COLORADO
Oil & Gas Conservation Commission
Department of Natural Resources

Model Sampling and Analysis Plan

Rule 615

Colorado Oil and Gas Conservation Commission

Version 3

January 2021

APEX

2019 Review and Revisions by
Apex Companies, LLC & COGCC staff

REVISION HISTORY

Effective Date	Reviewer/Approver	Description (Review or Nature of Revisions)
May 1, 2013	COGCC	Version 1 SAP approval and implementation
August 2019	H. Shideman (Apex) P. Gintautas (COGCC) A. Koepsell (COGCC)	Version 2 SAP review and updates
January 2021	COGCC	Version 3 SAP (rule change to 615)

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1.0 – INTRODUCTION

The Colorado Oil and Gas Conservation Commission ("COGCC") has prepared this model sampling and analysis plan ("SAP") for parties who engage in sampling and analysis activities for Rule 615 – Groundwater Baseline Sampling and Monitoring. This Rule applies to oil Wells, gas Wells ("Oil and Gas Wells"), Multi-Well Sites, and Class II UIC Wells for which a Form 2, Application for Permit to Drill (Form 2) or Form 4, Notice to Recomplete (Form 4), is submitted or pending on or after January 15, 2021. Oil and Gas Wells, Multi-Well Sites, and Class II UIC Wells operating under a Form 2 approved prior to January 15, 2021, will continue to follow the sampling protocols required by their permits at the time that the Form 2 was approved. This SAP 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 rules.

The Commission moved prior Rule 609 to Rule 615. The Commission expanded the scope of the Rule to include recompleted Wells, coalbed methane Wells regulated under prior Rule 608.b, Wells in the Greater Wattenberg Area previously regulated under prior Rule 318A.f, and Wells previously regulated under Commission orders for the Northern San Juan Basin. By consolidating all Groundwater baseline sampling rules into a single Rule, the Commission intends to provide simpler and clearer standards for Operators, local governments, and the general public, while also ensuring that Groundwater throughout the state receives the same baseline protections.

The timing and frequency of the sampling is described in the Rule 615 and will not be described in detail in this SAP. A separate document has been prepared to provide guidance related to selection of sampling sites as well as timing and frequency of sampling and analysis.

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 from representative aliquots of Groundwater for analysis. It is important to use well documented analytical processes so that different laboratories are capable of producing comparable accurate data. The goal of any environmental sampling program is to ensure precision, accuracy, representativeness, comparability, and completeness of the data. These principals must be carried forward for sampling and analysis efforts designed to meet requirements of Rule 615. Equally important is the 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 an available water source ("AWS") and its current use, along with field observations about the water sample, such as effervescence, reported taste, and odor, are also important. The field observations acquired at each site must be recorded and submitted into the COENV database in addition to the laboratory generated analytical data.

2.0 - PRE-SAMPLING ACTIVITIES

Water sources will be selected based on the definition in the COGCC 100 Series Definitions and further refined based on criteria contained in Rules 614 and 615. Water sources within the areas where sampling is required can be identified using the COGCC GIS Online interactive map as outlined in the COGCC guidance to operators (COGCC, 2021). An oil and gas operator (Operator) must make good faith efforts to identify the owner of the water source and obtain permission for site access, including the acknowledgement that the sample data will be accessible to the public through the COGCC website.

An Operator will review Division of Water Resources ("DWR") online permit records for water source construction, depth, casing diameter, reported static water level, and initial flow rate/yield prior to the water source sampling. During the initial sampling, the location of the water source must be surveyed in accordance with COGCC Rule 216. Confirmation of the location of the water source should be confirmed during subsequent sampling events.

Before or during the sampling, the landowner should be interviewed regarding current water source conditions and knowledge of any discrepancies between the DWR records and the current water source configuration. Data should also be collected on recent water source use(s) and water quality concerns such as observations or recent changes in appearance, taste, and odor.

3.0 - SAMPLE COLLECTION

All samples will be collected by individuals experienced with water quality sampling and sent to a laboratory accredited by the National Environmental Laboratory Accreditation Program ("NELAP") 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

(Reapproved 2019) Standard Guide for Sampling Ground-Water Monitoring Wells, ASTM D5358-93 (2019) Standard Practice for Sampling with a Dipper or Pond Sampler, and/or ASTM D5088-15a (2015) Standard Practice for Decontamination of Field Equipment used at Waste Sites.

A complete set of samples should be obtained from each available water source, as specified in Rule 615, and at a minimum analyzed for the required analytes listed in Table 3-1.

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

In order to prevent cross contamination of samples, disposable sampling equipment should be used whenever possible. Samples will be placed in clean laboratory-supplied, disposable polyethylene or glass bottles containing the appropriate preservative aliquot, as applicable. All non-disposable equipment (e.g., sampling pumps with non-disposable tubing, dippers, beakers, sample collection tubing, valve assemblies, etc.) and instruments that contact the samples must be decontaminated prior to use and between sample locations using the following ASTM D5088-15a procedures:

1) Remove gross contamination by dry brushing followed by a tap water rinse;
2) Wash with a laboratory grade detergent solution, such as Alconox® or equivalent;
3) Detergent solutions should be circulated through sampling pumps and non-disposable discharge tubing to decontaminate this equipment;
4) Rinse with tap water;
5) Rinse with distilled or deionized water;
6) Air dry; and
7) 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 during mobilization to the next site and prior to use.

