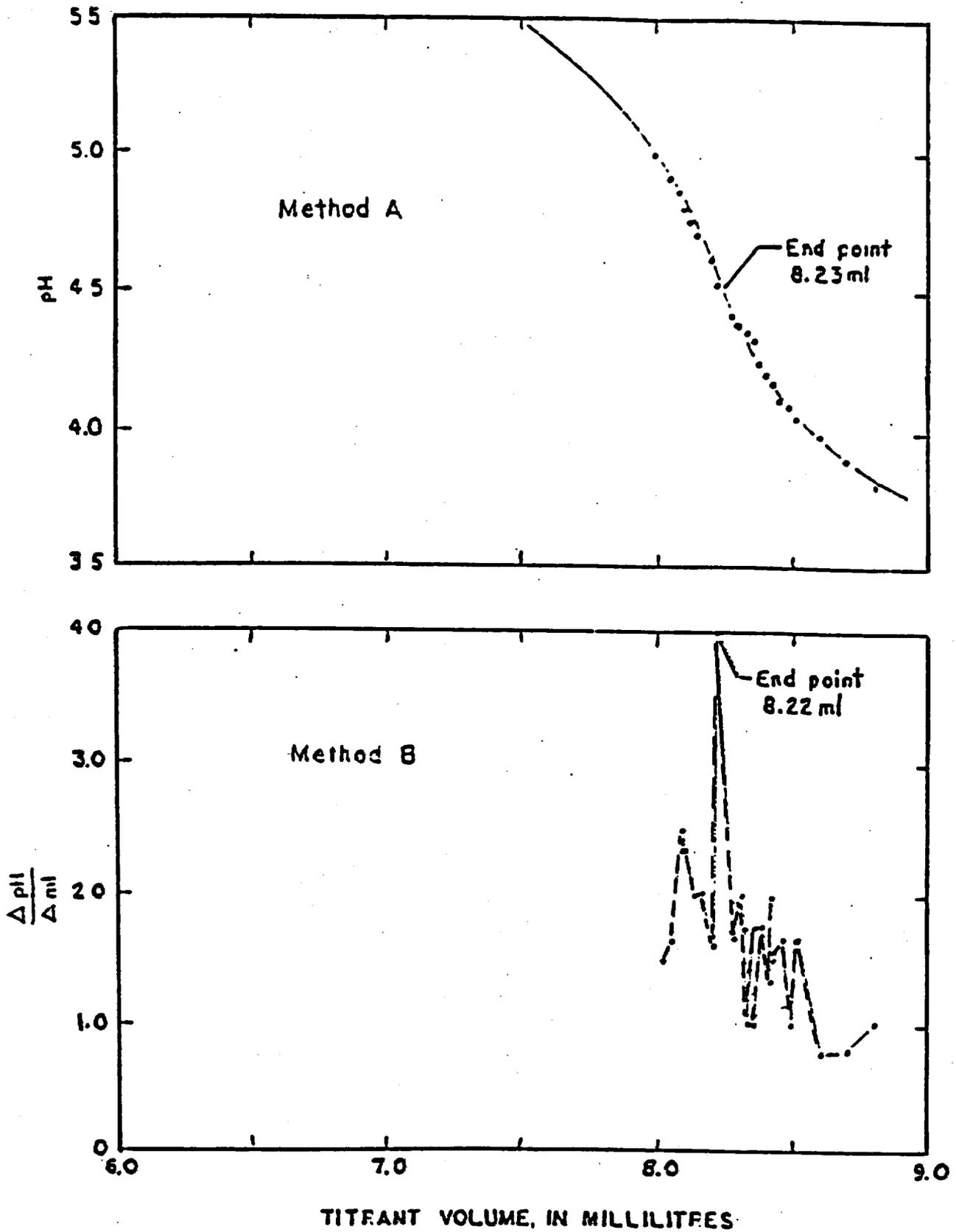


Figure 1.--Methods of determining the end point for alkalinity titrations.

6. If pH is greater than 8.3, add sulfuric-acid titrant by drops. Record titrant volume and pH value after turning off stirrer between each addition of acid. Record data as follows:

pH	Buret	Volume	$\Delta$ pH <sup>1</sup>
	level (ml)	of titrant (ml)	$\Delta$ vol. titrant
7.87	0.18	0.00	-
7.46	1.83	1.65	-0.25

- $\Delta$  pH is the change in pH between aliquots.
- $\Delta$  volume is the change in volume of titrant between aliquots.

7. When the pH of the sample decreases below 8.00, continue to slowly add acid until pH decreases to approximately 5.5. Record pH and amount of acid added. Subsequent titrant addition might be as large as 0.1 ml but should be decreased to single drops as pH decreases below 5.0 and the end point is approached. Be careful to get the 1st drops on the buret tip into the sample after each addition.

