



Model Sampling and Analysis Plan
Rules 609 and 318A.e(4)
Colorado Oil and Gas Conservation
Commission
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1.0 Introduction

The Colorado Oil and Gas Conservation Commission (COGCC) has prepared this model sampling and analysis plan for parties who engage in sampling and analysis activities for Rule 609 - Statewide Groundwater Sampling and Monitoring and Rule 318A.e(4) – Groundwater Baseline Sampling and Monitoring in the Greater Wattenberg Area (GWA). This document will be modified as necessary based on new procedures, protocols, and other information that need to be incorporated to meet the objectives of the new rules.

As stated in the statement of basis and purpose for these rules:

“The purpose of the new and amended water sampling rules is to gather baseline water quality data prior to oil and gas development occurring in a particular area, and to gather additional data after drilling and completion operations. The water quality data generated under the rules will be publicly available on the Commission’s web site. Acquiring this data and making it publicly available will inform relevant stakeholders, including public officials, of baseline groundwater quality, and may aid in early detection of any adverse impacts related to oil and gas activity. Similarly, the sampling program may identify existing groundwater contaminants, which can then be properly treated”.

The timing and frequency of the sampling events is described in the rules themselves and will not be described in detail in this SAP.

Sampling must be conducted in a way that employs “best practice protocols” designed for the collection of samples that are representative of groundwater at the site. Methods and techniques used in the analysis of the groundwater samples must be capable of providing both accurate and precise measurements and representative aliquots of a groundwater for analysis. It is important to use well documented analytical processes so that different laboratories are capable of producing comparable data. The goal of any environmental sampling program should be to ensure precision, accuracy, representativeness, comparability and completeness (PARCC) of the data. These principals should be carried forward for Rule 609 and Rule 318A.e(4) sampling efforts. Equally important, is assurance that the methods and processes of analysis will yield reproducible results at reporting thresholds that are adequate to evaluate potential changes in water quality.

The groundwater sampling and analysis procedures outlined in the SAP are designed to provide consistency in sampling and analytical techniques. The use of the original laboratory’s electronic data deliverable (EDD) files in the COGCC format is also an essential part of ensuring that the data are accurately captured for later evaluation. The upload process allows efficient data handling and transfer and can eliminate the need to check for data transcription errors that are an inevitable result of manual data entry. Documentation of sample location and condition of a water source and its current use, along with observations about the water sample, (such as effervescence, taste and odor) are also important.

2.0 Pre-sampling Activities

Use the COGCC GIS Online interactive map or other resources to identify potential water sources within the area where sampling is required. Select potential sites based on water source selection criteria contained in the rules. Obtain permissions for access, including acknowledgement that data will be accessible to the public through the COGCC website.

The operator or their consultants/contractors need to obtain Division of Water Resources (DWR) records on water well construction, depth, diameter, initial static water level and initial flow rate or yield from the well prior to a sampling event. At the time of sampling or before, the landowner should be interviewed regarding current conditions at the well and any knowledge of discrepancies between the DWR records and the current well configuration. At the time of sampling interview the landowner regarding recent use of well and water quality concerns noted by the owner such as observations regarding recent changes in appearance, taste and odor of water from the well.

3.0 Sample Collection

All samples shall be collected by individuals experienced with water quality sampling and sent to a laboratory accredited by the National Environmental Laboratory Accreditation Program in general and more importantly, for analytical procedures and analytes of concern in this SAP. Guidance for general sampling practices can be found in ASTM D4448-01 (2013) Standard Guide for Sampling Ground-Water Monitoring Wells.

The individual collecting the samples should wear new, disposable powder free gloves to prevent possible contamination of the samples. The gloves should be changed following the collection of samples from each sample location at a minimum, or more frequently as needed.

A complete set of samples should be obtained from each water source, as specified in the rules. Samples should be collected and preserved using the field methods for unfiltered samples, filtered samples, and dissolved gas samples according to the sampling protocols below.

In order to prevent cross contamination of samples, disposable sampling equipment should be used whenever possible. All sample containers must be new and pre-cleaned at the factory and generally provided in that condition by laboratories to their clients. All non-disposable equipment (e.g., sampling pumps with non-disposable tubing, dippers, beakers, sample collection tubing and valve assemblies, etc.) and instruments that contact the samples must be decontaminated prior to use and between samples using the following procedure:

- Remove gross contamination by dry brushing followed by a tap water rinse.
- Wash with a laboratory grade detergent solution, such as Alconox or equivalent.
- Rinse with tap water.
- Rinse with distilled or deionized water.
- Air dry.

Decontamination solutions should be pumped through sampling pumps and non-disposable discharge tubing to decontaminate this equipment.

Initial decontamination should be performed prior to arriving at the sampling location. All decontamination solutions should be collected and properly disposed. Decontaminated equipment should be stored in sealed containers such as zipper-lock plastic bags or boxes with tight lids to protect from airborne dust contamination prior to use.

3.1 Water Well Sampling

Instructions for acceptable well purging practices can be found in the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey-Collection of water samples -ver. 2.0: U.S. Geological Survey Techniques of Water-Resources Investigations, 2006), the U.S.EPA Region 9 Field Sampling Guidance Document #1220 Groundwater Well Sampling (September 2004), and in the ASTM D6452-99-Standard Guide for Purging Methods for Well Used for Groundwater Quality Investigations (2012)

Two processes for purging wells are recommended: 1) Fixed wellbore volume purging techniques or 2) purging until stabilization of water parameters. Each Operator and their contractors/consultants must document in detail their procedures and provide the procedures to the Commission staff upon request.