Initial decontamination should be performed prior to arriving at a sampling location. All decontamination solutions should be collected, properly disposed, and documented in accordance with applicable federal, state, and local regulations.

Table 3-1 – Minimum Required Laboratory Analytes

Analyte	Filter, Container, and Preservative	Lab Method	Holding Time	LLQ
General Water Quality Parameters				
pH	Unfiltered, Plastic, Unpreserved & 4°C	SM4500-H+ or SW846 9040C	< 15 minutes	NA
Specific Conductance (Conductivity)		SM2510B or SW846 9050A	28 days	NA
Solids, Total Dissolved (TDS)		SM2540C	7 days	10 mg/L
Bicarbonate, Carbonate and Total Alkalinity (as $CaCO_3$)		SM2320B	14 days	10 mg/L
Major Anions				
Bromide (Br)	Unfiltered, Plastic, Unpreserved & 4°C	EPA 300.0 or SW846 9056A	28 days	0.2 mg/L
Chloride (Cl)		EPA 300.0 or SW846 9056A	28 days	0.1 mg/L
Fluoride (F)		EPA 300.0 or SW846 9056A	28 days	0.2 mg/L
Sulfate (SO_4^{2})		EPA 300.0 or SW846 9056A	28 days	5 mg/L
Phosphorus (P)		EPA 365.1 or SM4500-PA	NA	0.05 mg/L
Nitrate as N (NO_3)		EPA 300.0 or SW846 9056A	48 hours	0.1 mg/L
Nitrite as N (NO_2)		EPA 300.0 or SW846 9056A	48 hours	0.1 mg/L
Nitrate & Nitrite as N		By summation of results of NO_3 and NO_2 analyses by 300.0 or 9056A (above)		
Nitrate & Nitrite as N	Unfiltered, Plastic, preserved with H_2SO_4 & 4°C unless analyzed in 24 hours of collection	SM4500-NO_3F or EPA353.3	28 days	0.1 mg/L
Major Cations (dissolved)				
Calcium (Ca)	Filtered (0.45µm) at lab, Plastic, HNO_3 Preserved to pH<2 at lab & 4°C May also be filtered in the field and then immediately preserved to pH<2	EPA 200.7/200.8 or SW846 6010D/SW846 6020A	180 days	1 mg/L
Iron (Fe)		EPA 200.7/200.8 or SW846 6010D/SW846 6020A	180 days	0.1 mg/L
Magnesium (Mg)		EPA 200.7/200.8 or SW846 6010D/SW846 6020A	180 days	1 mg/L
Manganese (Mn)		EPA 200.7/200.8 or SW846 6010D/SW846 6020A	180 days	0.1 mg/L
Potassium (K)		EPA 200.7/200.8 or SW846 6010D/SW846 6020A	180 days	1 mg/L
Sodium (Na)		EPA 200.7/200.8 or SW846 6010D/SW846 6020A	180 days	1 mg/L
General Water Quality Parameters				
Barium (Ba)	Filtered (0.45µm) at lab, Plastic, HNO_3 Preserved to pH<2 at lab & 4°C May also be filtered in the field and then immediately preserved to pH<2	EPA 200.7/200.8 or SW846 6010D/SW846 6020A	180 days	0.001 mg/L
Boron (B)		EPA 200.7/200.8 or SW846 6010D/SW846 6020A	180 days	0.1 mg/L
Selenium (Se)		EPA 200.7/200.8 or SW846 6010D/SW846 6020A	180 days	0.001 mg/L
Strontium (Sr)		EPA 200.7/200.8 or SW846 6010D/SW846 6020A	180 days	0.1 mg/L

NA - Not Applicable

Table 3-2 – Minimum Required Laboratory Analytes (continued)

