



**COLORADO**  
Oil & Gas Conservation  
Commission  
Department of Natural Resources

## **Colorado Oil and Gas Conservation Commission**

### **Sampling and Analysis Plan for Naturally Occurring Radioactive Material in Oil and Gas Produced Water**

**Prepared by  
Peter Gintautas, Ph.D.**

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## 1. Introduction, Purpose, and Approach

The Colorado Oil and Gas Conservation Commission (COGCC) seek to gain a better understanding of the activities of naturally occurring radioactive materials (NORM) in aqueous exploration and production (E&P) wastes. The study is also responsive to concerns and questions raised in the October 2011 review of COGCC rules, policies and practices by the State Review of Oil & Natural Gas Environmental Regulations (STRONGER). The STRONGER review noted that the COGCC did not have appreciable data concerning concentrations or activities of radioactive constituents in E&P waste streams in Colorado. The relative paucity of NORM data in COGCC records is in part because the COGCC has no statutorily granted authority over use or disposal of radioactive materials. The legislature in Colorado has solely invested regulatory authority over radioactive materials with the Colorado Department of Public Health and Environment (CDPHE) in all processes and wastes even though COGCC does, in general, regulate many other aspects of storage and disposal of E&P wastes along with requiring remediation of spills or releases of E&P wastes, when necessary, to ensure compliance thresholds established by rule.

COGCC staff addressed the STRONGER review concerns in part by the 2014 sampling of drill cuttings, soils into which cuttings had been mixed, and background soils with subsequent analysis of NORM constituents. Sampling and analysis of cuttings was a priority because cuttings are typically land-disposed under COGCC purview. Analysis of drill cutting also presents an opportunity to evaluate the activities of uranium and thorium and their radioactive progeny in the rocks that are in contact with water, gas and oil produced by a well. The rocks in which a well is completed are assumed to be the main source of NORM in E&P products and wastes that are brought to surface. In general, activities of NORM constituents in drill cuttings (COGCC, 2014b) were similar to or lower than activities of NORM analytes in background soils in the Wattenberg field. Two other data sets contain the bulk of the NORM constituent analyses from E&P wastes available to COGCC. Data on radioactivity in gas wells drilled near Project Rulison (Garfield County) and in wastes from those oil and gas wells is submitted to COGCC by operators in the area as prescribed under policies first adopted in 2007 (COGCC, 2010). One operator voluntarily provided a data set containing analyses of selected NORM constituents in produced water from just over 100 of their coal bed methane (CBM) wells in the Raton Basin. The Raton Basin dataset gathered in 1998 is the highest proportion of the Colorado produced water NORM analyses available to the COGCC. Analysis of produced water was chosen for this study as it is the E&P waste produced in greatest volume and is a primary source of NORM found as sediments and scale in storage or processing facilities. Radon (Rn) is a gas that is produced in the decay chain of both thorium and uranium and may be found in both the aqueous (waste) as well as in oil and gas (product) phases brought up well bores, as illustrated in Figure 1. When radon migrates out of the mix of liquids and gases produced from oil and gas wells, as gases by design do in liquid/gas separators used in-line at or near wells, then the progeny of radon (also NORM) might be more likely found in gas pipelines or further downstream in gas processing facilities. To better understand the fractionation of  $^{222}\text{Rn}$  between the produced water phase and the natural gas phase, a subset of samples of natural gas and produced water from the same wells will be analyzed for activities of  $^{222}\text{Rn}$ . Radon carried in the gas stream could result in presence of its progeny in production facilities processing gas but not receiving produced water.

Characterization of NORM constituents in aqueous E&P wastes from basins other than the Raton CBM field with different geologic settings and also different producing lithologies is needed to better understand what levels of NORM activities are present in water produced in other basins and from other geologic formations across the state. Significant variations in the geochemistry of produced waters are expected in general and are present even within waters produced from the same coal-bearing formations in the same basin. For example, some CBM-produced waters from the Raton Basin have concentrations of total dissolved solids (TDS) as low as 500 milligrams per liter (mg/l) while a few produced waters in the same formation in the same basin have TDS >25,000 mg/l. Aqueous wastes from production of gas in tight sandstones in the Piceance Basin of western Colorado may be expected to have different geochemical signature than produced water from wells completed in carbonate mineral bearing chalk and marl zones in the Niobrara Formation of the Wattenberg field in northeastern Colorado because the rocks the well produce from have very different overall mineralogy and chemical composition, and the produced water chemistry from each is expected to reflect those differences in chemistries of the rocks with which the waters are in contact.

