

COLORADO Oil & Gas Conservation Commission

Department of Natural Resources

# **Produced Water Quality Model Sampling and Analysis Plan**

# Rule 909.j Colorado Oil and Gas Conservation Commission Version 1 April 2022

**REVISION HISTORY** 

Effective Date	Reviewer/Approver	Description (Review or Nature of Revisions)
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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 909.j, *Produced Water Quality Analyses*. This Rule applies to oil wells and gas wells (Oil and Gas Wells) as required by Rules 909.j., 803.g(5)C, 803.g(5)D, 806.a, 806.b, 806.c, 809, 810, and 811. COGCC will modify this SAP as necessary based on new procedures, protocols, and other information needed to meet the objectives of the rules. The aqueous fluids co-produced with oil and natural gas are produced water and are generally referred to as produced water.

The timing and frequency of the sampling is described in the Rule 909.j.(1)-(5) and as applicable in Rules 803.g(5)C, 803.g(5)D, 806.a, 806.b, 806.c, 809, 810, and 811, and will not be described in detail in this SAP. Rules 803.g(5)C, 803.g(5)D, 806.a, 806.b, 806.c, 809, 810, and 811 reference sampling and analysis being performed pursuant to Rule 909.j.(1), (3), (4), and (5). Throughout the rest of this guidance document, references to Rule 909.j. are meant to include the 800-Series rules listed above.

Sampling must be conducted in a way that employs "best practice protocols" designed for the collection of samples that are representative of the aqueous fluids produced by one or more Oil and Gas Wells. Methods and techniques used in the analysis of these produced water samples must be capable of providing both accurate and precise measurements from representative aliquots of produced produced water 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 principles must be carried forward for sampling and analysis efforts designed to meet requirements of Rules 909.j., 803.g(5)C, 803.g(5)D, 806.a, 806.b, 806.c, 809, 810, and 811. Equally important is the assurance that the methods and processes of analysis will yield reproducible results at reporting thresholds that are adequate to evaluate produced water quality of the aqueous exploration and production (E&P) wastes entering permitted pits.

The produced water sampling and analysis procedures outlined in the SAP are designed to provide consistency in sampling and analytical techniques. The use and submission of the laboratory generated electronic data deliverable (EDD) files to COGCC via Form 43, Analytical Sample Submittal (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, current conditions of a sampling site, and field observations about the water sample, such as effervescence, color, and odor, are also important. The field observations acquired at each site must be recorded and submitted into the COGCC Environmental (COENV) database along with the laboratory-generated analytical data.

#### 2.0 PRE-SAMPLING ACTIVITIES

The Operator will identify appropriate sampling site(s) with respect to each of their permitted pits. Appropriate sampling sites will vary based on style and type of production. For example, sampling directly from the wellhead may be appropriate for many coal bed methane wells. In situations where organic liquids are produced, appropriate sampling sites may be at oil-gas-water separators that may be receiving fluids from one or more wells. In other situations, sampling directly from a pipe releasing produced water to a pit may be appropriate. Sampling water from the pit itself is not appropriate, as it is not considered to be representative of produced water composition for reasons such as loss of organic compounds by volatilization, changes in composition from evaporation, or from precipitation falling in the pit. Sampling from an open-top produced water vessel is also not appropriate for the same reasons.

During the initial sampling, the location of the sampling site must be surveyed in accordance with COGCC Rule 216. The location of the water source should be confirmed during subsequent sampling events.

#### 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 (NELAP) for the analytical procedures and analytes of concern in this SAP.

Samples should be collected from the following locations in order of decreasing preference:

- 1. As close to the well as possible, and collected from each well that produces water to a pit.
- 2. Each separator that separates water from the production stream for discharge into a pit. In these cases, record which well(s) produce to the separator.
- 3. A closed produced water tank, buried, or partially buried vessel.
- 4. The end of pipe that discharges into a pit.