Analyte	Filter, Container, and Preservative	Lab Method	Holding Time	LLQ
Dissolved Gases				
Methane (CH_4)	Preferred – In-line sample collection system container such as Isoflask® with bactericide present in sampling device, per laboratory specifications Alternate – Unfiltered, 40ml VOA vial, may be preserved with HCl to pH<2 & 4°C	Lab-specific SOP for analysis if in-line sample collection vessel such as IsoFlask® used.		
Ethane (C_2H_6)		RSK175 (for use with 40ml vials)	14 days preserved 7 days non-preserved recommend 48 hours	0.005mg/L
Propane (C_3H_8)				
Compositional and Isotopic Analysis (if [CH4, Dissolved]>1mg/L)				
Fixed Gases C1-C6 (Gas Chromatograph Concentrations of N_2, O_2, CO_2, Ar, H_2, He, CH_4, C_2H_6, C_3H_8, iC_4H_{10}, nC_4H_{10}, iC_5H_{12}, nC_5H_{12}, iC_4, nC_4, iC_5, nC_5, and C_6+).	Preferred – In-line sample collection system container such as IsoFlask® with bactericide in sampling device, per laboratory specifications Alternate – 1000ml plastic with septa sealed lid with bactericide preservative added by lab in gel capsule	Lab Specific SOP	6 weeks	NA
Mass spectrometric determination of $\delta^{13}C$ of CH_4, and δD of CH_4 and $\delta^{13}C$ of C_2H_6, and $\delta^{13}C$ of C_3H_8 (If present at concentrations great enough to yield accurate data)		Lab Specific SOP	6 weeks	NA
Organic Analytes				
Benzene, toluene, ethylbenzene, o-xylene, m-+p-xylene, total xylenes (by sum of xylene isomers)	Unfiltered, 40ml VOA vial, HCl to pH<2 & 4°C	SW846 8260D	14 days	1 µg/L
Total Petroleum Hydrocarbons (TPH) (volatile) as Gasoline Range Organics (GRO) using retention time window between 2-methylpentane to 1,2,4-trimethylbenzene (approx. C6 to C10 range)		SW846 8015C and modifications or SW846 8260D and modifications	14 days	0.05 mg/L
TPH (extractable) as Diesel Range Organics (DRO) using retention time window of C10-C28 Range	Unfiltered, 1L Amber Glass, & 4°C	SW846 8015C and modifications	7 days	0.05 mg/L
Bacterial Activity Reaction Tests				
Iron Related Bacteria	Unfiltered, Sterile Plastic, Unpreserved & 4°C	BART Method	days to reaction or 100cfu/100ml	test should be initiated within 24-48 hours of sample collection
Slime Forming Bacteria		BART Method	days to reaction or 100cfu/100ml	
Sulfate Reducing Bacteria		BART Method	days to reaction or 100cfu/100ml	

NA - Not Applicable

3.1 Sample Labeling

Sample containers should be properly labeled prior to, and/or during field work. Labels will be completed with indelible ink and will include the following minimum information:

1) Sample identification number (Facility ID created in the COGCC Environmental (COENV) database);
2) Water source name;
3) Sampler's initials;
4) Date and time of collection, and
5) Preservation type.

Labels can be waterproof stickers, tags, or written directly onto the container and 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. Containers should be free from all other labels to prevent confusion.

3.1.1 Facility Naming Convention

The facility name will be generated based on the following naming convention:

- Water sources such as permitted water wells, monitoring wells, or adjudicated springs will have a Facility name which includes the last name of the landowner followed by the permit number assigned by the DWR.
- Sources without an assigned permit number such as some livestock wells, other types of wells, or surface locations without an assigned permit number will have a Facility name created by entering the landowner's last name followed by Quarter-Quarter, Section, Township, and Range.

3.2 Water Source Sampling

Standard monitoring well sampling protocols require purging a specified number of well volumes prior to collecting water samples (ASTM D6452-18, 2018). However, most available water sources are used frequently, have longer screen intervals or open boreholes, are equipped with fixed depth high flow rate pumps, and water collection is not taken directly from the wellhead but rather through the closest practical sampling point; therefore, standard Groundwater monitoring well sampling protocols may not be appropriate at all sites (Molofsky et. al, 2018). It is recommended that a withdrawal point, upstream of ancillary equipment (e.g. holding tanks, pressure tanks, water softeners, water treatment systems, conveyance piping, etc.) be identified. If no withdrawal points upstream of ancillary equipment are available, best judgement should be utilized in purging to flush the water holding capacity of piping and any equipment upstream of the withdrawal point (US EPA, 2017a). Specifically, purge calculations should include the water holding capacity of the pressure tanks to limit the potential CH_4 loss (Molofsky et. al, 2018).

An Operator must document, in detail, their procedures and provide the procedures to COGCC staff, upon request. Once the purge method has been established at specific water sources, the same procedure will be utilized for all subsequent sampling at the specific water source (Molofsky et. al, 2018).

3.2.1 Water Source Purging

Instructions for acceptable water source purging practices can be found in ASTM D6452 - 18 Standard Guide for Purging Methods for Well Used for Groundwater Quality Investigations (2018); ASTM D6771-18 Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations (2018); Purging and Other Sampling Variables Affecting Dissolved Methane Concentration in Water Supply Wells (Molofsky et. al, 2018); Low-Flow (Minimal Drawdown) Ground-water Sampling Procedures (Puls and Barcelona, 1996); and EPA Operating Procedure Groundwater Sampling, Number SESDPROC-301-R4 (2017a).

Water sources will be purged prior to sampling to obtain a water sample representative of the aquifer. The purging methods described below are meant to be used as guidelines, but may change with site conditions, purpose of sampling, and or/landowner concerns. Two methods for purging water sources are recommended:

1) fixed wellbore volume purging techniques, or
2) purging until stabilization of water quality parameters.