Most standard monitoring well purging sampling protocols require purging a minimum of three well bore volumes prior to collecting water samples (ASTM D6452-99, 2012). Utilization of domestic wells for sampling should also take into account the normal use patterns of the well, and the recovery rate of the well. Many domestic water wells in Colorado may yield a few hundred gallons or less a day, which may still provide adequate water volumes to the users. As part of the pre-sampling activities, the samplers must determine if purging three well volumes is possible in a reasonable time frame, or if in normal use, the well has been purged frequently. If the well is used frequently and with more than small volumes pumped, it is recommended to use the parameter stabilization technique discussed below with detailed notes recorded on well use.

Purging based on stabilization of indicator parameters, such as temperature, pH, and specific conductance, is more suitable for wells with low yields or in cases where the landowner will not allow purging of three wellbore volumes. Landowners frequently wish to capture the purge water in a cistern or portable tank or to use in watering landscape features such as trees or shrubs.

It is always prudent to take a conservative approach and utilize low flow and/or low volume purging techniques (Puls and Barcelona, 1996) and in the COGCC Raton Basin Phase II report (COGCC, 2008). In either case, on-site collection of water quality parameters such as pH, temperature, specific conductance, dissolved oxygen and turbidity should be monitored during the purge period and recorded.

3.1.1 Water Well Sample Collection

Wells should be sampled immediately following, but no later than 2 hours after purging. The individual collecting the samples should wear disposable, powder free surgical gloves to prevent possible cross contamination of the samples and/or the domestic water supply. The gloves should be changed between sample locations.

Samples should be collected and preserved as unfiltered samples, filtered samples, or dissolved gas samples according to the sampling protocol listed on Table 1. Specific sampling methods for each type of sample are described below.

Unfiltered Samples. Unfiltered samples should be directed from the pump discharge, tap, or bailer directly into the laboratory-supplied sample containers. If sampling from a tap equipped with an aerator, remove the aerator prior to sampling, with landowner consent. The samples should be carefully transferred to the sample containers in a manner that minimizes agitation and aeration. For those sample containers with preservative, special care should be taken to not overfill the container.

Filtered Samples. Samples that will be field filtered must be collected using an in-line disposable 0.45-micron glass-fiber filter. When field filtering is performed, disposable tubing with the in-line filter should be connected to the tap (aerator removed) or pump discharge line. For hand bailed wells, a hand vacuum pump and tubing should be used to draw water from the bailer and push it through the filter. In all cases, the tubing and filter should be flushed and the filtered water should be collected directly into the pre-cleaned sample containers provided by the laboratory. New filters must be used for each sample location.

Filtration at the laboratory after receipt followed by appropriate preservation is an acceptable alternative to field filtration.

Dissolved Gases Samples. There are two methods for collection of water samples for dissolved gas analysis. The first, and preferred method, should be used for samples that are collected from wells using pumps and for effervescent water samples. The second sampling method is a traditional method of sampling and can be used for samples collected with bailers.

Method 1 – Wells with Pumps & Effervescent Samples

Samples may be retrieved from wells with permanent pumps or with temporary sampling pumps. Bailers **should not** be used to collect samples under this method. The samples should be collected in containers supplied by the laboratory (isotopic analysis).

To collect a sample from a tap or sampling pump, fill a clean 5-gallon bucket with water from the tap and set aside. Connect a section of clean 5/8-inch hose to the pump discharge or tap to be sampled. Attach a 6-inch length of small diameter 1/4-inch tubing to the end of the 5/8-inch hose nozzle using a step down valve. Adjust the flow through the valve so that the flow rate through the tubing is low. If necessary, attach a high flow bypass valve with another 6-inch length of 1/4-inch tubing to keep the flow

in the 1/4-inch sample line low. Maintain laminar flow through the hose and tubing assembly at all times. Submerge the closed sample container to the bottom of the 5-gallon bucket. While under water, open the sample container, insert the 1/4-inch sampling line and flush the sample container with water from

the sample line. Monitor the time to allow enough water volume to flow through the container to displace twice the volume of the container. Then slowly remove the sample line.

Isotopic analysis-For sample containers without integral antibacterial preparation, quickly insert a benzalkonium tablet into the container and replace the container screw cap while holding the container under water and as far down to the bottom of the bucket as possible. Effervescent water well samples should be collected with headspace gas.

Non-isotopic analysis- For non-isotopic gas analysis (methane, ethane, and propane) sample collection, no antibacterial tablet is required. The container should be held near the bottom of the bucket while the screw cap is replaced so that any dissolved methane is trapped under the pressure head of the water and the sample is not easily degassed. Make sure that no air is allowed into the sample container during sample collection. After the sample container is capped, take it out of the bucket, invert and inspect it to make certain that there are no bubbles in the container. If bubbles are visible, collect another sample. If it is not possible to collect a gas free sample because the water is too effervescent, a gas headspace in the VOA vial is acceptable, but the laboratory should be notified to analyze the gas headspace to determine the gas composition.