Each sample collected should be analyzed for the 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. The gloves should be changed following the collection of each set of samples, 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. Circulate detergent solutions through sampling pumps and non-disposable discharge tubing;
- 4. Rinse with tap water;
- 5. Rinse with distilled or deionized water;
- 6. Air dry; and
- 7. Store decontaminated equipment in sealed containers such as zipper-lock plastic bags or boxes with tight lids during mobilization to the next site and prior to use to protect from airborne dust contamination.

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.

In cases where reusable equipment is employed, it may be necessary to collect an equipment blank for analysis of the analytes in Table 3-1 as a field quality control sample.

Analyte	Filter, Container, and Preservative	Lab Method, Holding Time, LLQ					
General Water Quality Parameter	General Water Quality Parameters						
рН		SM4500-H+ or SW846 9040C, < 15 minutes, NA					
Specific Conductance (Conductivity)		SM2510 B or SW846 9050A, 28 days, NA					
Solids, Total Dissolved (TDS)	Unfiltered, Plastic, Unpreserved & 4°C	SM2540 C, 7 days, 10 mg/L					
Solids, Total Suspended (TSS)		SM2540D, 7 days, 10mg/L					
Bicarbonate Alkalinity, Carbonate Alkalinity and Total Alkalinity (as CaCO3)		SM2320 B, 14 days, 10 mg/L as $CaCO_3$					

Analyte	Filter, Container, and Preservative	Lab Method, Holding Time, LLQ			
Major Anions					
Bromide (Br)		SW846 9056A, 28 days, 0.2 mg/L			
Chloride (Cl)		SW846 9056A, 28 days, 0.1 mg/L			
Fluoride (F)		SW846 9056A, 28 days, 0.2 mg/L			
Sulfate (SO <sub>4</sub> <sup>2</sup> )	Unfiltered, Plastic, Unpreserved & 4°C	SW846 9056A, 28 days, 5 mg/L			
Phosphorus (P)		SM4500-P A, NA, 0.05 mg/L			
Nitrate as N (NO <sub>3</sub> )		SW846 9056A, 48 hours, 0.1 mg/L			
Nitrite as N (NO <sub>2</sub> )		SW846 9056A, 48 hours, 0.1 mg/L			
Nitrate & Nitrite as N		By summation of results of NO3 and NO2 analyses by 9056A (above)			
Nitrate & Nitrite as N	Unfiltered, Plastic, preserved with H2SO4 & 4°C unless analyzed in 24 hours of collection	SM4500-NO3 F, 28 days, 0.1 mg/L			
Major Cations (total)					
Calcium (Ca)		SW846 6010D/SW846 6020B, 180 days, 1 mg/L			
Iron (Fe)		SW846 6010D/SW846 6020B, 180 days, 0.1 mg/L			
Magnesium (Mg)	Unfiltered, Plastic, HNO <sub>3</sub> Preserved to pH<2 in field and confirmed at lab & 4°C	SW846 6010D/SW846 6020B, 180 days, 1 mg/L			
Manganese (Mn)	Preparation method SW-846 3010 to be utilized	SW846 6010D/SW846 6020B, 180 days, 0.01 mg/L			
Potassium (K)		SW846 6010D/SW846 6020B, 180 days, 1 mg/L			
Sodium (Na)		SW846 6010D/SW846 6020B, 180 days, 1 mg/L			
Other Elements (total)					
Barium (Ba)		SW846 6010D/SW846 6020B, 180 days, 0.001 mg/L			
Boron (B)	Unfiltered, Plastic, HNO <sub>3</sub> Preserved to pH<2 in field and confirmed at lab & 4°C	SW846 6010D/SW846 6020B, 180 days, 0.1 mg/L			
Selenium (Se)	Preparation method SW-846 3010 to be utilized	SW846 6010D/SW846 6020B, 180 days, 0.001 mg/L			
Strontium (Sr)		SW846 6010D/SW846 6020B, 180 days, 0.01 mg/L			