Many domestic water wells in Colorado yield a few hundred gallons, or less, per day, which may still provide adequate water volume to the users. As part of the pre-sampling activities, the samplers must determine if, during normal use, the water source has been purged frequently. If the well is used frequently, a representative sample can be collected after purging <1 wellbore volume (Molofsky et al., 2018). It is recommended to use the stabilization of water quality parameters method, discussed below, with detailed notes of well use recorded on the field sampling data sheet (Appendix A). It is always prudent to take a conservative approach, utilizing low flow and/or low volume purging techniques (Puls and Barcelona, 1996; COGCC, 2008).

Regardless of purge method, onsite collection of water quality operational and indicator parameters such as water volume purged, visual and olfactory observations such as presence or absence of odor, bubbles or effervescence, qualitative determination of color of water if any, presence or absence of sediment, quantitative measurements of pH, water temperature, and conductivity must be monitored during the purge and recorded on a field sampling data sheet. Field parameter measurements should be collected using a multi-parameter instrument, utilizing an in-line flow-through device (ASTM D4448-01, 2019; ASTM D6452-18, 2018; ASTM D6771-18, 2018; Puls and Barcelona, 1996). Parameter stabilization is defined in Table 3-3 and is achieved once three successive measurements, taken 3 to 5 minutes apart, are within recommended ranges (ASTM D6771-18; Puls and Barcelona, 1996). It is also recommended that quantitative instrumental determination of oxygen-reduction potential ("ORP"), dissolved oxygen ("DO"), and turbidity be measured and recorded at each sampling site.

Table 3-3 - Field Parameters

Field Parametes	Field Methods	Lower Limit of Quantification (LLQ)	Parameter Stabilization Criteria[1]
Required Parameters			
Volume Water Purged Prior to Sampling	Measured Volume	NA	NA
Odor	Olfactory	NA	NA
Water Color	Visual, Photo	NA	NA
Bubbles	Visual, Photo	NA	NA
Effervescence	Visual, Photo	NA	NA
Sediment	Visual, Photo	NA	NA
pH	Field Meter	NA	±0.2 SU
Specific Conductance	Field Meter	NA	±3 % µS/cm
Temperature (water)	Field Meter	NA	±0.3 % °C
Recommended Parameters			
Dissolved Oxygen	Field Meter	NA	±10 % or ± 2 mg/L, whichever is greater
Turbidity	Field Meter	NA	±10 % or ± 1 NTU, whichever is greater
Oxygen Reduction Potential	Field Meter	NA	±10 % or ± 10 mV, whichever is greater
%LEL and/or CH_4	4-Gas Meter	Range (0-100%)	NA

NA - Not Applicable

If the water source is not routinely operated under normal use, volumetric purging with a minimum of three to five casing volumes should be purged prior to sampling (EPA, 2017a). After the volumetric purge, flow rates will be decreased to avoid drawdown in the water source, turbulence in the well bore, and to ensure any gas is not agitated out of solution.

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. If purge water is not allowed to be discharged on location, it will be collected in portable tanks and stored on-site until the water can be transported and properly disposed off-site.

3.2.2 Water Source Sample Collection

Wells should be sampled immediately following purging. Samples should be collected and preserved as unfiltered, filtered, or dissolved gas samples, according to the specific sampling methods described below.

3.2.2.1 Collection of Unfiltered Groundwater Samples

Unfiltered sample(s) containers should be filled directly from the pump discharge point (or via ¼" polyethylene tubing connected to the pump) into the laboratory-supplied sample containers. If sampling from a tap equipped with an aerator, the aerator should be removed, with landowner consent, prior to the sampling. If an in-line flow-through device was used during the purging, it should be disconnected or bypassed during sample collection (Puls and Barcelona, 1996). Preservation of unfiltered Groundwater samples with acids should be done for certain analyses as listed in Table 3-1. The samples for analysis of volatile aromatic organic compounds and volatile petroleum range hydrocarbons will be collected in a manner that minimizes agitation, aeration, and overfill which would typically be done by direct fill of the 40ml vials.

3.2.2.2 Collection of Filtered Groundwater Samples

Filtration and preservation at the laboratory are preferred; however, in some instances, field filtration is necessary.

When field filtration is necessary, samples will be filtered during collection using an in-line disposable 0.45-micron (µm) glass-fiber filter. When field filtering is performed, disposable tubing with the in-line filter will be connected directly to the pump discharge spigot, if possible. The pressure from the spigot/discharge point will be used to push water through the filter into the sample bottle. Alternatively, the in-line filter can be connected with tubing to a peristaltic pump to draw water from a pre-cleaned container through the filter. In all cases, the tubing and filter will be flushed with at least one liter of sample water before sample collection, and filtered water will be placed into laboratory provided sample containers. New filters will be used for each sample and decontamination procedures will be strictly followed. Preserve samples for metals analysis as listed in Table 3-1 if the container did not have acid in the container provided by the lab.