This sampling and analysis plan (SAP) has been developed to provide COGCC staff procedures for the collection of representative aqueous E&P wastes (and one E&P product – natural gas) as well as for the accurate and precise determination of NORM activity levels in those aqueous wastes and gaseous products. This SAP has also been developed to provide documentation of the analytes of interest as well as to provide documentation of the laboratory methods to be used in the analysis of the specified target list. This SAP provides written guidance for record-keeping in the field and laboratory and also provides general Quality Assurance (QA) practices and procedures to be used in the field and laboratory.

Naturally occurring thorium (Th) and uranium (U) isotopes, and one radioactive isotope of potassium (K), are present in rocks and, together with the progeny produced by the decay of uranium and thorium, are the primary sources of NORM in E&P wastes (IAEA, 2003). Potassium is estimated to be the eighth most abundant element (1.84%) in the earth's crust (Greenwood and Earnshaw, 1997), and its long-lived, naturally occurring radioactive isotope ( $^{40}\text{K}$ ) is present as a fraction (0.0117%) of potassium present in the earth (Meija et al., 2016 and CIAAW, 2017) or approximately 2 milligrams per kilogram (mg/kg)  $^{40}\text{K}$  in the earth's crust. Although thorium and uranium were estimated to respectively be the 39<sup>th</sup> (8.1 mg/kg) and 47<sup>th</sup> (2.3 mg/kg) most abundant elements in the earth's crust by Greenwood and Earnshaw (1997), it is helpful to keep in mind that even small concentrations of radionuclides may represent a significant amount of radioactivity.

$^{232}\text{Th}$  (99.98%) and  $^{238}\text{U}$  (99.2742%) are the most abundant isotopes of thorium and uranium in the earth (Meija et al., 2016 and CIAAW, 2017) and are ubiquitous in the earth's crust with activities dependent on rock type (IAEA, 2003). The 23 radionuclides in the thorium and uranium decay chains are the primary NORM components in E&P wastes. These are listed in Figure 1 ( $^{238}\text{U}$ ) and Figure 2 ( $^{232}\text{Th}$ ) as modified from an International Atomic Energy Agency (IAEA, 2003) guidance document concerning management of NORM in E&P wastes. Thorium and, to a lesser extent uranium, are thought to be relatively immobile under the geochemical conditions present in many oil-producing rocks (Hem, 1985 and IAEA, 2003). Two elements found among the decay products of the uranium and thorium decay chains, radium and radon,

tend to be more soluble in groundwater and gas phases, respectively. Thus radium and radon are likely to be brought to the surface by production activities at oil and gas wells. Radium isotopes ( $^{224}\text{Ra}$ ,  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ) may be found in significant concentrations in waters while isotopes of radon gas ( $^{222}\text{Rn}$  and  $^{220}\text{Rn}$ ) are typically found in natural gas as discussed by Hem (1985) and IAEA (2003). These mobility concepts are illustrated in Figures 1 and 2 and are explained in more detail in the IAEA publication cited (IAEA, 2003). Potassium is relatively soluble in water (Hem, 1985) and is another potential source of NORM in produced water. The decay of  $^{40}\text{K}$  is directly to stable isotopes of calcium (Ca) by beta decay and to argon (Ar), so there are no radioactive progeny of  $^{40}\text{K}$  of concern in this study.

