

A Field Manual for Groundwater Sampling

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ABSTRACT

This document aims at standardizing the procedures for groundwater quality sampling at the Texas Water Development Board. It explains sample collection and chemical characterization procedures to be followed during any field sampling event by TWDB personnel or any other authorized party or agent. The sampling techniques presented are a blend of those used in the reference and may be revised as needs change or if better methods and procedures are developed. This manual supersedes all previous editions of TWDB groundwater sampling procedures.

INTRODUCTION

Groundwater sampling is done for a variety of purposes, including meeting regulatory requirements; waste disposal site monitoring; ambient groundwater quality monitoring; research; and general bacteriological and chemical quality monitoring. Each of these different objectives can result in a different set of protocols for sampling. This document is mainly focused on ambient and regional groundwater quality monitoring and describes the procedures for sampling from the well site to delivery at the laboratory.

TWDB's ambient groundwater quality sampling program is designed to monitor the quality of groundwater in the State's aquifers. Major and minor aquifers in Texas are monitored for groundwater quality on a 4-year cycle. The purpose of TWDB's groundwater quality sampling program is: 1) to monitor changes, if any, in the quality of groundwater over time; and 2) to establish, as accurately as possible, the baseline quality of groundwater occurring naturally in the State's aquifers. TWDB field personnel gather water quality data directly in accordance with procedures established in this Field Manual

for Groundwater Sampling. Additional data sources are the supplemental samples analyzed locally on TWDB's own Hach instruments, and samples collected and analyzed by other entities such as the Groundwater Conservation Districts, USGS, and other State and Federal Agencies.

In addition to its monitoring program, the TWDB also conducts water-quality evaluations as part of its groundwater studies, Priority Groundwater Management Area evaluations, well development control activities, cooperative agreements with other entities (such as Texas Alliance of Groundwater Districts), short term studies, and responses to public inquiries. In time, the combination of these programs will provide water-quality data on all groundwater sources of Texas. Field and analytical water-quality data are processed and stored by state well number, date of collection, and STORET code in the Board's groundwater database. Indicators of sample reliability, collecting entity, and analytical laboratory are also stored along with sample results. The data are available online at <http://wiiddev.twdb.state.tx.us/>, while TWDB's Map and File Room holds the data in hard-copy format.

The main aspects of groundwater sampling covered by this manual are:

1. Initial planning of a groundwater sampling trip
2. Well purging procedures
3. Determination of groundwater field parameters (temperature, specific conductance, pH, alkalinity, oxidation/reduction potential, and dissolved oxygen)

4. Recording of field data
5. Filtering of groundwater samples
6. Routine sampling procedures
7. Completing the chain of custody record and transport of sample to the laboratory
8. Health and safety issues.

INITIAL TRIP PLANNING AND PREPARATION

Careful planning and preparation of a groundwater-sampling trip can save time and help reduce the number of difficulties that commonly occur with fieldwork. The following are brief suggestions for things to consider before going on a groundwater sampling field trip. More details are provided in the following chapters.

1. Check with the Groundwater Conservation District(s) with jurisdiction over the area you will be sampling, and inform them about your fieldwork plans
2. By making combined use of the Groundwater Database and water quality fieldbooks and maps, decide which sites you will be sampling
3. Call well owners to inform them of what you are doing and to arrange access and a time for sampling
4. Organize and review well schedules, maps and location sketches, any past water-quality analyses, and field data sheets for the wells to be sampled

5. Fill out as much paperwork as possible before you leave, including chain of custody, field data sheets, and shipping forms - if appropriate. Carry a few business cards.

Correct sampling procedure begins with thorough preparation in the office and laboratory before sample collection. Each sample bottle is to be thoroughly cleaned and protected from any contamination during sample collection, preservation, and shipment to assure a high quality sample. If contamination is suspected, the contaminated sample should be discarded and not submitted to the laboratory. Filtering equipment is to be rinsed thoroughly to remove any mineral deposits in hoses or support container vessels. The sample containers and hoses for organic analyses are to be acid-washed and rinsed several times with deionized water. Glass jar sample containers for organic analyses are to be washed with methylene chloride/hexane, followed by an adequate laboratory detergent wash, and rinsed several times with deionized water. The rinsed bottles are to be air dried under the lab exhaust hood.

The next step is to select the wells to be sampled. The following information should be carefully researched:

1. Aquifer(s) or area
2. Well type
3. Water use
4. Study criteria
5. Previous work in the area and WQ data collected
6. Monthly, seasonal, or annual sampling schedule
7. Hydrogeologic characteristics.

Drilling history:

1. Well depth and diameter
2. Well stimulation program, acids used, final permeability, and yields realized
3. Drilling and geophysical logs
4. Well workovers – method and fluid type.

Well-completion data:

1. Casing sizes and depths
2. Casing material(s)
3. Cemented or grouted intervals and the type and chemical composition of the materials used
4. Plugs, stabilizers, etc., in casing
5. Gravel packing: volume, sizes, and type of material
6. Screened, perforated, or milled casing or other intervals which allow water to enter the well. Number of aquifers across which well is screened
7. Pump type, setting, intake location, construction materials, and pump column type and diameter
8. Pump fuel and lubricant.

Well pumping history:

1. Well yield in gallons per minute or per day
2. Frequency of well use

3. Static and/or pumping levels.

The sampler should then become familiar with the field parameters and laboratory analytes determined during various types of sampling events. There are four types of groundwater sampling that TWDB has been undertaking: routine, special, Hach, and grab sample collection. Routine sampling involves field parameter determination and lab analysis for major ions, dissolved metals, and nitrate. Special sampling is tailored to a project that might require determinations of groundwater radiogenic activity, organics, or other analytes not normally required in routine samples. Hach sampling involves the measuring of field parameters and analyzing for major ions using TWDB's HACH-2000 equipment.

Normally, field tests consist of pH, Eh, temperature, specific conductance, and alkalinity. They are performed for all suites except the grab sample. The contract laboratory is notified in advance of sampling trips as to the parameters to be analyzed. The contract lab will provide sampling containers, acids, and the chain of custody (COC) form. For Hach lab samples, paperwork and supplies will be provided by the TWDB.

A typical suite of parameters determined by both field tests and laboratory results of water taken from a well completed in the Dockum aquifer of Texas is shown in Figure 2. Since parameter suites are tailored to each aquifer, the composition of parameters for other aquifers may be slightly different.

For Hach samples, the normal suite of field tests is done. Samples are preserved and treated the same as for the contract laboratory. The typical laboratory analytes are: Ca, Mg, K, Fe, SO₄, Cl, F, SiO₃, and PO₄.

Grab samples are used as a screening tool. The analytical results yielded by grab samples are not as reliable as other types of samples. No field tests are conducted and the samples are unfiltered and not preserved. Specific conductance, pH, and alkalinity are determined in the lab. The samples are analyzed for Ca, Mg, K, Cl, SO₄, F, and SiO₂.

WELL PURGING PROCEDURES

In the field, before sampling any groundwater, the well must first be purged until pH, specific conductance (SC) and temperature (T) readings stabilize. The purpose of wellbore purging is to evacuate the stagnant water in the well casing prior to sampling so as to provide a representative sample of in-situ groundwater with minimum disturbance of the flow system and the collected sample.