3.2.2.3 Collection of Groundwater Samples from Water Sources for Dissolved Gas Analysis

Groundwater samples collected for dissolved gas analysis from water sources with permanent pumps will be collected in IsoFlask® or equivalent in line sampling devices or by direct fill into non-preserved 40mL VOA vials equipped with gas-tight septa as described on Molofsky et al. (2016). Collection of samples utilizing in line sample collection devices such as outlined in Molofsky et al. (2016) is the preferred means of sampling for dissolved gas analysis. If bubbles are visible in 40ml vials then another sample will be collected. If it is not possible to get a bubble-free 40ml sample because the water is too effervescent, a vial with gas headspace is acceptable. The Operator should note this on the chain-of-custody (“COC”) and notify the laboratory that headspace was present in the field. In-line sampling containers may contain bactericide as preservative thus no acid should be added to the in line sample device before or after sample collection. Samplers should follow preservation guidance from the laboratory if using 40ml vials to collect samples. Many reports by and to COGCC staff indicate that acid preservation of certain types of Groundwater samples (particularly those with elevated bicarbonate/carbonate alkalinity levels results in increased headspace in sealed 40ml vials which may lead to inaccurate analytical results of the dissolved gas analytes. Some laboratories have recommended use of a bactericide such as benzalkonium chloride for preservation of 40ml vial samples for dissolved gas analysis which may be preferable to acid preservation techniques for this analysis. Field documentation provided to the COGCC must include type of container, preservative (if any) and method of sample collection for dissolved gas analyses.

3.2.2.4 Collection of Groundwater Samples from Water Sources for Gas Composition and Isotopic Analysis

Groundwater samples collected for gas composition and isotopic analysis from water sources with permanent pumps will be collected in a closed-sample collection system container such as an IsoFlask® provided by the isotopic laboratory. Sample collection will be conducted using the manufacturer’s specified tubing configuration and procedures (Isotech, 2014). The sampling device as provided by the vendor should contain a bactericide capsule and samples collected in such an in-line sampling device should be shipped and stored as recommended by the laboratory. Field documentation provided to the COGCC must include type of container, preservative (if any) and method of sample collection for gas composition and isotopic analyses.

3.3 Spring and Seep Sampling

Collection of Groundwater samples from springs or seeps will be collected as near to the source as possible. Prior to sampling, the field parameters pH, conductivity, water temperature, sediment/turbidity, DO, ORP, effervescence, bubbles, water color, and odor (if present) will be measured and recorded on a field sampling data sheet. A clean, white 5-gallon bucket should be used when monitoring for color, odor, and effervescence.

3.3.1 Surface Water Sample Collection

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.

3.3.1.1 Collection of Unfiltered Surface Water Samples

Unfiltered samples should be collected by submerging a laboratory-supplied sample container or dipper directly into the spring and carefully transferring the sample to the 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 not to overfill the container.

3.3.1.2 Collection of Filtered Surface Water Samples

Filtration at the laboratory after receipt, followed by the appropriate preservation method will be the preferred method of filtering and preserving samples.

Alternatively, samples that will be field filtered must be collected using an in-line disposable 0.45 µm glass-fiber filter. 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 clean 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, and decontamination procedures will be strictly followed. For those sample containers with preservative, special care should be taken not to overfill the container.

3.3.1.3 Collection of Surface Water Samples for Dissolved Gas Analysis

Surface water samples collected for dissolved gas analysis from springs or seeps will be collected in non-preserved 40 mL VOA vials equipped with gas-tight septa. If the water is insufficiently deep to collect a sample, a depression will be made to create a pool of water, as close to the discharge point as possible, and to allow the flow of water to flush the suspended solids prior to sampling. Submerge a clean 500 mL or larger glass container and fill completely. Use the direct fill method outlined by Molofsky (2016) and decant water into the 40 mL VOA vial. If bubbles are visible, collect another sample. If it is not possible to get a gas-free sample because the water is too effervescent, a vial with gas headspace is acceptable. The Operator should note this on the COC and notify the laboratory that headspace was present in the field. Samplers should follow preservation guidance from the laboratory if using 40ml vials to collect samples. Many reports by and to COGCC staff indicate that acid preservation of certain types of Groundwater samples (particularly those with elevated bicarbonate/carbonate alkalinity levels results in increased headspace in sealed 40ml vials which may lead to inaccurate analytical results of the dissolved gas analytes. Some laboratories have recommended use of a bactericide such as benzalkonium chloride for preservation of 40ml vial samples for dissolved gas analysis which may be preferable to acid preservation techniques for this analysis. Field documentation provided to the COGCC must include type of container, preservative (if any) and method of sample collection for dissolved gas analyses.

3.3.1.4 Collection of Surface Water Samples for Gas Composition and Isotopic Analysis

Surface water samples for gas composition and isotopic analysis should be collected in a 1 liter plastic bottle with a gas tight septa cap provided by the laboratory with a bactericide capsule inside. Collection may require gentle transfer of water from a smaller glass bottle depending on depth and/or flow of surface water. Otherwise fill the 1 liter bottle by the direct fill method (Molofsky et al., 2016). In line sampling containers should be utilized for this test samples can be collected using an installed pump as described in section 3.2.3.4. Field documentation provided to the COGCC must include type of container, preservative (if any) and method of sample collection for gas composition and isotopic analyses.