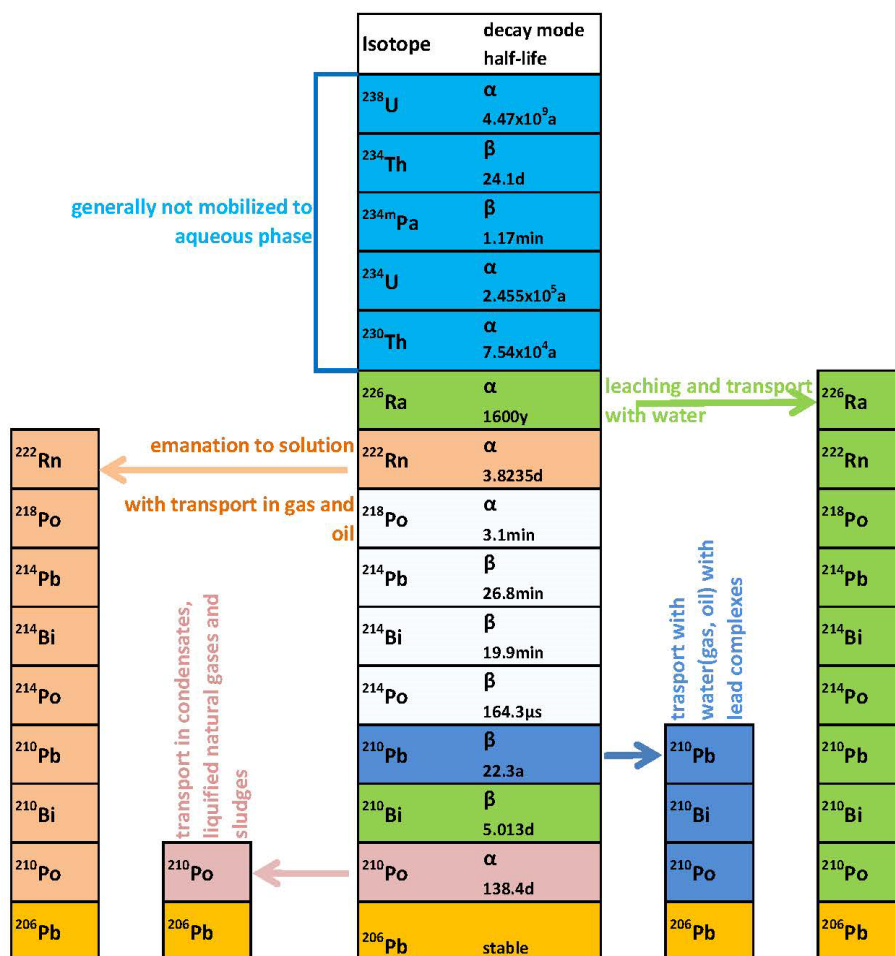
In Colorado, E&P activities for oil and natural gas are conducted in many parts of the state. These activities include drilling through various subsurface layers of rock containing uranium, thorium and their decay products with the intent of producing oil and natural gas from those geologic formations. Rock cuttings brought to the surface by drilling, and waters and gas co-produced when natural gas and crude oil are brought to surface, are expected to contain NORM. Rock cuttings from drilling activities in the Greater Wattenberg field of Colorado were analyzed for NORM activities in 2014 (COGCC, 2014b) Special Project 2136 utilizing a project-specific SAP (COGCC, 2014a).

In April 2013, Pennsylvania Department of Environmental Protection contracted with Perma-Fix Environmental Services, Inc. (PESI) to perform a comprehensive study of NORM and TENORM (technologically enhanced NORM) related to the oil and gas exploration activities throughout the Commonwealth of Pennsylvania. As part of this effort PESI prepared a sampling and analysis plan (PESI, 2013a and 2013b). The 2014 COGCC SAP and this document borrow from those documents.

Previous studies of NORM in Colorado E&P wastes include the COGCC study in 2014 and a nationwide 1989 survey (Otto, 1989) performed on behalf of the American Petroleum Institute (API) with screening type analyses reported from multiple sites in five counties in Colorado. NORM in produced waters from E&P wastes in Pennsylvania (PESI, 2016) were sampled and analyzed, and this data can be used for comparison to data from Colorado E&P wastes collected in the current study and also from the 2014 COGCC study (COGCC, 2014b). The United States Geological Survey (USGS) maintains a database containing produced water analyses from around the country, and recently they have incorporated radium activities/activity concentrations in their database (NASE&M, 2016 p.42). As with other available data, the USGS compiled data will be compared to data gathered in this study if the data is not already in the COGCC database.