### Table 3-1 - Minimum Required Laboratory Analytes

Analyte	Filter, Container, and Preservative	Lab Method, Holding Time, LLQ			
Organic Analytes					
Benzene, toluene, ethylbenzene, o-xylene, m-+p-xylene, total xylenes (by sum of xylene isomers)		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 C <sub>6</sub> to C10 range)	Unfiltered, 40ml VOA vial, HCl to pH<2 & 4°C	SW846 8015C and modifications or SW846 8260D and modifications, 14 days, 0.05 mg/L			
TPH (extractable) using retention time window of C <sub>10</sub> -C <sub>36</sub> Range	Unfiltered, 1L Amber Glass, & 4°C	SW846 8015C and modifications, 7 days, 0.5 mg/L			
NORM Analytes					
<sup>226</sup> Ra	Unfiltered, 1L LDPE, HNO <sub>3</sub> preserved to pH<2 in field and	E903.0, SW846 9315, or SM7500-Ra-B Radium and modifications, NA, 0.5pCi/L			
<sup>228</sup> Ra	confirmed at lab	E904.0, SW846 9320 or SM7500-Ra-D Radium and modifications, NA, 1pCi/L			

#### Table 3-1 - Minimum Required Laboratory Analytes

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:

- Sample identification number (Facility ID created [if necessary] in the COENV database);
- Where sampled (for example, wellhead, separator, pipe outfall to pit, or produced water vessel);
- Sampler's initials;
- Date and time of collection; and
- Preservation type.

Labels can be waterproof stickers or tags, or written directly onto the container and covered with clear plastic tape to keep the ink from running due to water during sampling or 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 shall be generated based on the following naming conventions:

- Samples collected from a single well should be named to reflect that well using the API well number.
- Samples collected at the pipe end at a pit should be named using the COGIS pit facility number.
- Multi-well samples collected at shared production equipment such as a separator or closed produced water vessel should be named using the production facility name from onsite signs.

#### 3.2 PRODUCED WATER SAMPLING

Standard monitoring well sampling protocols require purging a specified number of well volumes prior to collecting water samples. However, oil and gas wells that are continuously or regularly and routinely pumped do not necessarily require the type of multiple well volume purging suggested for infrequently sampled or infrequently used monitoring wells.

The Operator must document, in detail, their sampling procedures and provide the procedures to COGCC staff, upon request. If samples are collected from a separator treating fluids from multiple wells or a tank storing water from a multi-well separator, then all wells should be in operation for a minimum of 48 hours prior to sampling. Documentation of chemical products used downhole within 30 days prior to sampling at a single well or at any well that is part of a multi-well sample must be provided as part of field notes for the sampling event. At a minimum this list must include products used to treat mineral scale or paraffin buildup, and products used for emulsion control. Safety data sheets (SDS) for any products used downhole continuously or in individual treatments during the 30 days prior to sampling shall be uploaded as documents to the environmental database.

#### 3.2.1 PRODUCED WATER SAMPLING

Water quality, operational, and indicator parameters listed in Table 3-2 must be monitored prior to the sampling and recorded on a field sampling data sheet. Field parameter measurements may be collected using a multi-parameter instrument, utilizing an in-line flow-through device (ASTM D6452-18, 2018; ASTM D6771-18, 2018) or individual meters/instruments. Parameter stabilization is defined in Table 3-2 and is achieved once three successive measurements, taken 3 to 5 minutes apart, are within recommended ranges (ASTM D6771-18). 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.

Field Parameters	Field Methods	Lower Limit of Quantification (LLQ)	Parameter Stabilization Criteria <sup>1</sup>
Produced water volume per day or month	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
рН	Field Meter	NA	±0.2 SU
Specific Conductance	Field Meter	NA	±3 % µS/cm
Temperature (water)	Field Meter	NA	±0.3 % °C
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

#### Table 3-2 - Field Parameters

NA - Not Applicable

Required Parameters

Recommended Parameters

#### 3.2.2 PRODUCED WATER SAMPLE COLLECTION

Wells shall be sampled immediately following the determination of stable produced water parameters (pH, specific conductance, and temperature). Samples shall be collected and preserved unfiltered according to the specific sampling method(s) described below.