The containers should be packed in a baggie filled with ice, placed in a secure upside down position within a pre-cooled ice chest, and shipped overnight to the analytical laboratory. The samples should be kept on ice or refrigerated until they are analyzed.

Method 2 – Wells Sampled with Bailers

This method is only to be used for wells sampled with bailers. This method should not be used to sample water that effervesces. It should also not be used to collect samples of groundwater known to have high bicarbonate content as the sample preservatives may cause the samples to degas and lose methane.

Under this method, the samples are collected in 45-ml glass VOA vials equipped with a gas-tight Teflon septum containing an HCl or H₂SO₄ preservative. The sample should be collected by slowly filling the vial. Allow the water to run down the inside surface of the vial until the vial is full and a meniscus develops along the upper edge of the sample vial. Remove any bubbles floating on the top of the meniscus with the vial cap, and seal the vial. Be careful to not overfill the sample as over filling will result in a loss of the sample preservative. If that happens, collect a new sample.

After confirming that no gas bubbles are present in the sample vials, the vials should be packed in a baggie filled with ice, placed in a secure upside down position within a pre-cooled ice chest, and shipped to the analytical laboratory. The samples should be kept on ice or refrigerated until they are analyzed.

3.2 Spring or Seep Sampling

The following procedure shall be used for collection of groundwater samples from springs and seeps. Samples should be collected directly from the spring or seep if at all possible.

Prior to sampling, the field parameters (temperature, pH, specific conductance, color/appearance, and odor) should be measured and recorded. Measurements should be made with instruments calibrated in

accordance with manufacturer specifications. A clean, white 5-gallon bucket should be used to monitor the water for color, odor, and effervescence.

Sample Collection. Field personnel collecting the samples should wear disposable powder free surgical gloves to prevent possible contamination of the samples. The gloves should be changed as need and at a minimum following the collection of samples from each sample location. Samples should be collected and preserved using the field methods for unfiltered samples, filtered samples, and dissolved gas samples according to the sampling protocol listed below.

Unfiltered Samples. Unfiltered samples should be collected by submerging a pre-cleaned sample container or dipper directly into the spring and carefully transferring the sample to the laboratory-supplied sample container. If the sampling point is a seep, it may be necessary to use a pre-cleaned glass beaker to collect the water. Care should be taken to prevent the re-suspension of sediment into the water during sampling. The collected sample should be transferred from the dipper or beaker by allowing the water to run down the inside wall of the sample container to minimize sample disturbance. For those sample containers with preservative, special care should be taken to not overfill the container.

Field Filtered Samples. Samples that will be field filtered must be collected using an in-line disposable 0.45-micron glass-fiber filter with subsequent acidification to pH <2 with HNO₃. When field filtering is performed, the required water volume should be collected from the spring or seep using the dipper or beaker and placed in a pre-cleaned bucket. A hand vacuum pump and tubing should then be used to draw water from the bucket and push it through the in-line filter and into the sample container. In all cases, the tubing and filter should be flushed prior to sample collection and the filtered water should be collected directly into the pre-cleaned sample containers provided by the laboratory. New filters must be used for each sample location. For those sample containers with preservative, special care should be taken to not overfill the container. Filtration at the laboratory after receipt with subsequent acidification is an acceptable alternative to field filtration.

Dissolved Gases Sampling. There are two methods for collection of water samples for dissolved gases analysis. The first method can be used for most samples, including all effervescent water samples. The second sampling method is an alternate method of sampling which is expected to be less useful in Colorado due to relatively high alkalinity in many ground waters.

Method 1

This method is for most samples, including all effervescent samples. The samples should be collected in 40-mL VOA vials equipped with a Teflon gas-tight septum (methane, ethane, propane analysis) or other specialized glass containers supplied by the laboratory (isotopic analysis).

To collect a sample of spring or seep water, create a pool of water in a depression as close to the discharge point as possible. Allow the flow of water from the spring or seep to flush suspended sediment from the pool prior to sampling. Submerge a 500 mL beaker in the water. Allow water to slowly flow into the beaker until it is filled. Avoid getting suspended sediment into the beaker by allowing water to flow into the beaker close to the air-water interface. Keeping the beaker submerged in the pool of water, submerge the sample container in the beaker upside down, open it, and allow water to fill the sample container slowly by gradually increasing the tilt of the sample container. For the

isotopic analysis, for sample containers without integral antibacterial preparation, quickly insert a benzalkonium tablet into the container and replace the container screw cap while holding the container

under water and as far down to the bottom of the beaker as possible. For non-isotopic gas analysis or the methane, ethane, propane sample, the benzalkonium tablet is not required.

Seal the sample container and check for bubbles. If it is not possible to collect a gas free sample because the water is too effervescent, a gas headspace in the VOA vial is acceptable, but the laboratory should be notified to analyze the gas headspace to determine the gas composition. Empty the beaker outside of the pool and repeat the sampling procedure as necessary until all sample containers have been collected.

The sample containers should be packed in a baggie filled with ice, placed in a secure upside down position within a pre-cooled ice chest, and shipped overnight to the analytical laboratory. The samples should be kept on ice or refrigerated until they are analyzed, and the analyses should be completed no later than 48 hours after the samples are collected.