Remember, with each addition of titrant turn off the stirrer. Take the pH reading after another pre-determined time interval. This is to eliminate the streaming potential caused by protons (H<sup>+</sup>) moving past the electrode tip during stirring. Acid additions should continue until pH is less than 4 or until the maximum rate change has been observed.

#### 4.2.10.2 Calculations

- Calculate the carbonate content (if initial pH is greater than 8.3):

$$\text{CO}_3^{-2} \text{ (in mg/L)} = (\text{ml acid to end point near pH 8.3})$$

2. Calculate the bicarbonate content:

$$\text{HCO}_3^{-1} \text{ (in mg/L)} = \frac{\text{(ml acid between end point near pH 8.3 and pH 4.5)} - \text{(ml acid to pH 8.3)}}{\text{ml(s)}}$$

Where:

ml(s) = sample volume

ml(a) = volume of standard 0.01639 N sulfuric acid.

End point is determined as in Figure 1.

4.3 Alternative Method(s) Considered: Similar, but slightly different procedures could be used to produce approximately the same results. However, the methods described herein represent standard USGS procedures and fulfill the requirements of the project.

4.4 Materials/Equipment Required: A copy of HP-91, R0 is required for performing all work described herein.

4.4.1 Filtration - Equipment Needed For Large-Volume Sample:

- o Geotech (#0800) 142-mm backflush filter, or equivalent.
- o Geotech Series I (#0740) or Series II (#0760) 115-V AC, or C-12V DC peristaltic pump, or equivalent.
- o Power supply - 12V DC storage battery or 115V AC outlet.
- o Schleidner & Schuell membrane filters (or equivalent):
  - 142-mm 0.45 nitrocellulos (#BA85)
  - 142-mm 0.10 nitrocellulos (#PH79)
  - 142-mm glass fiber prefilter (#25)
- o Small tubing clamps
- o Four acid-rinsed polyethelene 500-ml sample bottles and one acid-rinsed 250-ml sample bottle with polyseal or polypropylene caps. Acid-rinsed bottles are available from the Central Laboratory. They are designated as acid rinsed when they have red caps. If not available, rinse twice regular polyethelene bottle and cap with double-distilled reagent-grade nitric acid.
- o Deionized water.
- o Label tape.
- o Permanent marker.
- o Ice chest filled with ice (if preserving sample by cooling rather than acidification.)

- o 500-ml wash bottle filled with deionized water.

#### 4.4.2 Hydrogen & Oxygen Isotopic Ratios Equipment Needed

- o 50-ml glass sample bottle with polyseal cap.
- o  $\text{HgCl}_2$  tablets - 10 mg  $\text{HgCl}_2$  in a NaCl base (available from Centfal Laboratory).
- o Label tape.
- o Permanent marker.
- o Filtration equipment as noted in para 4.2.1, filtration.

#### 4.4.3 Stable Carbon Isotopes Equipment Needed

- o One-liter glass sample bottle with polyseal cap.
- o A 50-ml volumetric pipet and pipet bulb and 50-ml capacity plastic syringe may also be used. Attach approximately 15 cm of Tygon tubing to tip.
- o Filtration equipment as described in para 4.2.1.
- o Ammoniacal strontium chloride hexahydrate solution:  
Dissolve 450 g of reagent grade  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  in 1800 g of concentrated reagent grade  $\text{NH}_4\text{OH}$ . The volume can be calculated by dividing 1800 g by the density. Allow the solution to remain undisturbed for 2 days. Decant the clear solution into glass field-reagent bottles and seal tightly. Solution is stable for several years as long as it is kept tightly sealed thereby preventing contamination with atmospheric  $\text{CO}_2$ .

- o Label tape.
- o Permanent marker.

#### 4.4.4 Tritium Analyses Equipment Needed

- o Two 250-ml glass sample bottles with polyseal caps.
- o Black plastic electrical tape.
- o Label tape.
- o Permanent marker.

#### 4.4.5 Carbon 14 Analyses Equipment Needed for Large-Volume Sample

- o 2 plastic-lined 55-gallon drums.