#### 3.2.2.1 COLLECTION OF UNFILTERED PRODUCED WATER SAMPLES

Fill unfiltered samples directly from the well, separator, tank, or pipe into the laboratory-supplied sample containers. If an in-line flow-through device was used to obtain field measurements, it should be disconnected or bypassed during sample collection (Puls and Barcelona, 1996). Preservation of unfiltered produced water samples with acids must be done in the field for certain analyses as listed in Table 3-1. The samples for analysis of volatile aromatic organic compounds (VOCs) and volatile petroleum range hydrocarbons shall be collected in a manner, such as direct fill of the 40ml vials, that minimizes agitation, aeration, and overfill.

Follow the manufacturer's calibration and maintenance procedures detailed in the equipment's technical manuals for calibration of field instrumentation. Replace solutions on or before the manufacturer's expiration date printed on each container; and dispose of unused, expired standards per manufacturer's instructions. Temperature corrections of pH and conductivity measurements are typically done by multiparameter 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 produced water, before data is submitted to the COGCC.

#### 4.0 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 VOCs, should follow the preservation guidance developed in EPA SW 846 Chapter 4 (U.S. EPA, 2018) and guidance identified in Table 3-1.

With the exception of water samples for analysis of radium isotopes, water samples will be placed in a cooler, with ice or other coolant, immediately following collection, unless otherwise indicated by the laboratory. Samples that require storage at 4°C will be stored in refrigerated conditions that prevent freezing. If shipping is required, samples requiring storage at 4°C 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 Chain-of-Custody (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.

#### 5.0 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, 1<sup>st</sup> subsequent, 2<sup>nd</sup> subsequent, to closure);
- Sample reason (e.g., 909.j. or other rules requiring use of 909.j protocols);
- 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 seals (ASTM D4840-99, 2018).

#### 6.0 ANALYTICAL PROCEDURES AND QUANTITATION LIMITS FOR LABORATORY AND FIELD METHODS

Analysis will be conducted using EPA SW-846 analytical methods, as incorporated by reference in Rule 901.b or listed in Table 3-1. With the Director's approval, analytical methods other than those listed in Table 3-1 may be accepted. Other methods suggested must be published by nationally recognized organizations and shown to be valid for non-potable water. Analysis of samples must be completed by laboratory(ies) accredited by NELAP, in general, and more importantly, for analytical procedures and analytes of concern in this SAP. NELAP accreditation extends to both matrix (such as produced water, 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). For

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.

Analytes, appropriate methodology, and expected achievable detection limits are included in Table 3-1. There are potentially acceptable methods used for determination of the analytes in the anions and general water quality parameters other than those listed in Table 3-1, but any methods utilized must be validated on or listed for non-potable water matrices and not solely for use on potable water matrices.

#### 7.0 FIELD AND LABORATORY QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Data integrity will be assured and verified through:

- Field sampling practices that comply with this SAP;
- Sample analysis by accredited analytical laboratory(ies);
- Laboratory practices that follow approved analytical methods appropriate for not-potable aqueous matrices;
- Collection and analysis of field quality assurance samples, when available; and
- Data quality reviews of the laboratory and field practices.

All samples will be analyzed by laboratory(ies) that are NELAP accredited for the required matrices and analytical processes, where such accreditation exists. Approved and accepted analytical methods, such as test methods for Evaluating Solid Waste SW846 or 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. Produced water typically can be categorized as non-potable. Methods used for potable water supplies such as those used for Safe Drinking Water Act (SDWA) compliance monitoring, have generally not been validated for non-potable matrices and should not be used to meet the requirements of Rule 909.j.

Where Standard Methods or EPA SW-846 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 shall be provided as part of the laboratory report.