The amount of water to be pumped before collection of water samples depends upon well depth, hydraulic properties, sampling methodology and program requirements. There is no set number of volumes to be pumped that fits all situations. It is generally agreed that a minimum of three casing volumes of water should be evacuated as well as attaining the stabilization of pH, temperature and electrical conductivity of the discharging water. At least three pH, SC, and T readings of the discharging water should be taken at three (3) - to five (5) - minute intervals. These parameters are deemed to have stabilized when three successive measurements, taken at intervals of three (3) to five (5) minutes, are within the following ranges:

pH: ± 0.1 pH units

Temperature: $\pm 3\%$

Specific Conductance: $\pm 3\%$

If the chemical stability has not been attained after four casing volumes of water have been removed, it is advised that sampling can commence if notes are made clearly describing the stabilization problem.

The following formula can be used to estimate the quantity of water to be purged equivalent to three well volumes:

$$V = 3C\pi(D/2)^2H$$

where:

V = total purge volume (i.e., three well volumes, in U.S. gallons)

π = Pi constant (=3.1416)

C = constant (=7.48) converts ft^3 to U.S. gallons

D = inside diameter of well casing (feet)

H = height of water in well (feet). This is calculated by subtracting the depth to water from the pump setting, or from bottom of completion interval, or from the depth of the well (in that order of priority).

EXAMPLE: An irrigation well with a 16-inch casing is pumping at a rate $Q = 750$ gallons per minute. The static water level was 205 feet, and the screened interval is 205 – 305 feet. How much water needs to be purged and for how long?

$$V = 3 \cdot 7.48 \cdot 3.1416 \cdot (1/2)^2 \cdot (305 - 205) = 1,761.5 \text{ gallons}$$

The time (t) required to pump this amount of water out of the well will be:

$$t = \frac{V}{Q} = \frac{1,761.5}{750} = 2.34 \text{ minutes}$$

Low transmissivity wells may require less purging to obtain fresh aquifer water. Caution should be taken so that a low yield well does not drawdown to such an extent that the well pumps “dry” or the pump trips off line. If this should happen, wait until the pressure rebuilds in the well before sampling.

When the field parameter readings have become stable, begin sampling. The sample is to be collected near the wellhead before the water has gone through pressure tanks, water softener, or other treatment. Wells equipped with faucets at the wellhead are ideally suited for sample collection.

The purpose for groundwater sampling is to obtain results that most accurately reflect the water quality conditions within the aquifer. The procedures employed for sample preservation and storage are to minimize reactions within the water sample after it has been collected and placed in a container.

Accurate lab analysis of certain parameters requires preservation of the sample with an additive. In the case of dissolved metals, nitric acid is often added to insure that ions stay in solution and not adsorb onto sample container walls. Other constituents, such as nitrate, may be preserved with sulfuric acid. The type of acid preservative used must be consistent and compatible to the lab analysis procedure used (USBR, 1984). Acidified sample collection bottles must be properly labeled. Anion and nutrient samples are to be kept on ice following collection in the field and all samples brought to the lab within established timelines.

It is the responsibility of the personnel conducting sampling to make sure the integrity of the sample is maintained. This is accomplished by avoiding sample contamination and observing requirements for sample holding time.

DETERMINATION OF FIELD PARAMETERS

Several analyses must be made in the field at the time of sampling. Measurements of pH, temperature, and specific conductance are used to establish that the well has stabilized before sampling may begin. Other parameters, such as oxidation reduction potential, alkalinity, and dissolved oxygen, are measured at the time of sampling because the dissolved gases may react during the holding time. These reactions change the chemical composition of the water, thus making any laboratory analysis at a later time inaccurate. Many of the instruments used for field measurements require batteries or other means of electrical power. Prior to going to the field, always check all meters and their power supply. Have an extra set of fresh batteries in the event of a malfunction.

Determination of pH

pH is the measure of effective hydrogen-ion concentration, or the negative logarithm of the hydrogen-ion activity concentration in moles per liter. In aqueous solutions, pH is controlled by reactions that produce or consume hydrogen including practically all dissociations of acids, bases, and hydrolysis (Wood, 1976). It is strongly influenced by the temperature of the groundwater. The primary control of pH in most potable groundwater is the carbonate system including gaseous and dissolved carbon

dioxide, bicarbonate, and carbonate ions. Other dissolved gases, such as hydrogen sulfide and ammonia, and hydrolyzable metal ions can also affect the pH of the solution. Most natural ground waters have pH of 4 to 9. Groundwater affected by industrial or mining activities may range from 2 to 12.

The epoxy-type electrode is better suited to field use than the older glass-type electrode. Avoid placing any equipment to be used in the pH measurement from coming into contact with soil particles or any foreign material that might contaminate the readings.

This procedure is for pH meters equipped with a combination electrode, thermistor, thermocompensator (ATC), and autolock. If using pH meters without such options, consult the instrument manual for the correct procedure. pH is extremely temperature sensitive, and meters may not always read the exact value of the standardizing solutions or buffers.

Required Equipment:

1. pH meter and electrode
2. pH buffer solutions 4, 7, and 10; 500 ml each
3. Clean plastic manifold, source connections, and hose
4. Thermistor
5. Deionized water
6. Plastic wash bottle for deionized water
7. Box of kimwipes or equivalent tissue paper
8. Plastic beakers or cups

Procedure:

1. Connect plastic hose to well and connect the manifold to the hose. Turn water on so that the manifold fills and a gentle stream of water comes out the overflow.
2. Inspect the pH electrode and fill with new solution if needed.
3. Remove electrode from protective boot, rinse with deionized water, and blot dry with tissue paper. Remove thermistor from case, rinse with deionized water, and blot dry.
4. Connect pH electrode and thermistor to the pH meter. Turn the meter on and push the CLR button to clear any previous calibrations.
5. Immerse the pH electrode and thermistor into the 7 buffer solution. Buffers may be immersed in a container of well discharge water to allow them to stabilize to well temperature, thus obtaining a more accurate calibration. Gently stir the electrode, taking care to keep the bulb immersed while not hitting the sides of the beaker or bottle. Push the STD button on the meter. A flashing display indicates that the meter is computing the pH. When the display stops flashing, a pH reading near 7 should be displayed, along with the temperature.
6. Remove the electrode and thermistor from the 7 buffer solution, rinse with deionized water, and blot dry.
7. Immerse the pH electrode and thermistor onto the 10 buffer solution. Gently stir the electrode as in step 5. Push the STD button on the meter. The display

will again flash until the meter computes the value of the second standard.

When the display stops flashing, a pH reading near 10 should be displayed, along with the temperature.

8. Remove the electrode and thermistor from the 10 buffer solution, rinse with deionized water, and blot dry.
9. Place the pH electrode and thermistor in the manifold and push the pH button on the meter. After one minute push the AUTO button. When the display stops flashing, record the time, pH, and temperature.
10. Repeat step 9 at five-minute intervals until the pH stabilizes (± 0.1 units).
While waiting for the well to stabilize, set up conductivity meter.
11. After well stabilizes, remove the pH electrode and the thermistor from the manifold, rinse with deionized water, and blot dry. Disconnect the electrode, place it in the ring stand clamp (preparatory to the alkalinity titration), and lower into beaker of water to keep the bulb wet. Keep the thermistor ready for further use to measure Eh.