Method 2

This method can be used when site conditions prevent collection of the sample using Method 1 described above. Extreme caution should be used if this method is used to collect samples where water effervesces. It should also not be used to collect samples of groundwater known to have high bicarbonate content as the sample preservatives may cause the samples to degas and lose methane. Under this method, the samples are collected in 40-mL glass VOA vials equipped with a Teflon gas-tight septum containing HCl as preservative. The sample should be collected by using the dipper or beaker to retrieve the sample and slowly transfer it to the vial. Allow the water to run down the inside surface of the vial until the vial is full and a meniscus develops along the upper edge of the sample vial. Remove any bubbles floating on the top of the meniscus with the vial cap, and seal the vial. Be careful to not overfill the sample as over filling will result in a loss of the sample preservative. If that happens, collect a new sample. After collecting the sample, invert the VOA vial to confirm there are no air bubbles in the vial. If an air bubble is present, collect a new sample.

After confirming that no gas bubbles are present in the sample vials, the vials should be packed in a baggie filled with ice, placed in a secure upside down position within a pre-cooled ice chest, and shipped to the analytical laboratory. The samples should be kept on ice or refrigerated until they are analyzed.

4.0 Field Analyses and Observations

Physically or chemically unstable analytes should be measured in the field, rather than solely at a laboratory. Some examples of potentially unstable parameters include pH, dissolved oxygen, and temperature. Although the specific conductance (i.e., electrical conductance) of most groundwater samples should be relatively stable during and after sampling, it is required that specific conductance be measured in the field both as part of the evaluation of the effectiveness and completeness of the purge and as a reportable analyte for the groundwater at the time of sampling. Submission to the COGCC Environmental Database of the pH and the temperature of groundwater at the time of sampling is also required. Other recommended field analyses are dissolved oxygen content of the groundwater as well as the turbidity of the groundwater at the time of sampling. Measurement of the oxidation reduction potential of groundwater at the time of sampling is also recommended if an in-line flow cell for measurements is used for analysis. Any field analyses performed must be reported.

Calibration of field instrumentation should follow at a minimum the manufacturer's guidance. Daily calibration and checks of reference solutions for pH and conductivity meters/electrodes is required. Temperature corrections of pH and conductivity measurements are typically done by meters equipped with temperature probes, but if the pH and specific conductance meters are not capable of performing temperature corrections to 25°C, then manual corrections must be performed based on the measured temperature of the groundwater before data is entered in the COGCC Environmental Database.

The required field parameters and field observation data are summarized in the following table.

Table 4-1 Field Parameters and Field Observation Data

Analyte	Method(s)	Lower Limit of Quantification
volume water purged	Measured volume	NA
pH	Electrometric	NA
specific conductance	Electrometric	NA
temperature (water)		NA
odor	Olfactory	NA
water color	Visual	NA
effervescence	Visual	NA
sediment or turbidity	Visual or Light-scattering instrument	NA
%LEL or %CH ₄	4-gas meter	2%LEL

5.0 Sample Preservation and Handling

Preservation of samples prior to shipment to a laboratory is done in several ways depending on analyte and method guidance. Recommended preservation for many organic analytes may be as simple as storing and shipping at 4°C with a range of acceptable temperatures on receipt at a lab of 0-6°C. Other samples, such as water samples for analysis of volatile organic compounds, should follow the preservation guidance developed by the Colorado Department of Public Health and Environment (1998).

Table 5-1 provides a more complete summary of bottle types used for sample collection and storage and preservation techniques by method or type of analyte. Laboratory specific requirements may supersede the procedures summarized in Table 5-1.

Table 5-1 Sample Preservation and Handling

Analyte	Container and Preservative	Laboratory Method(s)	Holding Time (days)
pH	Plastic, 4°C	SM4500-H+, EPA 150.1 or SW-846 9040C	As soon as practicable
Specific Conductance		SM-2510 SW-846 9050A	28 days
Total Dissolved Solids		SM-2540C	7 days
Dissolved Gases	Glass 40ml VOA vial may be preserved with HCl to pH <2	RSK-175(mod)	Not established, but 14 days assumed
Alkalinity	Plastic, 4°C	SM2320B	14
Major Anions Br, Cl, F, SO ₄ NO ₃ and NO ₂ (individually)	Plastic, 4°C	EPA 300.0, SW-846 9056	28 nitrite 48 hours
Nitrate/Nitrite	Plastic 4°C and H ₂ SO ₄ if analysis not within 24 hours	353.3	28 days
Phosphorous	Plastic	SM-4500-P 365.3	
Dissolved Major Cations Ca, Fe, Mg, Mn, K, Na	Plastic (0.45µm filtered in field and acidified to pH<2 with HNO ₃) or shipped unfiltered at ambient pH in plastic container and filtered and acidified on receipt at	200.7/200.8 SW-846 6010C/6020A	180
Other Elements Ba, B, Se, Sr			

	laboratory		
TPH (extractable) C10-C26 range	Amber glass, 4°C	SW-846 8015C and modifications	7
TPH (volatile) (2-methylpentane to 1,2,4-trimethylbenzene range	Glass 40ml VOA vial, pH <2 with HCl or as per CDPHE guidance	SW-846 8015C and modifications	14
benzene, toluene, ethylbenzene, o-xylene, m-+p-xylenes, and total xylenes		SW-846 8260B SW-846 8260C	14
Bacterial Activity Reaction Tests	Sterile plastic	BART documentation	As soon as practicable
Gas Composition and Isotopic Ratio Analyses	1 liter poly bottle with septa cap 4°C, bactericide (benzalkonium chloride)	Laboratory Specific SOPs	Not established but 28 days assumed