- o C-14 precipitator and connecting hoses.
- o pH meter and combination electrode.
- o pH 7 and pH 10 buffers.
- o 50-ml glass beakers
- o 2 small-mouth glass Ball or Mason jars.
- o Pump, 12V battery-operated or gasoline-powered, and hose.
- o 8 liters of 12N HCl (reagent-grade concentrated HCl)
- o Deionized water.
- o Garden hose, with spray head; if possible, water supply.
- o Nitrogen gas tank with two-stage regulator and connecting hoses.
- o Barium chloride/lanthanum chloride reagent (two 2-liter aliquots required per sample): Boil for ten minutes enough deionized water to make the desired amount of solution. Add 580 g of reagent-grade  $BaCl_2$  and 10 g of reagent-grade  $LaCl_3$  to a polyethylene bottle for each 2-liter aliquot desired. Pour 2 liters of boiling, deionized water into each bottle and cap the container to provide an airtight seal. Shake to dissolve salts. NOTE: Prepare only enough solution for several days' use.
- o Sodium hydroxide reagent (500 ml is sufficient for approximately three samples): Boil for ten minutes enough deionized water to yield 500 ml. Pour boiling water into a pyrex container, seal and cool. Place a magnetic stir bar in the container, and add 200 g of reagent grade NaOH pellets in 5-g increments, stirring until each 5-g addition has dissolved. Store in an air-tight bottle. NOTE: If NaOH pellets appear glossy and adhere firmly to each other, discard and use fresh pellets. Mix fresh solution monthly.

#### 4.4.6 Temperature Analyses Equipment Needed

- o Calibrated, partial-immersion thermometer graduated in  $0.5^{\circ}C$  or  $1.0^{\circ}F$  with the range of  $0-50^{\circ}C$ . Partial-immersion thermometer should have etched line indicating depth of immersion to be used. The thermometer should be accurate to  $\pm 0.5^{\circ}C$  as checked against a NBS calibrated thermometer.

A thermocouple calibrated over the range  $0-50^{\circ}C$  or expected used to an accuracy of  $\pm 0.5^{\circ}C$  as checked against a NBS calibrated thermometer is also acceptable.

#### 4.4.7 Specific Conductance Analyses Equipment Needed

- o Lab-line Lectro Mho-Meter with the cell constants of 0.1 and 1.0, or an equivalent direct-reading meter.
- o Calibrated thermometer, 0-50<sup>0</sup> graduated in 1.0<sup>0</sup>C.
- o Two reference-calibration standards with conductivities bracketing the expected sample values.

#### 4.4.8 pH Analyses Equipment Needed

- o Orion 399 A/F or 407AF pH meter or equivalent. An expandable scale is not necessary for surface water work.
- o Orion-Ross combination pH electrode or equivalent. Spare electrodes desirable.
- o pH buffer solutions 4.01, 6.86, 7.41, 9.18, and 10.4 in 100-ml containers. (Buffers should be prepared fresh regularly by dissolving Fisher Scientific Dry Buffer Salts in deionized water and diluting to 1 liter in a volumetric flask, or equivalent available commercially prepared standards.)
- o Filling solution for reference electrode.
- o Calibrated thermometer.
- o Deionized water.
- o Plastic squeeze wash bottle for deionized water.
- o Small box of Kimwipes or equivalent.
- o Four small beakers or plastic bottles.

#### 4.4.9 Carbonate and Bicarbonate Alkalinity Analyses Equipment Needed

- o All equipment and reagents used for pH determinations, para 4.2.9.1.
- o Buret, 25-ml or 50-ml capacity with 0.1-ml graduation and Teflon stop cock. Schellback burets are helpful for field conditions.

4.5 Assumptions Affecting the Procedure: The quality of the results is dependent on the quality of the work performed. Assumptions inherent in the methods are described in the individual method summaries.

4.6 Data Information: Data generated by this procedure includes values for temperature, specific conductance, pH, carbonate, and

bicarbonate. Data type and form are described in each method.

4.6.1 Quantitative/Qualitative Criteria: The uniqueness of surface-water measurements to the location and environmental conditions negate the ability to predetermine results. If previous work has been done at the site of measurement these results can be used to judge if current results are reasonable but should not be considered as absolute limits.

Proper completion of SIF's field notebooks and/or data sheets represent qualitative criteria by which proper implementation of this procedure may be evaluated.

4.7 Limitations: Accuracy requirements for each measured parameter are listed in the individual methods sections.

4.7.1

Method	Accuracy	Limits/Range
Filtration	NA	pressure 20 psi
Acidification	NA	2ml/liter
Isotopic Ratios	NA	NA
Carbon Isotopes	NA	NA
Tritium Analysis	NA	NA
Carbon-14	NA	NA
Temperature Analysis	NA	NA
Specific Conductance	5%	1 to 1,000,000 s/cm <sup>2</sup>
pH	+0.05	0 to 14 pH units
Alkalinity	check reference section 9.0	

4.8 Other: None.

5.0 CALIBRATION REQUIREMENTS. Calibration is required as a part of this technical procedure. When calibrations are required, all instruments and methods when applicable, will be calibrated in compliance with the Instrument Calibration Procedure (NNWSI-USGS-QMP-12.01) prior to obtaining data that will be cited to support licensing the NNWSI Project.

5.1 Calibration Responsibility: The PI is responsible for calibrations required by this procedure. Calibration will be in accordance with procedures described or referenced in Para. 5.2. Maintenance of all calibration records described in Para. 5.3 may be done by a contributing investigator under the direct supervision of the PI.