4.0- FIELD ANALYSES AND OBSERVATIONS

Physically or chemically unstable parameters, such as pH, DO, and water temperature must also be measured in the field, rather than solely at a laboratory. Although the conductivity of most Groundwater samples should be relatively stable during and after sampling, it is required that conductivity be measured in the field both as part of the evaluation of the effectiveness and completeness of the purge and as a reportable parameter for the Groundwater at the time of sampling. Other recommended field parameters are DO content of the Groundwater, as well as the turbidity of the Groundwater at the time of sampling. Measurement of the ORP of Groundwater at the time of sampling is also recommended if an in-line flow-through device for measurements is used for analysis. Any field analyses performed must be reported on the field sampling data sheet. The required field parameters and observation data are summarized in Table 3-3 - Field Parameters. General guidance for documentation of a Groundwater sampling event can be found in ASTM D6089-15 (2015).

Calibration of field instrumentation should follow the manufacturer's calibration and maintenance procedures detailed in the equipment's technical manuals. Calibration solutions should be replaced on or before the manufacturer's expiration date printed on each container, and unused, expired standards should be disposed of per manufacturer's instructions. Temperature corrections of pH and conductivity measurements are typically done by multi-parameter meters equipped with temperature probes, but if the pH and conductivity 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 submitted to the COGCC.

5.0- Sample Preservation, Handling, and Shipping

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 water temperatures on receipt at a laboratory of 0 to 6°C. Other samples, such as water samples for analysis of volatile organic compounds ("VOCs"), should follow the preservation guidance developed in SW 846 Chapter 4 (U.S. EPA, 2018) and guidance identified in Table 3-1.

Water samples will be placed in a cooler, with ice or other coolant, immediately following collection unless otherwise indicated by the laboratory. Collected samples will be stored in refrigerated conditions that prevent freezing. If shipping is required, samples will be packed in a cooler with sufficient ice to maintain water temperature until the samples reach the laboratory. The coolers should be clearly labeled in order to expedite delivery to the selected laboratory and transported or shipped in a timely manner (preferably overnight) to minimize the potential for failure to meet method-specified hold times. Laboratory-supplied trip blanks and temperature blanks will be included with each cooler. After the cooler is properly packed, a signed custody seal will be placed across the opening edge of the cooler, signed over to the laboratory or freight carrier, and a copy of the COC form retained, demonstrating transfer of custody.

Table 3-1 provides a summary for sample collection, storage, and preservation techniques by method or type of analyte. Laboratory specific requirements may supersede the procedures summarized and any deviations should be approved by the COGCC staff.

6.0- Chain of Custody Documentation and Records Management

Guidance for general COC practices can be found in ASTM D4840-99(2018)e1, Standard Guide for Sample Chain-of-Custody Procedures.

Samples must be handled, stored, and shipped in accordance with 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. The analytical laboratory will provide a COC form that includes the following:

- Operator;
- Sample identifications (facility name, facility ID, legal location);
- Sample frequency (e.g., initial, 1st subsequent, 2nd subsequent, to post-closure);
- Sample reason (e.g. 614.d or 615);
- Date and time of collection;
- Requested analysis;
- Preservatives;
- Matrix, number of bottles;
- Field parameters (optional); and
- Signatures.

The sampler must also 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 courier. The laboratory also signs the COC form accepting custody of the samples at the time of delivery by the sampler or the shipping courier. The COC form and any other documentation (shipping receipts, bills of lading) should be sealed in a zipper lock plastic bag and taped to the inside top of the cooler to limit the potential for water damage to the form. Once the cooler is prepared to insure sample integrity, 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 (ASTM D4840-99, 2018).

7.0- ANALYTICAL PROCEDURES AND QUANTITATION LIMITS FOR LABORATORY AND FIELD METHODS

Analysis of samples must be completed by laboratory(ies) accredited by the 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). As an example, an acceptable laboratory 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 at this time for some analytes or analytical technology such as the specialized isotopic ratio determination of the carbon and hydrogen present in CH_4, dissolved gases and/or the use of bacterial activity reaction test (“BART”) biodetectors.

Analytes, appropriate methodology, and expected achievable detection limits are included in Table 3-1. There are many acceptable methods used for determination of the analytes in the anions and general water quality parameters and not all are listed in Table 3-1.

8.0- FIELD AND LABORATORY QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Data integrity will be assured and verified through:

1) Field sampling practices that comply with this SAP;
2) Sample analysis by an accredited analytical laboratory(ies);
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 laboratory(ies) that are NELAP accredited for the matrices and analytical processes that will be used for sample analysis, where such accreditation exists. Approved and accepted analytical methods, such as test methods for Evaluating Solid Waste SW846 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 as indicated in Table 3-1. Deviations to the analytical methods should be approved by the COGCC staff prior to sampling.