Since most natural groundwaters have a pH at or slightly above 7, the buffers used to calibrate the pH meter should be 7 and 10. If more acidic groundwater is encountered, it may be necessary to recalibrate using the 4 and 7 buffers.

Because the pH is extremely temperature-sensitive, all pH meters should be calibrated at least once a day before sampling. If extreme weather conditions are encountered in the field (i.e., an increase or decrease of 12°C or 25°C or more in ambient air temperature from the time of calibration), the pH meter should be recalibrated.

The filling and storage solution required for the pH electrode is 4M KCl saturated with AgCl. A supply of this solution must be on hand while on a water-quality monitoring field trip.

Temperature Determination

Record the temperature as a separate parameter using the thermistor on the pH meter. There is no calibration for the thermistor.

Specific Conductance Determination

The specific conductance of a water sample is the measure of its ability to carry an electrical current under specific conditions. Groundwater contains dissolved constituents, most of which occur as positive-charged and negative-charged ions. The concentration gradients of these charged ions cause a potential for the electrons to flow in groundwater, thereby creating an electrical current. The degree to which the solution conducts the current depends on the concentration and the rate at which the charged ions move under the electrical charge potential (voltage).

Electrical conductivity is the inverse of resistivity. Since resistivity is measured in ohms meter squared per meter ($\text{ohms m}^2/\text{m}$), the unit of electrical conductivity is mhos/meter, or siemens/meter (S/m) in SI units. The normal unit of electrical conductance used in groundwater is micromhos per centimeter ($\mu\text{mhos}/\text{cm}$) or microsiemens per centimeter ($\mu\text{S}/\text{cm}$).

The mobility of the charged ions is influenced by temperature; as the temperature increases, so does the electrical conductivity of water. The conductivity of groundwater

should be reported at a specific temperature, normally at 25⁰C. The primary reason for determining the specific conductance of a sample in the field at the time of collection is to aid in establishing that the well has stabilized and that the groundwater is representative of the aquifer. The specific conductance of a sample can change with time as a result of the precipitation of minerals from the water once the sample is in the container. A sample that has been acidified will not yield an accurate representation of the specific conductance. Therefore, it is essential to obtain an accurate field specific conductance determination within five minutes after withdrawing a water sample from the well (Wood, 1976).

Specific conductance gives an indication of the concentration of dissolved solids (TDS) in the water. Many of the newer conductivity meters compute the TDS from the conductivity reading. The relationship between the concentration of total dissolved ions in groundwater is linear in dilute solutions (below 1000 $\mu\text{mhos/cm}$). But as the concentration of the total dissolved ions increased and the solution approaches saturation, the relationship between TDS and conductivity ceases to be linear.

A specific conductance value that is markedly different from those obtained in nearby wells may indicate a different source of the groundwater, contamination from surface infiltration, or leakage from a formation that contains water of a different quality. Detection of an anomaly may also indicate that more detailed sampling or evaluation of the well is required.

Required Equipment:

1. Specific conductance meter
2. Thermistor

3. Clean plastic manifold
4. Standard solution for instrument calibration
5. Deionized water
6. Plastic wash bottle
7. Kimwipes

Procedure:

1. Insert the gray calibration module plug in the back of the meter marked CELL (it is keyed to fit properly). Set the range switch to 2,000 and the function switch to MICROMHO. The display should read approximately 1,000. Using a small screwdriver in the hole in the back of the meter marked DELTA CELL, adjust the set screw until the exact reading of 1,000 is obtained. Disconnect the calibration module plug, and the reading should change to approximately 0. This step insures that the meter is working properly.
2. After placing the pH electrode and thermistor into the manifold, remove the conductivity meter and probe from case. Rinse the probe with deionized water and blot dry. Connect the probe to the meter and place the probe in one of the standardizing solutions. Set the selector knob to conductivity and allow the reading to stabilize. Adjust the reading using the knob on the back of the instrument until the reading matches that of the standard.
3. Remove the conductivity probe from the standard solution, rinse with deionized water, and blot dry. Place the conductivity probe in the manifold.

4. Immediately after taking a pH measurement, read the conductivity and record it next to the pH and temperature measurements. Turn the selector knob back to conductivity.
5. Repeat procedure at five-minute intervals until the well stabilizes and sampling may begin.
6. Remove probe from manifold, rinse with deionized water, and blot dry. Turn meter off, disconnect probe, and pack both in their case.

Oxidation Reduction Potential (ORP) Determination

The transfer of electrons from one ion to another in an aqueous solution is called an oxidation-reduction reaction, or redox reaction. This redox reaction takes place in two half reactions which are always coupled in nature. The oxidation reaction results in an ion losing or donating its electron(s) to another ion, and the reduction reaction results in an ion gaining or accepting electron(s).

The oxidation potential of an aqueous solution is called the Eh, which is synonymous with oxidation reduction potential (ORP). The sign of the potential is positive if the reaction is oxidizing and negative if it is reducing.

Required Equipment:

1. pH meter
2. Platinum electrode with pin-to-BNC adapter
3. Reference electrode
4. Thermistor

5. Clean plastic manifold
6. Deionized water
7. Plastic wash bottle
8. Kimwipes

Procedure:

1. The measurement is taken immediately after those of pH, temperature, and conductivity. Remove the platinum electrode from the case, rinse with deionized water, blot dry, and place in the manifold. Connect the platinum electrode to the “pH” connection on the pH meter.
2. Remove the reference electrode from the case, rinse with deionized water, blot dry, and lace in the manifold. Connect the reference electrode to the REF connection on the pH meter.
3. Check to see that the thermistor is in the manifold and is connected to the pH meter.
4. Turn pH meter on. Press the mV button to read millivolts. Press the AUTO button and the display will begin to flash. Wait while the meter computes the Eh reading. When the display stops flashing, record the value.
5. Turn pH meter off and disconnect the electrodes and thermistor. Rinse the electrodes and thermistor with deionized water and blot dry. Pack the electrodes in the case and place the thermistor in beaker with pH probe.

Alkalinity Determination

Alkalinity is the capacity to neutralize acid. In water chemistry it is the capacity to accept protons (De Zuane, 1990). The primary components of alkalinity in groundwater are carbonate ions (CO_3), bicarbonate ions (HCO_3), and hydroxyl ions (OH); of these three, carbonate and bicarbonate are the most common. Measurements must be made in the field at the time of sampling since alkalinity is controlled by dissolution or degassing of CO_2 which can shift the source of alkalinity.

The alkalinity value gives an estimate of non-acid constituents of water. When the “basic” constituents are limited to salts of calcium and magnesium, alkalinity equals hardness. When alkalinity is greater than hardness, basic salts such as those of sodium and potassium, may also be present. When alkalinity is less than hardness, the presence of salts of calcium and magnesium are more likely to be sulfates instead of carbonates (De Zuane, 1990).

Two methods for determining alkalinity are normally run in ground water sampling. These procedures are run on water collected through the filtration system at the end of the sampling event. The equipment and procedures required for both tests are presented.