All sample containers should be pre-labeled using an indelible ink pen. Sample container labels will include the sample identification number (Facility ID created in the COGCC Environmental Database), date and time the sample is collected, requested laboratory analyses, and sampler initials. Labels can be covered with clear plastic tape after being filled out to keep the ink from running due to contact with water during sampling and moisture in the sample shipping cooler. A Facility ID must be used so that the EDD can be uploaded into the COGCC Environmental Database. (COGA, 2011)

After the samples have been collected they should be immediately placed on ice in a pre-cooled insulated ice chest. The cooler should be kept at or below 4°C during storage and shipment to the analytical laboratory. Each cooler should be packed and sealed in a manner to help minimize potential damage to sample containers, help maintain the required temperature, and to help prevent tampering. The coolers should be clearly labeled in order to expedite delivery to the selected laboratory and shipped in a timely manner (preferably, nightly) to minimize the potential for failure to meet method specified hold times.

6.0 Chain of Custody Documentation and Records Management

Samples must be handled, stored, and shipped in accordance with Chain-of-Custody (COC) procedures. COC procedures require that all samples be maintained under the control of the sampler (i.e., in sight or in a secure, locked environment controlled by the sampler) from the time of collection until delivery to the analytical laboratory or release to a third-party shipping company. Request for Analysis and Custody forms should be provided by the analytical laboratory and filled out completely. The sampler must sign the COC form releasing the samples to the laboratory at the time of delivery to the lab or at the time of release to the shipping company. The laboratory must sign the COC form accepting custody of the samples at the time of delivery by the sampler or the shipping company. The COC form, Request for Analysis, and any other documentation should be sealed in a zipper lock plastic bag and taped to the inside top of the cooler. The cooler should be secured with shipping tape and custody seals (adhesive labels signed and dated by the sampler) should be securely placed on the cooler such that the cooler cannot be opened without breaking the seal (COGA, 2011).

Retention of records is an essential part of this program. Records of laboratory analyses will be transferred to COGCC Environmental Database within 3 months of sampling including EDD and PDF reports. Other records such as field observations and measurements will be transferred to COGCC Environmental Database within 3 months of sampling.

7.0 Analytical Procedures and Quantitation Limits for Laboratory and Field Methods

Analysis of samples must be by laboratories accredited by the National Environmental Laboratory Accreditation Program (NELAP) in general and more importantly for analytical procedures and analytes of concern in this SAP. NELAP accreditation extends to both matrix such as groundwater which has been listed as non-potable water (NPW) matrix in NELAP terminology as well as to analytical technology such as gas chromatography/mass spectrometry (GC/MS) and to individual analytes such as benzene or toluene. An example is that an acceptable lab would be accredited for analysis of benzene and toluene by purge and trap GC/MS techniques for the non-potable water matrix.

State or national accreditation may not be possible for some specialized analyses such as isotopic ratio determination of the carbon and hydrogen present in methane which is one exception to the statement above. State or national accreditation for analysis of dissolved gases is another field of testing in which there may be exceptions to the requirement. There also may be an exception to the accreditation requirement for the use of bacterial activity reaction test (BART) kits.

Analytes, appropriate methodology, and expected achievable detection limits are included in Table 7-1 below. There are many methods used for determination of the analytes in the anions and general water quality parameters. Please consult with COGCC before use of other methods than those listed in any of the table below.

Table 7-1 Analytical Parameters

Anions and General Water Quality Parameters (Unfiltered in Field)		
Analyte	Method(s)	Lower Limit of Quantification
pH	SM-4500-H+ 150.1 SW-846 9040C	NA
specific conductance	SM-2510 SW-846 9050A	NA
total dissolved solids	SM-2540C	10mg/l
total alkalinity as CaCO3	SM 2320	10mg/l
bicarbonate alkalinity as CaCO3		10mg/l
carbonate alkalinity as CaCO3		10mg/l
bromide	300.0 SW-846 9056	0.2mg/l
chloride		0.1mg/l
fluoride		0.2mg/l
sulfate		5mg/l
nitrate (as individual analyte instead of combined analysis)		0.1mg/l
nitrite (as individual analyte instead of combined analysis)		0.1mg/l
nitrate and nitrite as N	353.3	0.1mg/l
phosphorous	SM-4500-P 365.3	0.05mg/l
Dissolved Gases		
Analyte	Method(s)	Lower Limit of Quantification
methane	RSK SOP 175 and modifications	0.005mg/l
ethane		0.005mg/l
propane		0.005mg/l
Well Bore Bacterial Indicators		
iron related bacteria	BART manuals	1 day to reaction or 100cfu/100ml
sulfur related bacteria		
slime forming bacteria		