Where Standard Methods or EPA published methods are not available, standard industry practices will be followed. Laboratory quality assurance samples, such as method blanks, matrix spike/matrix spike duplicates, laboratory duplicates, and laboratory control samples, 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 including the COGCC EDD, and an analytical narrative will be provided as part of the laboratory report.

8.1 Field Control Samples

Field quality control samples will be collected following an Operator’s specified procedures. All field quality control sample results will be submitted to the COGCC. Guidance for general protocols can be found in ASTM D7069-04(2015), Standard Guide for Field Quality Assurance in a Groundwater Sampling Event. Generally recommended practices are provided below.

8.1.1 Field Duplicate Samples

The following protocol will be followed for field duplicate sample collection:

- One complete set of duplicate samples should be collected for every 20 Groundwater samples collected, but not less than one per year.

- Duplicate samples should be collected at approximately the same time as the original sample using identical sampling methods (ASTM D7069-04, 2015).
- Each duplicate sample should be given a fictitious sample identification number, which is recorded on the field sampling data sheet.
- The laboratory will not be informed that the sample is a field duplicate, ensuring no analytical bias will occur; and
- Duplicate samples should be analyzed for the same analytes as the original sample.

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 ≤ 20% will be used for original and duplicate sample values that are greater than five times (5x) the practical quantitation limit (U.S. EPA 2017b). In instances when RPD is ≥ 20%, field and laboratory data will be reexamined to identify potential causes for the observed differences, and, if necessary, update SOPs as appropriate to minimize future variances.

8.1.2 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 to be analyzed for major cations (dissolved) and/or VOCs. One equipment blank sample will be collected for every 10 Groundwater samples taken with decontaminated sampling equipment, 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.

The use of equipment that requires decontamination will be minimized to reduce cross-contamination and reduce the cost of field equipment blanks, where possible.

8.1.3 Trip Blanks

Trip blanks should be used to assess contamination introduced during shipping and/or field handling procedures. Trip blanks should be collected at a frequency of one blank per cooler. Trip blanks should be collected at a frequency of one blank per cooler. Trip blank VOA vials are filled by the analytical laboratory staff under controlled conditions, transported to the sampling site, and transported back to the laboratory without being exposed to sampling procedures. Trip blanks will be analyzed for VOCs. Trip blank results should have concentrations less than the laboratory method detection limit ("MDL"). An Operator should verify negative results on all trip blanks and will adjust procedures accordingly if results above the MDL are identified.

8.1.4 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 CH_4 (i.e., the water source is located adjacent to hydrocarbon or CH_4 storage or fueling area).

Field blanks will be collected by filling a clean glass VOA vial, equipped with a 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 benzene, toluene, ethylbenzene, and xylene ("BTEX") and dissolved gasses (CH_4, ethane, and propane). BTEX and dissolved gases concentrations should be less than the MDL.

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 (see Appendix B) which should be stored in the project files with the field sampling data sheet and the laboratory analytical data reports. The objective of the data quality review sheet is to confirm that all data was properly collected and is suitable for release to COGCC. The data quality review should:

- Review all field sampling data sheets to confirm that:
    - The water source was properly purged;
    - The flow rate was reduced prior to sampling;

    - Water quality field parameters had stabilized prior to sampling, if necessary; and
    - No site 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 to laboratory receipt;
    - All samples were analyzed for the requested analyses;
    - Proper laboratory methods were used for analyses;
    - 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; and
    - Field quality control samples meet the data quality objectives, listed above.
- Specify corrections needed and dates by when those actions should be completed.
- Certification by the data reviewer confirming that the data was collected in accordance with the SAP and that the data is suitable for incorporation into the COGCC database.

9.0- EVALUATION OF DATA QUALITY

An Operator is expected to review field sampling records to ensure that samples were collected in accordance with this SAP or if re-sampling may be required prior to submittal to the COGCC COENV database. COC records and the condition of samples upon receipt at the laboratory should also be evaluated to ensure the use of proper sample containers and preservatives by the samplers. A basic review of laboratory results and QC processes will also be completed and will include the following minimum data quality checks (SM1030 Data Quality, 2017). If values are identified outside of the listed acceptance ranges, the sample should be re-analyzed.

Calculation of TDS from the concentrations of major cations and anions, sum of the following constituents (mg/L):

$$TDS = 0.6\,(alkalinity\ as\ CaCO_3) + Na^{+} + K^{+} + Ca^{2+} + Mg^{2+} + Cl^{-} + SO_4{}^{2-} + SiO_3{}^{2-} + NO_3{}^{-} + F^{-}$$

1) Calculation of cation-anion balance must be done and reviewed with typical criteria acceptance as follows:

$$\%\ difference = 100\ x\ \frac{\Sigma\ cations - \Sigma\ anions}{\Sigma\ cations + \Sigma\ anions}$$

Anion Sum *(meq/L)*	Acceptable Difference
0-3.0	± 0.2 meq/L
3.0-10.0	± 2%
10.0 – 800	5%