5.2 Calibration Procedure: The following instruments require calibration: temperature measuring instruments, Lab-line Lectro Mho-meter, Orion 399 A/F pH meter (or equivalent).

5.2.1 Calibration of the Lab-line Lectro Mho-meter is described in Para 4.2.8.1; Orion pH meter is described in para 4.2.9.1. Calibration of temperature measuring instruments is described in Para 4.2.7.1.

- 5.3 Calibration Records: Calibration data will be entered in a notebook or other organized documentation. A field notebook will be used if the test equipment is used in the field. These notebooks or other documents shall be maintained as described in the Document Control Procedure (NNWSI-USGS-QMP-6.01) and stored in accordance with the QA Records Management Procedure (NNWSI-USGS-QMP-17.01). Minimum data will include instrument type, its identification and location, calibration procedure used, its date, the standard used, its range and accuracy, recalibration due date, responsible division subunit, any pertinent observations and the name of the person calibrating the instrument. Calibration entries shall be signed and dated by the person performing the calibration and filed with the QA Office.
- 5.4 Labeling of Equipment Calibration Status: In compliance with NNWSI-USGS-QMP-12.01, a sticker will be affixed to each piece of equipment used in this procedure denoting the calibration status according to one of the following three categories:
- a) Equipment identification, date calibrated, date recalibration is due, procedure number and calibrator;
  - b) Equipment identification, "OPERATOR TO CALIBRATE", and the procedure number; or
  - c) Equipment identification and "NO CALIBRATION REQUIRED".
- 6.0 IDENTIFICATION AND CONTROL OF SAMPLES. Samples will be collected as part of this procedure.
- 6.1 Sample Identification: As part of the data records and documentation, and in compliance with QMP-8.01, all samples will be identified as follows: As described in method summaries and using a SIF for each collected sample.
- 6.2 Control and Storage: In compliance with QMP-8.01, the collected and identified samples shall reside in the custody of the Project Chief who shall store them at the Denver Federal Center or Nevada Test Site.
- 6.3 Special Treatment: Is described in each procedure and summarized in Table 1.
- 7.0 QUALITY ASSURANCE RECORDS. All information collected and recorded under this procedure that is to be used in support of the NNWSI Project licensing process is required to be a part of the official USGS record. Input needed to process the information as a record includes: title or description, subject, originator, date of the document, and whether it is an original, a revision or an addendum.
- Specific items from this procedure that will constitute a record are all SIFs, field notebooks, data sheets, instrument calibration records.
- 7.1 Notebooks or other organized documentation will be prepared as appropriate by the PI or a contributing investigator to record data

from this procedure and shall include any information considered by the originator to be pertinent. When data are kept in loose-leaf form, each page will be numbered consecutively and chronologically. All documents will be signed or initialed and dated by the investigator on a daily basis when entries are made. Any revisions will be lined out, initialed, and dated.

7.2 All data collected and the applicability of methods used in this procedure will be reviewed and cosigned by a peer or supervisor of the investigator knowledgeable with the objectives of this procedure in accordance with NNWSI-USGS-QMP-6.01, Para. 4.2.2; and as such are acknowledged by both the investigator and the reviewer to be acceptable and meaningful data that meet appropriate quantitative and qualitative acceptance criteria. Unacceptable data shall be identified appropriate to the form of the data.

8.0 MODIFICATIONS. When field modifications become necessary, per Para. 4.8, QMP-5.01, the PI shall fully document the changes, submit the documentation for the same review signature and distribution process as for the original procedure, and indicate whether the change should result in a subsequent revision to the technical procedure. The documentation will be reviewed within 30 days.

9.0 REFERENCES CITED.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., Duncan, S. S., 1979, Methods for determination of inorganic substances in water and fluvial sediments, U. S. Geological Survey, Techniques of water-resources investigations of the United States Geological Survey, 626 p.

10.0 ATTACHMENTS. There are no attachments for this technical procedure.

11.0 **APPROVAL.** This technical procedure shall become effective upon its approval as noted by completion of all the following signatures and dates.

Patrick W. McKinley  
Prepared by: P. W. McKinley

30 March 1987  
Date

F. Eugene Rush  
Technical Reviewer: F. E. Rush

Aug. 27, 1987  
Date

K. W. Causseaux  
NHP QA Coordinator: K. W. Causseaux

Sept 28, 1987  
Date

W. E. Wilson  
NHP Chief: W. E. Wilson

9-30-87  
Date

L. R. Hayes  
Chief, Branch of NNWSI: L. R. Hayes

9/30/87  
Date

J. R. Willmon  
Quality Assurance: J. R. Willmon

10/7/87  
Date