Table 7-1 Continued

Metals and Other Elements (Filtered in Lab or in Field)		
Analyte (dissolved)	Method(s)	Lower Limit of Quantification
calcium	200.7/200.8	1mg/l
iron	or	0.1mg/l
magnesium	SW-846 6010C/SW-846	1mg/l
manganese	6020A	0.01mg/l
potassium		1mg/l
sodium		1mg/l
barium		0.001mg/l
boron		0.1mg/l
selenium		0.001mg/l
strontium		0.01mg/l
Dissolved fraction metals(filtered and acidified at lab or filtered and acidified in field)		
Organic Compounds and Indicators (Unfiltered in Field)		
benzene	SW-846 8260B	1µg/l
toluene	Or	1µg/l
ethylbenzene	SW-846 8260C	1µg/l
o-xylene		1µg/l
m-xylene and p-xylene		1µg/l
total xylenes		1µg/l
total petroleum hydrocarbons (see fraction description below)		
TPH-volatile hydrocarbons (from 2-methylpentane-1,2,4-trimethylbenzene)	SW-846 8015C and modifications	0.05mg/l
TPH-extractable hydrocarbons (from C10-C28 alkanes)	SW-846 8015C and modifications	0.5mg/l

Table 7-1 Continued

Gas Composition and Isotopic Analyses (Unfiltered in Field)		
Analyte	Method(s)	Lower Limit of Quantification
hydrogen	GC/TCD*	0.0001mol%
argon	GC/TCD*	0.0001mol%
oxygen	GC/TCD*	0.0001mol%
nitrogen	GC/TCD*	0.0001mol%
carbon dioxide	GC/TCD*	0.0001mol%
methane	GC/FID**	0.0001mol%
ethane	GC/FID**	0.0001mol%
ethene	GC/FID**	0.0001mol%
propane	GC/FID**	0.0001mol%
propene	GC/FID**	0.0001mol%
iso-butane	GC/FID**	0.0001mol%
n-butane	GC/FID**	0.0001mol%
iso-pentane	GC/FID**	0.0001mol%
n-pentane	GC/FID**	0.0001mol%
hexanes +	GC/FID**	0.0001mol%
$\delta^{13}\text{C CH}_4$ (VPDB)	IRMS***	NA
$\delta\text{D CH}_4$ (VSMOW)	IRMS***	NA

*GC/TCD gas chromatography thermal conductivity detector

**GC/FID gas chromatography flame ionization detector

***IRMS -Isotope-ratio mass spectrometry

8.0 Field and Laboratory Quality Assurance/Quality Control

Data integrity will be assured and verified through:

- 1) Field sampling practices that comply with this Sampling and Analysis Plan,
- 2) Sample analysis by accredited analytical laboratories,
- 3) Laboratory practices which follow approved analytical methods,
- 4) When available, collection and analysis of field quality assurance samples, and
- 5) Data quality reviews of the laboratory and field practices.

All samples will be analyzed by laboratories that are accredited by the National Environmental Laboratory Accreditation Program for the analytical procedures that will be used for sample analysis, where such accreditation exists. As specified in Table 1, U.S. Environmental Protection Agency (EPA) analytical methods such as Test Methods for Evaluating Solid Waste SW-846 or other methods such as

Standard Methods for the Examination of Water and Wastewater, which are recognized standard industry practice, will be used for sample analysis (COGA, 2011).

Where EPA-approved methods are not available, standard industry practices will be followed. Laboratory quality assurance samples, such as matrix spike/matrix spike duplicates, will be prepared in the laboratory and analyzed as specified by the designated method. Laboratory quality assurance sample results must be reported along with the original sample results on the laboratory report, and an analytical narrative shall be provided as part of the laboratory report.

8.1 Field Control Samples

Field quality control samples shall be collected following Operator and/or their environmental consultant protocols. All field quality control samples collected shall be submitted to the COGCC. Generally recommended practices are provided below:

Field Duplicate Samples. One complete set of duplicate samples should be collected for every twenty groundwater samples collected by the operator, but not less than one per year. Duplicate samples should be collected immediately following the original sample using identical sampling methods. Each duplicate sample should be given a fictitious sample identification number, which is recorded on the Field Data Sheet, and then submitted, to the laboratory as a blind duplicate. Duplicate samples should be analyzed for the same parameters as the original sample.

Data Quality Objectives- Field duplicate sample results should be evaluated based on the Relative Percent Difference (RPD) between the sample result and the duplicate. RPD is calculated as:

$$RPD = \frac{|S - D|}{0.5(S + D)} \times 100$$

Where,

RPD = Relative Percent Difference

|S-D| = Absolute value of S - D

S = Sample Result (original)

D = Duplicate Result

A data quality objective of $RPD \leq 20\%$ will be used for original and duplicate sample values that are \geq five times (5x) the practical quantitation limit (PQL, COGA, 2011).

Field Equipment Blanks. Equipment blanks should be collected if decontaminated sampling equipment (e.g. sampling pump with dedicated discharge hose, sample dipper, beaker, etc.), is used to collect the samples. One equipment blank sample shall be collected for every ten (10) groundwater samples taken with decontaminated sampling equipment by the operator, but no less than one per year. Equipment blanks should be collected immediately following equipment decontamination by running distilled or deionized water through or over the sampling equipment and collecting the rinse water in the sample container. Equipment blanks should be analyzed for major cations (dissolved) and BTEX (COGA, 2011).

Data Quality Objectives- Equipment blanks should have individual cation and BTEX constituent concentrations below method detection limits.

Trip Blanks. Trip blanks should be used to assess contamination introduced during shipping and field handling procedures. Trip blanks should be collected a frequency of 1 blank/cooler containing volatiles. The trip blanks should consist of a clean sample matrix that is prepared in the laboratory, transported to the sampling site and transported back to the laboratory without having been exposed to sampling procedures. The trip blanks should only be analyzed only for volatile compounds.