Required Equipment:

1. Phenolphthalein indicator solution
2. Bromocresol green, methyl red reagent
3. Deionized water
4. Plastic wash bottle

5. Sulfuric acid (H_2SO_4) – 0.020 Normal
6. Two 200 ml plastic beakers
7. 250 ml pyrex beaker
8. 50 ml volumetric pipette
9. 25 ml pyrex buret
10. pH meter
11. Thermistor
12. pH combination electrode
13. Calculator
14. Ring stand
15. Clamp for holding buret
16. Clamp for holding pH electrode and thermistor
17. Teflon stir bar
18. Stir box

Phenolphthalein Alkalinity as CaCO_3 (Carbonate) Test Procedure

If the pH of the sample is greater than 8.3 or is unknown, this procedure must be performed.

1. Set buret in clamp on ring stand. Place stir box at or on the base of the ring stand.
2. Fill buret with dilute H_2SO_4 taking care to get all of the air bubbles out of the buret and to accurately “zero” the top (set the top of the column and record the

level). Use the second plastic beaker to collect any acid during the “zeroing” step.

3. Collect 100 ml (or other measured amount) of sample filtrate in one of the plastic beakers.
4. Using the volumetric pipette, place 50 ml sample in 250 ml pyrex beaker.
Place clean stir bar in bottom.
5. Place the beaker with the sample on the stir box and turn the power on.
Adjust the speed of the stir bar so that it is stirring gently on the bottom of the beaker.
6. Connect the pH electrode and thermistor to the pH meter. Place the electrode and thermistor in the clamp and lower into the sample, making sure that the bulb of the electrode is sufficiently covered yet not touching the bottom. Take care not to allow the stir bar to hit the electrode or thermistor.
7. Turn pH meter on and push the pH button.
8. Add 2 drops of phenolphthalein indicator solution. If carbonate is present, sample will turn pink. If carbonate is not present, sample will not turn pink; and the remainder of this procedure may be omitted. If the pH of the water is known to be 8.3 or greater, follow the remainder of the procedure, even if the sample did not turn pink when phenolphthalein indicator was added. Use a pH reading of 8.3 as the end-point for the titration.
9. Add H_2SO_4 by drops, recording volume accurately within 0.5 ml increment off buret until reaching the end point at pH 8.3. The sample will turn clear as

the titration proceeds, but the identification of the end point is determined by pH meter.

Calculation of Phenol Alkalinity:

$$\text{Phenol Alkalinity} \frac{1000}{\text{ml of Sample}} \times \text{ml of Acid}$$

$$\text{meq/l CO}_3 = \text{Phenol Alkalinity} \times 0.04$$

$$\text{mg/l CO}_3 = \text{meq/l CO}_3 \times 30.0047$$

Total Alkalinity as CaCO₃ (Bicarbonate) Test Procedure

1. If not already done, set up titrating equipment as in steps 1 through 7 according to the Phenolphthalein Alkalinity procedure.
2. Add H₂SO₄ by drops, recording volume accurately within 0.5 ml increment off buret until reaching the end point at pH 4.5. The end point of this titration is determined by pH although a colorimetric method may be used if the pH meter ceases to function.

Colorimetric Method for Total Alkalinity as CaCO₃ (Bicarbonate)

This method is to be used only as a back-up method in the event that the pH meter malfunctions. It gives an approximate measurement for total alkalinity; but since the color change is a judgement call, the pH should be used as the true end-point indicator.

1. If not already done, set up titrating equipment as in steps 1 through 7 according to the Phenolphthalein Alkalinity procedure.
2. Add one powder pillow of bromcresol green, methyl red reagent. The sample will turn blue-black to dark green.

3. Add H₂SO₄ by drops, recording volume accurately within 0.5 ml increment off buret, until the sample turns to a gray-pink color (end point near 4.5).

Calculation of Total Alkalinity:

$$Alk_{tot} = \frac{1000}{V_s} \times (V_p + V_{mo})$$

where:

V_s = sample volume (ml)

V_p = volume of acid required to reach pH 8.3 (ml)

V_{mo} = volume of acid required to reach pH 4.5 (ml)

Dissolved Oxygen Determination

Dissolved oxygen in groundwater usually comes from contact with the atmosphere before recharging the aquifer. The solubility of oxygen in the water is dependent upon the partial pressure of oxygen in the atmosphere, the dissolved solids content of the groundwater, and the temperature within the aquifer. The presence of dissolved oxygen in groundwater is a more common occurrence than is generally believed. This is particularly true in hydrologically stressed systems. Dissolved oxygen can exist at great depths in aquifers which have little or no oxidizable material in the water flow path and can also be present in any aquifer where the residence time of the water is short compared to the rate of oxygen consumption. The measured amount of dissolved oxygen is used to determine redox potential for use in geochemical studies.

Required Equipment:

1. 250 ml burette

2. 10 ml pipettes
3. Deionized water
4. Plastic wash bottle
5. Manganous sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) powder pillow #1
6. Alkaline iodide-azide powder pillow #2
7. Sulfamic acid powder pillow #3
8. Starch indicator solution
9. PAO titrant (phenylarsine oxide)
10. BOD bottle and cap

Procedure (modified Winkler titrimetric method):

1. Fill BOD bottle carefully to overflow the brim, allowing no air bubbles to form or to be entrapped.
2. Add reagent pillows #1 and #2 to sample and stopper or tighten the bottle cap.
3. Mix by inverting the bottle at least 15 times.
4. When precipitate settles, leaving a supernatant above the manganese hydroxide $\text{Mn}(\text{OH})_2$ floc, shake again.
5. Let solution settle for two minutes. Floc should be gray to brown in color if DO is present and the test should continue. If DO is absent, floc will be white, and the test should end at step #5.
6. Add reagent pillow #3, being careful not to get acid on your clothes or body.
7. Shake vigorously until floc has disappeared.

8. Measure 200 ml of solution in burette. Discard remainder of solution in BOD bottle and return the 200 ml of solution to BOD bottle.
9. Titrate with PAO until straw color attained.
10. Add 4 or 5 drops of starch indicator. Solution should turn blue-black.
11. Titrate with PAO until end point of color (clear) is attained. Take reading directly off the pipette. The volume of titrant in ml equals the DO content in mg/l.

Measuring DO by Dissolved Oxygen Meter

The following procedure is for an oxygen meter equipped with a thermistor and a thermocompensator. If using an oxygen meter without such options, consult the instrument manual for the correct procedure.

Calibration

1. Switch the instrument to OFF and adjust meter mechanical zero.
2. Switch to ZERO and adjust to "0" on mg/l scale.
3. Switch to FULL SCALE and adjust to "15" on mg/l scale.
4. Prepare probe for operation, plug into instrument, and wait up to 15 minutes for probe to stabilize. Probe can be located in calibration chamber or ambient air.
5. Switch to CALIB.O₂ and adjust CALIB control until meter indicates local altitude on short scale in upper right corner of meter. It is desirable to calibrate probe in a high humidity environment.

Measurement

1. Place probe in sample and stir.

2. Allow sufficient time for probe to stabilize to sample temperature and dissolved oxygen.
3. Switch to READ TEMP AND SET DIAL. Set O₂ SOLUBILITY FACTOR dial to sample temperature. Take care to properly index salinity on sloped white bar.
4. Switch to READ O₂ and read mg/l, dissolved oxygen while stirring.
5. Instrument should be left on between measurements to avoid the necessity to re-polarize the probe.