#### 7.1 FIELD CONTROL SAMPLES

Field quality control samples shall be collected following the Operator's specified procedures. All field quality control sample results shall 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.

#### 7.1.1 FIELD DUPLICATE SAMPLES

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

- Collect one complete set of duplicate samples for every 20 produced water samples collected, but not less than one per year.
- Collect duplicate samples at approximately the same time as the original sample using identical sampling methods (ASTM D7069-04, 2015).
- Give each duplicate sample 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.
  - 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 - DS = 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 greater than five times (5x) the practical quantitation limit (U.S. EPA 2020). In instances when RPD is > 20\%, field and laboratory data will be reexamined to identify potential causes for the observed differences and, if necessary, the SOPs updated as appropriate to minimize future variances.

#### 7.1.2 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, anions, and VOCs. One equipment blank sample shall be collected for every 10 produced water 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, where possible, to reduce cross-contamination and reduce the cost of field equipment blanks.

#### 7.1.3 TRIP BLANKS

Trip blanks should be used to assess contamination introduced during shipping and/or field handling procedures. Collect trip blanks at a frequency of one blank per cooler. Trip blank volatile organic analysis (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). The Operator should verify negative results on all trip blanks, and adjust procedures accordingly if results above the MDL are identified.

#### 7.1.4 FIELD BLANKS

Field blanks will be collected only if the sampling technician believes that site conditions might cause the sample to become cross-contaminated by VOCs (i.e., the water source is located adjacent to hydrocarbon storage or fueling area).

A field blank is collected in a clean, glass VOA vial equipped with a gas-tight septum. Fill the vial with distilled water and leave the sample container open during the entire period of volatile sample collection. Immediately prior to capping, add a few drops of distilled water to the vial to create a positive meniscus, then cap and invert the vial to check for air bubbles. If bubbles are present, open the vial, add additional water, and reseal and check the vial again for air bubbles. This procedure should be repeated until a bubble-free container is achieved.

Field blanks should be analyzed for benzene, toluene, ethylbenzene, and xylenes (BTEX). BTEX concentrations should be less than the MDL.

#### 7.2 DATA QUALITY REVIEWS

Data quality reviews should be performed after all data reports have been received from the laboratory. Data quality reviews are documented on data quality review sheets (see Attachment 2), which are 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 include the following:

- 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 those actions should be completed.
- Certify that the data was collected in accordance with the SAP and that the data is suitable for incorporation into the COGCC database.

#### 8.0 EVALUATION OF DATA QUALITY

The Operator is expected to review field sampling records to ensure that samples were collected in accordance with this SAP or determine 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 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):

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

• Calculation of cation-anion balance after conversion to milliequivalents per liter (meq/l) and reviewed with typical criteria acceptance as follows:

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

Anion Sum (meq/L)	Acceptable Difference
0-3.0	$\pm 0.2$ meq/L
3.0-10.0	± 2%
10.0 - 800	5%

• Measured TDS concentration (mg/l) should be larger than the calculated TDS calculation and reviewed with acceptance levels of:

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

• Calculated EC calculation should be larger than measured EC value ( $\mu$ mhos/cm), and reviewed with acceptance levels:

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

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

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

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

calculated TDS / conductivity = 0.55 to 0.7

#### 9.0 HEALTH AND SAFETY

The health and safety of personnel must be addressed by the Operator's health and safety program and include protocols to be followed at sample sites. General aspects of the safety plan need to address personal protective equipment (PPE), such as hard hats, safety glasses, chemical resistant gloves, sturdy boots, long pants, etc., and under what conditions PPE should be used during the collection of samples.

#### 9.1 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.

#### 10.0 DATA SUBMISSION

The Operator will upload all required data into the COENV database through a Form 43 within 3 months of the sampling event as directed by 909.j. Prior to submission of the Form 43 or submittal to landowners, all data, reports, and communications will receive a QA/QC check.