2) Measured TDS concentration should be larger than the calculated TDS calculation and reviewed with acceptance levels of:

$$1.0 < \frac{\mathit{measured\ TDS}}{\mathit{calculated\ TDS}} < 1.2$$

3) Calculated EC calculation should be larger than measured EC value, and reviewed with acceptance levels:

$$0.9 < \frac{\mathit{calculated\ EC}}{\mathit{measured\ EC}} < 1.1$$

4) Calculation of anion and cation sums should be approximately 1/100 of the measured EC, and reviewed with acceptance levels of:

$$100\ x\ \mathit{anion\ (or\ cation)\ sum, meq/L} = (0.9 - 1.1)\ EC$$

5) Calculated TDS to EC ratio and reviewed with acceptance levels of:

$$\mathit{calculated\ TDS\ /\ conductivity} = 0.55 - 0.7$$

6) Measured TDS to EC Ratio should be between 0.55 and .07

10.0 - HEALTH AND SAFETY

The health and safety of personnel and water source owners must be addressed by an Operator's health and safety program and include protocols 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 sampling, the field staff will explain to the water source owner or representative what and why PPE is required.

10.1 Materials and Waste Management

All materials and wastes, whether fluid or solid, generated during sampling and monitoring activities, must be properly handled, disposed, and documented in accordance with applicable federal, state, and local regulations.

Under special circumstances for large volume well purging, a sample will require coordination of waste water handling instructions, storage, transport, disposal resources, and any necessary manifesting or alternative tracking documents.

11.0 - DATA SUBMISSION

An Operator will upload all required data into the COENV database and submit to respective well owner(s), within 3-months of the sampling event as directed by Rules 614.d or 615. Prior to upload into the COENV database or submittal to landowners all data, reports, and communications will receive a QA/QC check.

11.1 COENV Database

An Operator will upload and submit the following electronic information into the COENV database through a Form 43, Analytical Sample Submittal (Form 43):

- Facility ID (already in existence or newly created) in the COENV database;
- Division of Water Resources 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 coordinates need to be in decimal degrees of latitude and longitude using the NAD83 reference, surveyed in accordance with COGCC Rule 215 with an accuracy of five decimals in the North American Datum 1983 (NAD 83);
- 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;
- Collection point (e.g. domestic, stock, irrigation, industrial, or municipal water supply well, or bradenhead);
- Laboratory name;
- Sample reason (e.g. Rule 614.d or Rule 615); and
- Results of field monitoring and observations must be submitted electronically to the COGCC. A simplified spreadsheet EDD can be utilized for this purpose, or results may be included on the COC and submitted with the laboratory provided EDD.

All samples submitted to the COGCC will include the following information and file types:

1) Correctly formatted laboratory EDD (Either XML or Excel);
2) A portable document format ("PDF") copy of the complete lab report including QA/QC data; and

3) A PDF copy of the field sampling data sheet that includes all the location information, purge information, and field parameters collected.

Laboratory results for each sample collected will be submitted via a Form 43 using the laboratory's XML or spreadsheet EDD, formatted appropriately for the COENV 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. PDF copies of calibration logs, field sampling data sheets, photographs, and laboratory results must also be uploaded to the database.

11.1.1 Electronic Data Deliverables

There are two accepted versions of the COGCC EDD that may be uploaded to the COENV database via Form 43. One is an XML EDD that is based on the EPA Water Quality Data ("WQX") XML schema. The second is a Microsoft Excel-based EDD. Both the XML and Excel-based EDD are in hierarchical format. The EDDs do not look, 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 be 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:
https://cogcc.state.co.us/documents/about/COGIS_Help/EnviroDB/EnviroDB.htm

Help regarding the EDD Form 43 upload process can be found at:
https://cogcc.state.co.us/documents/reg/Forms/instructions/Form_Instructions/Form_43_Instructions_09282018.pdf

11.1.2 Special Circumstances Reporting

In accordance with the COGCC Operator Guidance, an Operator will notify the water source owner and the COGCC immediately and will submit a Form 42, Notice of Field Operations (Form 42) if:

1) Methane concentration increases by more than 5 mg/L between sampling;
2) Methane concentration is detected at or above 10 mg/L;
3) Composition/isotopic data test results indicate thermogenic gas or a mixture of thermogenic and biogenic gas; and/or
4) BTEX compounds or TPH are detected.

Immediate notification is considered within 24 hours of receipt of analytical data from the laboratory. If analytical results are being re-analyzed, timely reporting is expected after the results have been confirmed. Delays in timely reporting due to third party consultants or additional internal data review should be avoided; the raw data can be reported immediately, with a caveat that additional review may be undertaken, and the results are therefore to be considered preliminary.

An operator may use any reasonable means to provide notifications to the water well owners. In-person or verbal notifications should be followed with written correspondence; written correspondence may be provided through e-mails or formal letters with delivery or receipt confirmation.

The report to the water source owner will include a description of the findings and an explanation if potential health risks for continued use of the water were determined to be present. A written letter to the landowner detailing the sample findings and potential health risks will also be provided and the findings will be reported to the COGCC.

12.0 - REFERENCES

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