RECORDING FIELD DATA

All pertinent data should be recorded in a field book or directly onto the Water Quality Field Data sheet (Figure 3). All blanks should be completed except total cations and anions, total hardness, and dissolved solids. These will be calculated from analytical data. The following data are most important: state well number (SWN); sample number; date of collection; final pH, Eh, and conductivity; alkalinity titration; and well owner's correct mailing address. Data entered on field sheet should be neat and easily deciphered.

2003FY TWDB Water Quality Field Data Sheet

Newly inventoried Well _____
 Sample ID Number: _____
 Date: _____
 Sampler(s): _____

State Well Number: _____ Name: _____
 County: _____ Address: _____
 County Code: _____ Phone Number: _____
 Aquifer Code: _____ Attention: _____
 Aquifer Id: _____ Well Name or #: _____

CIRCLE EACH SAMPLE FRACTION COLLECTED:				
1	2	3	4	5
500ml (filtered) Anions / Total Alk. Ice	500ml (filtered) Cations Nitric (HNO3)	250ml (filtered) Nitrate Ice + H2SO4	40 ml (unfiltered) Atrazine Ice and in dark	

Proper preservation requires adding enough of the correct acid to each sample fraction to bring the pH below 2.0.

Calibration Verification Readings	
pH	7 = _____
	4 or 10 = _____
SLP =	7.38 = _____
Conductivity	500 = _____
	1000 = _____
	2000 = _____
	5000 = _____

Time In: _____ Time Out: _____
 W. L. depth from LSD (ft.): _____ W.L. remark: _____ M.P. = _____
 Pumping Since: _____ Sampling Point: _____

Field Alkalinity Titration:	
Start pH	End pH
50.0 mL Sample Size	
mL Acid added for Phenol (> 8.3)	
mL Acid added for Total (8.3 - 4.5)	
<small>Items below calculated from: mL acid added x 20 = Alkalinity</small>	
Phenol Alkalinity (82244):	mg/L
Total Alkalinity (39986):	mg/L

Well Use: _____
 Lift: _____
 Power: _____
 Casing Type: _____
 Sample Time: _____

Items Below Calculated Later From Results:	
Dissolved Solids (mg/L):	
Hardness (as CaCO3):	
Balanced:	

FIELD G.P.S. readings
 Latitude: ° ' " _____
 Longitude: ° ' " _____
 Casing Size: " _____
 Filter pressure: hand pump / line

Water Quality Stabilization Parameters Table (at least 3 readings at five minute intervals)

Time:					
pH:					
Celsius Temp. (00010)					
Conductivity (uS/cm):					

Notes: _____

 Data Entered By: Sampler Into Database: _____ yes / no

Figure 2 The TWDB Water Quality Field Data Sheet

In the other notes block, enter useful information such as well yield, duration of pumping prior to sampling, depth, pump data, water use, and possible contaminants near the well. GPS coordinates would also be a valuable addition. Upon completion of the sampling trip, this recorded data should be updated in the groundwater database.

For Hach and grab samples, the form shown in Figure 4 should be completed and submitted to the TWDB with the sample. For Hach samples, a field data sheet will also be required showing field determined parameters.

If the sampled site does not have a SWN, then complete a Well Schedule form (Figure 5). This will require additional data, a location sketch, and obtaining a drillers' (if possible).

FILTERING OF GROUNDWATER SAMPLES

To determine concentrations of dissolved constituents in water, the sample must be filtered during collection. The recommended field filtration unit is the 102 mm backflush filter plate or any other approved filter kit.

Filtration Procedure

The filter kit should be fitted with two 0.45 μm cellulose filters, unless the constituent/property being tested requires otherwise. These filters will effectively remove all but dissolved inorganic species. A 0.45 μm filter paper should be placed between the two cellulose filters, the filtration unit assembled, and connected by a clean plastic hose to the well.

Texas Water Development Board

HACH / Grab Sample Analysis Sheet (circle one)

TO BE COMPLETED and ENTERED BY SAMPLER:

State Well Number: _____

Sample Number: _____

Sampler: _____

Sample Date: _____

Sample Time: _____

Phenol Alkalinity (82244) _____ mg/L

Total Alkalinity (39086) _____ mg/L

Specific Conductivity (screen 3) _____

pH (screen 4) _____

Temperature (00010) _____ C

TO BE COMPLETED and ENTERED BY ANALYST:

Analysis Date: _____

Analysis Time: _____

Analyst: _____

		Screen 3	Screen 4
Silica	_____ mg/L	x	
Magnesium	_____ mg/L	x	
Calcium	_____ mg/L	x	
Sodium (calculated)	_____ mg/L	x	
Potassium	_____ mg/L	x	
Sulfate	_____ mg/L	x	
Chloride	_____ mg/L	x	
Fluoride	_____ mg/L	x	
Nitrate (as N)	_____ mg/L		00618 or 00620
Nitrate (as NO ₃)	_____ mg/L	calculated	
Iron	_____ mg/L		01046
Phosphate	_____ mg/L		00671

Analyzed using HACH DR2000 spectrophotometer.

OHT= Out of Hold Time

BTL = Below Detection Limits of HACH DR2000 spectrophotometer

Figure 3 TWDB form for Hach and grab sample

**Texas Water Development Board
Well Schedule**

State Well Number 5313101 Previous Well Number _____ County PECOS 371
 River Basin RIO GRANDE 23 Zone 3 Latitude 305104 Longitude 1022743 Coordinates Accuracy 0
 Owner's well No. 10 Location: _____ 1/4, _____ 1/4, Section _____ Block _____ Survey _____

Owner DOMAINE CORDIER Driller _____
VINEYARDS

Address Box 146, I-10 Exit 285 Ft. STOCKTON TX 79735 Tenant/Oper. _____

Date Drilled _____ Depth 295.5 Source of Depth 0 Altitude 2681 Source of Alt. Data M

Aquifer Edw-Trinity(PLM) 218 EDDT Aquifer ID _____ Well Type W User _____

Well Construction Const Method _____ Casing Material STEEL S
 Completion Method _____ Screen Material _____

Casing or Blank Pipe (C)	
Well Screen or Slotted Zone (S)	
Open Hole (O)	
Cemented from _____ to _____	
Diam. (in.) _____	Interval of C.S. or O. From _____ To _____

Lift Data Pump Mfr. _____ Type of Lift SUMP. S Pump Depth Setting (ft) 288 ft.

Motor Mfg FRANKLIN Power ELITE B H.P. 30 HP

Yield Flow Rate _____ Pump Rate _____ GPM Meas Rept Est Date of Test _____

Performance Test Length of test _____ hr Production Rate 250 GPM Meas (Rept) Est Date of Test 9/18/02

Static Level 117' ft. Pumping Level _____ ft. Amount of Drawdown 195.6 ft. Specific Capacity _____ GPM ft.