#### 10.1 COENV DATABASE

The Operator will upload and submit the following electronic information into the COENV database through a Form 43:

- Facility ID (already in existence or newly created, as appropriate, in the COENV database);
- GPS coordinates for the site where sampling was conducted;
  - 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 incremental annual sampling;
- Date and time each sample was collected;
- Collection point (e.g. wellhead, separator, produced water vessel, end of pipe);
- Laboratory name;
- Sample reason (e.g. Rules 909.j., 803.g(5)C, 803.g(5)D, 806.a, 806.b, 806.c, 809, 810 and 811); and
- Results of field monitoring and observations.
  - 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 shall include the following information and file types:

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

• A PDF copy of the field sampling data sheet that includes all the location information, water production rate information, SDS for downhole products used at well(s), 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, downhole product SDS, and laboratory results must also be uploaded to the database.

#### 10.1.1 ELECTRONIC DATA DELIVERABLES

There are two accepted versions of the COGCC EDD that may be uploaded to the COENV database via Form 43: an XML EDD based on the EPA Water Quality Data (WQX) XML schema, or 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: <a href="https://cogcc.state.co.us/documents/about/COGIS\_Help/EnviroDB/EnviroDB.htm">https://cogcc.state.co.us/documents/about/COGIS\_Help/EnviroDB/EnviroDB.htm</a>.

Help regarding the EDD Form 43 upload process can be found at: <a href="https://cogcc.state.co.us/documents/reg/Forms/instructions/Form\_Instructions/Form\_43\_Instructions\_09282018.pdf">https://cogcc.state.co.us/documents/reg/Forms/instructions/Form\_Instructions/Form\_Instructions/Form\_43\_Instructions\_09282018.pdf</a>.

#### 11.0 REFERENCES

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ASTM D7069-04(2015), Standard Guide for Field Quality Assurance in a Groundwater Sampling Event, ASTM International, West Conshohocken, PA, 2015, <u>www.astm.org</u>.

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SM1030 Data Quality (2017), Standard Methods for the Examination of Water and Wastewater. <u>https://www.standardmethods.org</u>.

United States Environmental Protection Agency (EPA), 2020. National Functional Guidelines for Inorganic Superfund Methods Data Review (OLEM 9240.1-66), Office of Superfund Remediation and Technology Innovation (OSTRI), Washington, D.C., November 2020. EPA-542-R-20-006. <u>https://www.epa.gov/clp/superfund-clp-national-functional-guidelines-data-review</u>

United States Environmental Protection Agency (EPA), 2018. SW-846 Update VI chapter 4 revision 6 (Table 4-1). Accessed on 29 July, 2019 at <a href="https://www.epa.gov/hw-sw846/chapter-four-sw-846-compendium-organic-analytes">https://www.epa.gov/hw-sw846/chapter-four-sw-846-compendium-organic-analytes</a>.

#### 12.0 ATTACHMENT 1 - EXAMPLE FIELD SAMPLING DATA SHEET

# **Field Sampling Data Sheet**

COGCC Pit Facility #	Facility Name	Date of Sample
Sample Reason (e.g., Rules	909.j., 803.g(5)C, 803.g(5)D, 806.	a, 806.b, 806.c, 809, 810 and 811):
O&G API Number(s) (if m	ulti-well sample list all API #s)	
Pit Operator Name and Ind	ividuals Present (Who was on-site o	during the sampling?)
Sample Site Information		
GPS Location (field):		
GPS Location (post-process	sed):	
Legal Location (qtrqtr Sect	ion Township Range PM):	
Photo(s) Taken? Y N		
Weather conditions:		
Where was the sample take	n? (e.g., Wellhead, Separator, Prod	uced Water Vessel, Pipe to Pit et cetera)
Had the well(s) been in pro shutdown?	duction for a minimum of 48 hours	before sampling event? If not what was the reason for
Is well(s) routinely treated t	for mineral scale buildup and if yes	what product(s)?
Is well(s) routinely treated	for paraffin buildup and if yes what	product(s)?
Is well(s) routinely treated	with emulsion control product and i	if yes what product(s)?