Data Quality Objectives- Trip Blanks should have individual VOC constituent concentrations below method detection limits.

Field Blanks. Field blanks will only be collected if the sampling technician believes that site conditions might cause the sample to become cross contaminated by VOCs or methane (e.g. the well is located adjacent to hydrocarbon or methane storage or fueling area). Field blanks will be collected by filling a clean glass VOA vial equipped with a Teflon gas-tight septum with distilled water and leaving the sample container open during the entire period of volatile sample collection. Immediately prior to capping, a few drops of distilled water should be added to the vial to create a positive meniscus. The vial should then be capped and inverted to check for air bubbles. If bubbles are present, the vial should be opened, additional water should be added, and the vial should be resealed and checked again for air bubbles. This procedure should be repeated until a bubble-free container is obtained. Field blanks should be analyzed for BTEX and dissolved gasses (methane, ethane, and propane).

Data Quality Objectives- BTEX and dissolved gases concentrations should be below method detection limits in field blanks.

8.2 Data quality reviews

Data quality reviews should be performed after all data reports have been received from the laboratory. Data quality reviews should be documented on a Data Quality Review Sheet (Appendix B) which should

be stored in the project files with the Field Sampling Data Sheet and the laboratory data reports analytical data. The objective of the Data Quality Review Sheet is to confirm that all data were properly collected and are suitable for release to COGCC (with land owner approval). The data quality review should include:

- Review all field sampling data sheets to confirm that:
 - The wells were properly purged,
 - The flow rate was reduced prior to sampling,
 - The water quality field parameters had stabilized prior to sampling, and
 - No conditions were noted that suggest the samples may not be representative.
- Review all laboratory data reports to confirm that:
 - Proper custody was maintained from the time of sampling until receipt by the laboratory.
 - All samples were analyzed for the requested analyses.
 - Proper laboratory methods were used.
 - All sample holding times were met.
 - Laboratory quality assurance samples such as matrix spikes and matrix spike duplicates were collected and analyzed according to the laboratory method, and all laboratory quality control sample results were within method acceptance limits).
 - All field quality control samples meet the data quality objectives listed above.
- Specify corrective actions needed and dates by when those corrective actions should be completed.
- Certification by the data reviewer confirming that the data were collected in accordance with the SAP and that the data are suitable for incorporation into the COGCC database.

9.0 Evaluation of Data Quality

Operators or their consultants are expected to review field sampling records to ensure that samples were collected in accordance with this SAP or re-sampling may be required. Operators are expected to review chain of custody records and lab's condition of samples upon receipt to ensure the use of proper sample containers and preservatives by the samplers.

Operators or their consultants/contractors are expected to do basic review of data. At a minimum the calculation of cation-anion balance must be done and reviewed with general acceptance levels of <10% difference. Corrective actions may include re-analysis of samples already in custody of a lab or re-sampling and re-analysis of new sample aliquots.

Other measures of data quality also expected are relatively simple calculations such as calculation of specific conductance from pH and the concentration of major anions and major cations and calculation of total dissolved solids from the concentrations of major cations and anions followed by comparison of the calculated values to the measured values of these two water quality indicators. In general it is expected that data will not be submitted from labs to operators or their consultants/contractors if major

elements of lab QC were outside criteria such as low recovery of target compounds in a laboratory control sample associated with an extraction batch the groundwater samples are part of. Operators and their consultants/contractors do need to perform basic review of lab data to ensure that only data of good quality is submitted to the COGCC (COGA, 2011).

10.0 Health and Safety

The safety of personnel and landowners participating in activities at a water well sampling must be addressed by development of a health and safety protocol to be followed at sample sites. General aspects of the safety plan need to address what personal protective equipment (PPE), such as hard hats, safety glasses, chemical resistant gloves, sturdy boots, long pants, etc., should be used and under what conditions during the collection of samples. While at the home and water well, the field staff should explain to the landowner or representative what PPE is required at their home and why it is required (COGA, 2011).

11.0 Data Submission

The operator will enter or will have entered the following information from each sampling event for electronic submission and uploading into the COGCC's Environmental Database:

- Facility ID (already in existence or newly created) in the COGCC system
- Division of Water Resources well permit and receipt number for the sampling location (if permitted)
- Name and address of water source owner
- GPS coordinates for the water source (wellhead or spring) and need to be in decimal degrees of latitude and longitude using the NAD83 reference.
- API number(s) for the associated oil and gas well(s)
- Sample type – initial or baseline, one year post-completion or five year post-completion
- Date and time each sample was collected
- Results of field monitoring and observations must be submitted electronically to the COGCC. A simplified spreadsheet EDD can be utilized for this purpose.

All samples submitted to the COGCC shall include the following information and File types:

- 1) Correctly formatted Laboratory EDD (Either XML or Excel),
- 2) A PDF copy of the complete lab report including QA/QC data, and
- 3) A PDF copy of the Field Data sheet that includes all the location information purge information and field parameters collected in the field.

11.1 Environmental Database

Laboratory results for each sample collected will be submitted using the laboratory's XML or spreadsheet EDD formatted appropriately for the COGCC Environmental Database. The EDD must include quality control data such as results of method blanks, results of matrix spike or laboratory control samples, results of duplicate samples and surrogate or tracer recoveries. At this time the database cannot accommodate initial or continuing calibration information and the acceptable EDD format does not include that aspect of laboratory quality control practices. The laboratories PDF formatted report of results must also be uploaded to the database.