Water Use Primary IRRIG I Secondary _____ Tertiary _____

Water Quality (Remarks: _____)

Other Data Available Water Level _____ Water Quality Y Logs _____ Other Data _____

Water Levels Date _____ Meas. _____ Remarks _____ M.P. + _____ - _____

Date _____ Meas. _____ Remarks _____

Date _____ Meas. _____ Remarks _____

Recorded by R. Boghici Date Record Collected or Information Updated 05/20/2003 Reporting Agency 01

Remarks	1	
	2	
	3	
	4	
	5	
	6	

218 EDDT
Aquifer
53.13-101
Well Number

Figure 4 TWDB well schedule

After the water begins to flow, discard the first 150 to 200 ml of filtrate. This rinses the filtration unit of any dirt without contaminating the sample. After collection, the filtration unit should be disassembled, the 0.45 μm filter paper discarded, and the cellulose filters thoroughly rinsed with deionized water.

If total recoverable inorganic constituents are desired, save the filter paper for analysis. Digest the material collected on the membrane filter in nitric acid, hydrochloric acid, or both (aqua regia), dissolving all or most of the particulate matter. The resulting digestate may be analyzed by standard laboratory methods.

Total inorganic constituents can also be determined using a second, unfiltered sample collected at the same time as the sample for dissolved constituents. Acidify this sample to avoid precipitation and adsorption unless selective extraction techniques are to be used.

When filtering samples for analyzing organic constituents, use a glass-fiber or metal-membrane filter and collect the sample in a suitable container, usually glass. Because most organic analyses require extraction of the entire sample, do not discard any of it. After filtering, the membrane containing the suspended fraction can be sealed in a glass container and analyzed separately as soon as practicable.

Water that appears to be clear may contain considerable amounts of particulate matter in suspension. This must be removed prior to most analyses, particularly if the sample is to be acidified; because the addition of acid will cause much of this matter to dissolve. This point to the main purpose of the groundwater monitoring program to characterize representative water in the aquifer without interference from matter derived

from well construction and pumping equipment. Most of our results involve dissolved inorganic constituents, and to this end, filtration in the field is of utmost importance.

ROUTINE SAMPLING PROCEDURES AT TWDB

The objective of each sampling program is to provide data for a particular study. Some studies will be routine updates of the major and minor aquifers of the State, while others may be in response to special joint agency projects. Because each study has different objectives, the sampling program and constituents may differ. Careful planning before the field work will ultimately result in savings of time, money, and manpower.

Equipment Needed For Groundwater Sampling

The following checklist should be used as a guide for field preparation:

- Assorted sample containers
- Concentrated nitric and sulfuric acids
- Stir box with teflon stir bar
- Ring stand with clamps
- 0.02 N sulfuric acid
- 50 ml Pyrex beaker
- 10 ml plastic volumetric pipette and bulb
- 25 ml Pyrex burette
- Container labels and waterproof pens
- Filtration equipment
- Water-level and yield measurement equipment

Water-quality meters

Extra batteries

pH buffer solutions: 4, 7, 10.

Conductivity solutions tailored to the range in the study area

2 gallons of deionized water

Litmus paper for pH checks

Plastic manifold, beakers, and wash bottle

Box of kimwipes

Phenolphthalein indicator solution

Bromocresol green and methyl red reagent

Tools and plumbing fixtures

Coolers for ice and water samples

Safety equipment

Sampling run sheets, well schedules, and chain of custody forms

GPS Unit

Notebook computer downloaded with pertinent county data

County and topographic maps

Pertinent GW database printouts for your area

Observation well books and copies of drillers' reports

Cellular phone

Prior to filling, label all containers with the well number, type of sample, any preservative and amount, and sample number. Mark any container lid with an "X" if the sample will be acidified.

After purging and stabilizing the well, water sample collection may begin. When collecting groundwater samples, fill the container approximately half-full, swirl the water around the sides of the container, and discard. This rinses the container of any dirt while keeping the sample free of external contamination. To save time during each sampling run, unfiltered samples are to be collected first. The water flow can be briefly stopped to allow the filter unit to be connected, and then sampling can resume. After adding preservatives, check samples with litmus paper to insure that the correct pH was reached.

The following is a list of procedures for the common collections done by TWDB personnel. There are many other standard methods which may be more suitable if sampling for specific chemicals or chemical groups.

Routine Cations and Heavy/Trace Metals

Collect **filtered water** into a 1-liter plastic (polyethylene) container. Fill, acidify with concentrated nitric acid (HNO₃) to a pH \leq 2, top off any remaining head space, cap tightly, and chill to 4°C.

Routine Anions, Boron, Bromide, and Iodide

Collect **filtered water** into a 500-ml plastic (polyethylene) container. **Do not acidify.** Fill completely, cap tightly, and chill to 4°C.

Nutrients

Collect **filtered water** into the 250-ml plastic container provided. Fill, acidify with concentrated sulfuric acid (H_2SO_4) to a $\text{pH} \leq 2$, top off any remaining head space, cap tightly, and chill to 4°C .

Organics

Pesticide Screen (Gas Chromatograph): Collect **unfiltered water** into a 1-quart glass jar. **Do not acidify.** Fill to overflowing and seal tightly with teflon-lined cap. Chill to 4°C .

Total Organic Carbon (TOC): Collect **unfiltered water** into a 1-quart glass jar. **Do not acidify.** Fill to overflowing and seal tightly with teflon-lined cap. Chill to 4°C .

Volatile Organic Chemicals (VOCS): Collect **unfiltered water** into two 40-ml amber glass vials. **Do not acidify.** Fill to overflowing and cap tightly. Chill to 4°C .

Gas Chromatograph/Mass Spectrophotometer (GC/MS) Screen: Collect **unfiltered water** into a 1-quart glass jar. **Do not acidify.** Fill to overflowing and seal tightly with teflon-lined cap. Chill to 4°C .

Radioactivity

Collect **filtered water** into a 1-gallon plastic (polyethylene) container. Fill, acidify with concentrated nitric acid (HNO_3) to a $\text{pH} \leq 2$, top off remaining head space,

cap tightly, and chill to 4°C. If only sampling for gross alpha (α) and gross beta (β), collect 1 quart.

Radon Gas

Radon gas is a daughter product of U^{238} and has a half-life of only 3.5 days. It is an inert gas, but is dangerous to human health because it and its highly reactive daughter products are alpha-emitters. Radon is reactive with hydrocarbons; therefore, any groundwater to be analyzed for radon must be kept in glass containers. All samples for radon analysis are to be delivered to the laboratory within 48 hours.

1. Remove needle from container and screw it on the needle/tube holder so that the short end of the needle is inside the tube holder.
2. Remove cover off the long end of the needle and direct the tip of the needle to the running water to be sampled. Insert the rubber-capped end into the tube holder and push it until the needle punctures it. Keep it in place while holding the exposed needle tip in the water. Because the tube is vacuum-sealed, the water will flow into the tube.
3. The tube will fill, leaving a small space. Remove the tube from the holder and chill to 4°C.
4. Remove the needle from the tube holder and slide the covers on both ends as a safety precaution.

Stable Isotopes

These isotopes include O^{16}/O^{18} ; N^{14}/N^{15} ; C^{12}/C^{13} ; 2H , 3H ; and S^{32}/S^{34} . Check standard methods for the individual isotope to be collected for any filtering requirements. Collect water into a 1-quart approved container, fill to overflowing, cap tightly, and chill to 4°C.