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### Produced Water Quality Model Sampling and Analysis Plan

### Field Sampling Data Sheet – Page 2

Facility Name:\_\_\_\_\_

General Sampler Comments :\_\_\_\_\_

#### Water Quality Field Parameters

Clock Time	Elapsed Time	Water Level	Flow Rate (calc)	Temp (°C)	рН	EC (uS/cm)	ORP (mV)	DO (mg/L)	Turbidity	Odor	Color / Sediment	Bubbles / Effervescence

#### **Additional Information:**

Sampler's Name	(Print)	Company:	
Sampler's Signature		Date:	
Sampler's Signature		Date	

#### 13.0 ATTACHMENT 2 - EXAMPLE DATA QUALITY REVIEW SHEET

# **Data Quality Review Sheet**

COENV	Facility ID	Facility Name	Date of Sample
Sample	Reason (specific	rule)	
O&G A	PI Number(s)		
Oil & G	as Well(s)		Pit Facility #
Field Sl	heet Review		
1)	Was the well(s)	in use for 48 hours?	
	a. Please provi	ide approximate produced water volume pe	er day
2)	Were field parar	neters measured prior to sampling?	
3)	Did field parame	eters stabilize prior to sampling?	
4)		ons or other factors suggest that the sample ibe	es may not be representative of groundwater? If
Labora	tory Data Review	N	
1)	Were the sample	es received at the recommended water temp	perature of $\leq 6^{\circ}$ C?
2)	Were the sample	s properly preserved? If no, please explain	1
3)	Was proper chai	n-of-custody maintained? If no, please exp	plain
4)	Were all sample	s analyzed for the requested analyses?	
	a. If no, can th	e remaining sample be analyzed within the	e recommended hold time?
5)	Were the proper	methods used?	e recommended hold time?
	a. If no, can th	e remaining sample be analyzed within the	e recommended hold time?
6)	Were all sample	holding time limits met? If no, please expl	lain
7)	Were the correct	reporting limits used? If no, please explain	n
8)		y quality assurance samples collected and rding to laboratory methods? If no, please	d analyzed (i.e., matrix spikes & matrix spike explain

9) Were laboratory quality assurance sample results within acceptance limits? If no, please describe\_\_\_\_\_

#### Produced Water Quality Model Sampling and Analysis Plan

## Data Quality Review Sheet – Page 2 Facility Name:

#### **Field Control Samples**

- 10) Were field duplicate samples submitted? \_\_\_\_If no, proceed to trip blank questions.
- 11) Were the original and duplicate samples  $\geq 5x$  the practical quantitation limit (PQL)\_\_\_\_\_
- 12) Was the Relative Percent Difference (RPD)  $\leq 20\%$ ? If no, please describe\_\_\_\_\_
- 13) Were **trip blanks** submitted?\_\_\_\_\_\_ *If no, proceed to equipment blank question.*
- 14) If trip blanks were submitted, were the VOC constituent concentration results below method detection limits?
- 15) If **equipment blanks** were submitted, did the results meet the equipment blank data quality objectives specified in the Sampling and Analysis Plan?
- 16) If **field blanks** were submitted, did the results meet the field blank data quality objectives specified in the Sampling and Analysis Plan?

#### **Corrective Actions**

17) Are corrective actions required to remedy any data quality issues? If yes, please describe\_

18) Date by when corrective actions must be completed

19) Summary of Corrective Actions (once completed)

#### **Data Suitability Statement**

Based upon this data quality review and your professional judgment, have the data been collected and analyzed in general accordance with the COGCC Model Sampling and Analysis Plan? Yes No

(Circle one)

Are the data suitable for release for incorporation into the Colorado Oil and Gas Conservation Commission environmental database? Yes No *(Circle one)* 

Data Quality Reviewer's Name:		Company:	any:	
	(Print)			
Data Quality Reviewer's Signature:		Date:		