Access to the portion of the database where facilities can be created and data uploaded is controlled and credentials must be obtained prior to any attempt to use the Environmental Database. Operators or their designated agents (i.e., contractors, consultants or laboratories) can obtain necessary logon credentials in a manner similar to that used in E-Forms.

11.1.1 Electronic Data Deliverables

There are two accepted versions of the COGCC Electronic Data Deliverable (EDD) that may be uploaded to the COGCC Environmental database. One is an XML EDD that was based on the EPAs WQX XML

schema. The second is a Microsoft Excel based EDD. Both the XML based and Excel based EDD are in hierarchal format. The EDDs do not look like nor do they function like a common flat file EDD. The EDDS are designed to transfer data to the COGCC database and should not be used as an analytical tool by themselves.

Prior to being accepted into the database the EDDs go through a rigorous automated QA/QC check. If the information provided in the EDD fails to meet the valid value requirements the EDD will be rejected. If an EDD is rejected it will necessary to make corrections and resubmit the EDD. Once an EDD has been accepted by the database COGCC staff will conduct a brief review of the information in the EDD. Once the review process has been completed the EDD will be verified and saved into the database.

Data received by the COGCC will be posted to the COGCC website and be available for public review. Once verification has been completed by the COGCC Staff the data will be available within a couple of hours.

Help Regarding the EDD requirements can be found at:
http://cogcc.state.co.us/COGIS_Help/EnviroDB/EnviroDB.htm

Help regarding the EDD upload process can be found at:
http://cogcc.state.co.us/COGIS_Help/SampleData.pdf

Attachment 1
General References for Groundwater Sampling

Attachment 1

General References for Groundwater Sampling

COGCC Report 2008, Phase II Seep Investigation Final Report.PDF.

ASTM D4448-01 (reapproved 2013), Standard Guide for Sampling Ground-Water Monitoring Wells.

ASTM D6089-97 (reapproved 2010), Standard Guide for Documenting a Groundwater Sampling Event.

ASTM D6452-99 (reapproved 2012), Standard Guide for Purging Methods for Wells Used for Groundwater Quality Investigations.

ASTM D7069-04 (reapproved 2010), Standard Guide for Field Quality Assurance in a Groundwater Sampling Event.

Colorado Department of Public Health & Environment (CDPHE). 1998. Groundwater VOC Sample Preservation Policy.

Colorado Oil & Gas Association (2011), Voluntary Baseline Groundwater Quality Sampling Program – Example Sampling and Analysis Plan.

Gorody, A.W, 2005, What's In Your Water Well?, presented by Dr. Anthony W. Gorody at the 11/18/2005 North West Colorado Oil and Gas Forum.

LT Environmental, (2007), Phase II Raton Basin Gas Seep Investigation, COGCC Project 1925.

Puls, Robert W., and Barcelona, Michael J., (1995) Low-Flow (Minimal Drawdown) Ground-water Sampling Procedures, EPA/540/S-95/504.

U.S. EPA September 2004, U.S.EPA REGION 9 FIELD SAMPLING GUIDANCE DOCUMENT #1220 GROUNDWATER WELL SAMPLING.

U.S. Geological Survey, 2006, Collection of water samples (ver. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, September 2006, accessed May 6, 2013, at <http://pubs.water.usgs.gov/twri9A4/>

Attachment 2
Example Sampling Documentation Work Sheet

Field Sampling Data Sheet

COGCC Facility ID: _____
Site Address: _____
Site Contact: _____
Phone #: _____
Date of Sample: _____
Sample Type (baseline, post-drill, complaint): _____
Oil & Gas Well API Number: _____

Property Owner Name: _____
Property Owner Phone Number: _____
Property Owner Mailing Address: _____

Individuals Present (Who was on-site during the sampling event?)

Water Well Information from Permit Records

Permit No.: _____
Receipt No.: _____
Total Depth (ft.): _____
Static Water Level (ft.): _____
Yield (GPM): _____
Well Diameter (in.): _____

Water Well Information Onsite

GPS Location (field): _____
GPS Location (post-processed): _____
Water well casing height (in.): _____
Ground Elevation (ft.): _____ How determined: _____
Approximate distance to the Oil & Gas well pad: _____
%LEL at wellhead (if measured): _____
%CH₄ at wellhead (if measured): _____
Weather conditions: _____
Photo(s) Taken? **Y N**
Handed Out Landowner Introduction Letter? **Y N**
Handed Out FAQ Sheet? **Y N**
Handed Out "How Well Do You Know Your Water Well" Pamphlet? **Y N**

Where was the Sample Taken? _____
(Outside Tap, Well House, Kitchen Tap, Spring, Seep, etc.)

Condition of the Well, Spring or Seep (Wellhead sealed? Does the ground slope away from the well?, Visible contamination of spring/seep?, etc.):

Landowner Comments on Water Quality: _____

Time	Purge Vol. (gal)	pH	Conductivity	Temp	Color/Appearance /Sediment	Odor	Bubbles/Effervescence?

Sampling flow rate (gpm): _____

[illegible]

 Sampler's Signature _____ Date: _____