Grab Samples

After purging the well sufficiently, fill a rinsed 1-liter container with unfiltered water. Do not preserve this sample. Fill the container completely, cap tightly, and chill to 4°C.

SAMPLE SHIPMENT AND CHAIN OF CUSTODY

All samples collected for water-quality studies will follow these procedures:

1. Sample containers are to be clearly labeled with the well identification number, date of collection, type of parameter to be analyzed, and the preservative used.
2. The sample container (ice cooler) should be kept in a safe place. The ice cooler may be taped tightly with masking tape so that if the tape seal is broken, interference with the samples will be evident.
3. When samples change hands during shipment, a chain of custody form (Figure 1) is to be signed by both parties.

4. Samples may be shipped via another carrier, including common carriers. If using a third-party carrier, follow steps 1 to 3 and provide clearly written instructions on handling of samples.

HEALTH AND SAFETY

It is the responsibility of all personnel sampling groundwater to avoid danger by preventing exposure to chemical spills or by inhaling the fumes from any chemicals. When sampling groundwater from aquifers with historical known cases of contamination, the proper sampling gear and/or protective equipment is to be taken to the field. All personnel are to be thoroughly trained on the proper use of such equipment.

When the containers and preservatives are received from the laboratory, check to see that none have leaked. Be aware that many preservatives can burn eyes and skin, and must be handled carefully. Sample bottles should be labeled with the type of preservative, type of analysis to be done, and be accompanied by a Material Safety Data Sheet (MSDS).

ENVIRONMENTAL LABORATORY SERVICES CHAIN OF CUSTODY RECORD
(Do Not Write in Shaded Areas)

Company/Facility: TWDB Page: _____
Billing TO: RAOU, BOGHICA PO: _____
Results TO: GARY FRANKLIN TAT requested: _____ working days
Phone No.: 512.463.6543

NOTE: Submission of samples to Environmental Lab Services obligates the submitter to all terms and conditions outlined on the back of this form.

Check Special Regulatory Permitting Requirements
 None NPDES RCRA SDWA _____
 Sampled By: _____

Relinqu By: L. Boghica Rec'd. By: _____ Relinqu By: _____
 Date: 5/27/03 Date: _____ Date: _____
 Time: 8:25 AM Time: _____ Time: _____

Reporting Requirements
 Faxed Fax Number: _____
 EDD
 Additional copies How many? _____

Sample ID	Description	SC	ANAL	Date	Sample Time	Containers Volume	Type	Preservatives
53-30-401	55	1572	212	5/22	14:20			
53-30-701	56	557	190	6/22	16:00			
53-08-104	57	3070	190	5/23	14:10	500 ml	cat. HNO ₃	+ ice
53-08-601	58	1037	240	5/23	16:00	500 ml	anion	ice
54-10-703	59	706	216	5/23	17:30	2.504	HNO ₃	H ₂ SO ₄ + ice
53-29-401	60	817	176	5/24	14:30			
53-31-202	61	1081	208	5/24	16:30			
45-57-801	62	6610	302	5/25	14:30			

Lab Mgmt. Approval for Batch: _____ Login Review: _____

INORGANICS	ORGANICS	METALS (by ICP unless specific DL requested)	TNRCC 7-DAY LEACHATE
<input type="checkbox"/> Alkalinity, Total <input type="checkbox"/> Bicarbonate <input type="checkbox"/> Carbonate <input type="checkbox"/> Hydroxide <input type="checkbox"/> Phenolphthalein <input type="checkbox"/> BOD5 <input type="checkbox"/> Bromide <input type="checkbox"/> Carbon, Tot. Org. (TOC) <input type="checkbox"/> CBOD5 <input type="checkbox"/> Chloride <input type="checkbox"/> Chlorine, Residual <input type="checkbox"/> Chlorophyll <input type="checkbox"/> Color <input type="checkbox"/> COD <input type="checkbox"/> Conductivity <input type="checkbox"/> Cyanide, Amenable <input type="checkbox"/> Cyanide, Total <input type="checkbox"/> Dry Weight <input type="checkbox"/> Fluoride <input type="checkbox"/> Grain Size (12 sieves) <input type="checkbox"/> Hardness, Total	<input type="checkbox"/> Nitrogen, Ammonia <input type="checkbox"/> Nitrogen, Ammonia (Dist.) <input type="checkbox"/> Nitrogen, Nitrate <input type="checkbox"/> Nitrogen, Nitrate/Nitrite <input type="checkbox"/> Nitrogen, Nitrite <input type="checkbox"/> Nitrogen, Organic <input type="checkbox"/> Nitrogen, Total <input type="checkbox"/> Nitrogen, Total Kjeldahl <input type="checkbox"/> Oil and Grease (IR or Grav) <input type="checkbox"/> Oil and Grease (1664) <input type="checkbox"/> pH <input type="checkbox"/> Phenolics, Total <input type="checkbox"/> Pheophytin <input type="checkbox"/> Phosphorus, Ortho <input type="checkbox"/> Phosphorus, Total <input type="checkbox"/> Silica <input type="checkbox"/> Solids, Settleable <input type="checkbox"/> Sulfate <input type="checkbox"/> Sulfide <input type="checkbox"/> TS <input type="checkbox"/> TDS <input type="checkbox"/> Texture (Sand, silt, clay, gravel) <input type="checkbox"/> TPH (418.1) <input type="checkbox"/> TPH (TX 1005) <input type="checkbox"/> TSS <input type="checkbox"/> Turbidity <input type="checkbox"/> VSS	<input type="checkbox"/> Screen <input type="checkbox"/> Chlorinated Pesticides <input type="checkbox"/> PCBs <input type="checkbox"/> Org. Phos. Pesticides <input type="checkbox"/> Herbicides <input type="checkbox"/> VOAS <input type="checkbox"/> BTEX only <input type="checkbox"/> BTEX/MTBE only <input type="checkbox"/> THMs only <input type="checkbox"/> and Lib. Search (may not be requested alone) <input type="checkbox"/> Semi VOAs (BNAs) <input type="checkbox"/> Semi VOA (A) only <input type="checkbox"/> Semi VOA (BN) only <input type="checkbox"/> PAHs only <input type="checkbox"/> and Lib. Search (may not be requested alone)	<input type="checkbox"/> Total <input type="checkbox"/> Dissolved <input type="checkbox"/> Other
<input type="checkbox"/> Aluminum <input type="checkbox"/> Antimony <input type="checkbox"/> Arsenic <input type="checkbox"/> Barium <input type="checkbox"/> Beryllium <input type="checkbox"/> Bismuth <input type="checkbox"/> Boron <input type="checkbox"/> Cadmium <input type="checkbox"/> Calcium <input type="checkbox"/> Chromium <input type="checkbox"/> Cobalt <input type="checkbox"/> Copper <input type="checkbox"/> Iron <input type="checkbox"/> Lead <input type="checkbox"/> Lithium <input type="checkbox"/> Magnesium <input type="checkbox"/> Manganese <input type="checkbox"/> Mercury by CVAA <input type="checkbox"/> Molybdenum <input type="checkbox"/> Nickel <input type="checkbox"/> Potassium <input type="checkbox"/> Selenium	<input type="checkbox"/> Silver <input type="checkbox"/> Sodium <input type="checkbox"/> Strontium <input type="checkbox"/> Thallium <input type="checkbox"/> Tin <input type="checkbox"/> Titanium <input type="checkbox"/> Vanadium <input type="checkbox"/> Zinc	<input type="checkbox"/> Total TNRCC <input type="checkbox"/> TNRCC Metals <input type="checkbox"/> All Organics <input type="checkbox"/> Volatiles <input type="checkbox"/> BNAs <input type="checkbox"/> Pesticides <input type="checkbox"/> Herbicides <input type="checkbox"/> RCRA <input type="checkbox"/> TCLP <input type="checkbox"/> SPLP <input type="checkbox"/> TPH <input type="checkbox"/> PAH <input type="checkbox"/> All <input type="checkbox"/> All Organics <input type="checkbox"/> BNA's <input type="checkbox"/> Herbicides <input type="checkbox"/> Pesticides <input type="checkbox"/> VOA's <input type="checkbox"/> Benzene only <input type="checkbox"/> RCRA8 Metals <input type="checkbox"/> Lead only <input type="checkbox"/> RCI <input type="checkbox"/> Corrosivity <input type="checkbox"/> Reactivity <input type="checkbox"/> Ignitability	

Special Instructions: _____

Figure 5 Chain of custody record

APPENDIX 1

QUICK REFERENCE FIELD GUIDE FOR WATER QUALITY SAMPLING

1. Prior to going to the field, clean and inspect all sampling equipment and supplies. Prepare an appropriate type and number of sampling containers for the constituents to be measured. Pack all forms that will be required for proper chain of custody and laboratory analysis. Always practice quality assurance (QA) and quality control (QC) as discussed in this sampling procedure manual. Avoid contamination of sampling equipment, buffer and standard solutions, pipettes, reagent acids, and meter/electrodes.
2. If possible, obtain a pre-purging water level measurement and measure or estimate well yield during the purging of the well.
3. All equipment should be inspected as necessary while setting up on site. While well is purging: (1.) set up and calibrate meters; (2.) label appropriate sub-sample bottles; and (3.) begin entering information on the Water Quality Sampling Run form and well schedule, if newly inventoried.
4. While well is purging, measure and record: water temperature, pH, and conductivity. Repeat this step at five minute intervals until well equilibrates. The pH will be the last parameter to stabilize, and readings should be within ± 0.1 pH units. Record the final results on the appropriate water analysis forms.
5. If Dissolved Oxygen measurements are to be taken, do so at this time either by DO meter or Winkler Titration method. Avoid the introduction of atmospheric oxygen in the sample or the loss of oxygen by degassing.

6. Measure and record the Oxidation Reduction Potential (ORP) or Eh in millivolts using the Eh meter. Use the platinum electrode (**NOT** the pH electrode) when measuring the ORP or Eh of the water.
7. Collect any samples which do not require filtration, i.e., TOC, VOC, pesticides, or GCMS. Rinse the containers by filling approximately half full, swirling the water, and discarding the water. Then the sample can be filled to overflowing and capped. Note on the sampling form that the sample was not filtered.
8. Begin filtering water. Always discard the first 150-200 ml of filtrate.
9. Rinse and fill a 500-ml container for anion analysis. Do not acidify this sample. Note on the label and the sampling form that the sample was filtered but not acidified.
10. Rinse and fill a 1-quart container for routine cations and dissolved heavy/trace metals. Preserve with 2 ml of concentrated nitric acid (HNO_3). Note on the label and the sampling form that the sample was filtered and acidified.
11. Check the pH of the cation water sample using litmus paper. The pH should be less than 2; if not, add more concentrated nitric acid and recheck pH.
12. Rinse and fill a 250-ml opaque container for nutrient sample (if required). Acidify with .5 ml concentrated sulfuric acid (H_2SO_4). Do NOT use the dilute sulfuric acid used for alkalinity titration. Note on the label and the sampling form that the sample was filtered and acidified.
13. Check the pH of the nutrient sample as in step #11.

14. Rinse and fill a 1-gallon container for the radioactivity sample (if required). If only sampling for ___ and ___, a 1-quart container may be used. Acidify with 5 ml concentrated nitric acid (HNO₃) to 1 gallon; 2 ml for 1 quart. Note on label and the sampling form that the sample was filtered and acidified.
15. Check the pH of the radioactivity sample as in step #11.
16. Take any other samples as may be required for a particular study. Label all containers and forms indicating what filtering and preservatives may have been used. Check pH to insure that all preservatives are sufficient.
17. Fill 100 ml graduated cylinder for alkalinity test.
18. Shut off water flow from well.
19. Test for carbonate (CO₃) alkalinity.
 - a.) Set up ring stand and stir box apparatus. Fill buret with dilute sulfuric acid and zero. Pipette 50 ml of filtered water into beaker and place on stir box.
 - b.) Connect pH electrode and place in beaker. Turn on pH meter.
 - c.) Add 2 drops of phenolphthalein indicator. If no color change is apparent, go to the bicarbonate alkalinity test. If sample turns pink, titrate with dilute sulfuric acid (0.02 N H₂SO₄) until sample turns clear. This color change should appear at pH of 8.3 to 8.5. Record the amount of acid used to reach the end point.
 - d.) Carbonate (phenol) alkalinity computation:

$$Alk_p = \frac{1000}{V_s} \times V_p$$

where:

V_s = sample volume (ml)

V_p = volume of acid required to reach pH 8.3 (ml)

20. Test for bicarbonate (HCO_3) alkalinity.

a.) Continue using the same sample from the carbonate alkalinity test.

b.) Titrate with the dilute sulfuric acid until reaching the end point of pH 4.5.

Record the amount of acid used.

c.) If pH meter is not available for use in this procedure, a colorimetric method using bromcresol green may be used (see section on Alkalinity Determination).

d.) Alkalinity computations:

$$Alk_{tot} = \frac{1000}{V_s} \times (V_p + V_{mo})$$

where:

V_s = sample volume (ml)

V_p = volume of acid required to reach pH 8.3 (ml)

V_{mo} = volume of acid required to reach pH 4.5 (ml)

21. Place the anion and nutrient samples in an ice cooler and chill. While in the field, periodically check the amount of ice in the cooler. During hot weather, try to limit the amount of time that the cooler must be in an enclosed vehicle.

22. Be sure that your forms are properly completed. Deliver all samples and paperwork to the lab in a timely manner.
23. Quality assurance/quality control: Avoid sample contamination by not using dirty or contaminated sampling equipment (pipettes, acid-reagents, sample containers, unrinsed conductivity/pH electrodes). Remember, a contaminated sample is useless and has not meaning in characterizing groundwater quality.
24. Chain of custody: Whenever samples are shipped on a public transportation system, or through a second or third party, a record of all persons who handled the samples must be kept. Upon delivery to the laboratory, the laboratory representative will sign the chain of custody form showing that the samples were received.
25. Upon returning to headquarters, all equipment will be cleaned and inspected. All chemicals, reagents, and supply of distilled water will be refurbished to make everything ready for the next trip. Please take care with fragile and sensitive equipment.