For purposes of this plan, any water emerging from the well is considered to be produced water, even if was previously injected for hydraulic fracturing or is from aqueous liquids added to a wellbore such as KCl brines used to control pressure in wells or for other purposes, as all of those liquids are considered E&P wastes. The primary focus of the plan will be to sample and analyze aqueous E&P wastes from oil- and gas-producing formations in sedimentary basins across the state. At a subset of sites, sampling and analysis of source water for drilling and completion activities will be conducted. The source waters may include fresh water, recycled and possibly treated produced water/flowback, as well as water from other sources. Another

subset including sampling and analysis of water produced soon after hydraulic fracture stimulation, oftentimes referred to as flowback fluids, will also be attempted.

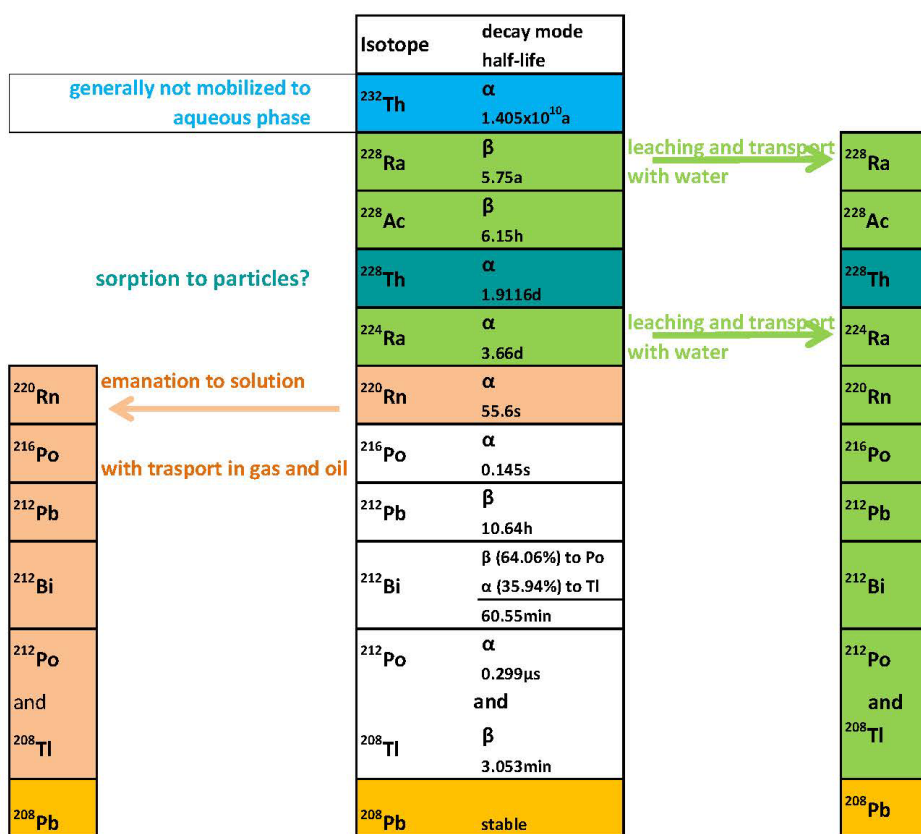


**Figure 1.** Decay chain of  $^{238}\text{U}$ . Decay modes are alpha =  $\alpha$  and beta =  $\beta$ . Abbreviations for time units as follows: a=year, d=day, min=minute and  $\mu\text{s}=10^{-6}\text{seconds}$ . Modified from IAEA, 2003.

Sampling activities, in order of priority with estimated numbers of samples, will include:

- produced water (44 including 4 field duplicates)
- source water (3 including 1 field duplicate)
- flowback (3 including 1 field duplicate)
- natural gas (10 including 1 field duplicate)

This SAP defines protocols for sampling, chain-of-custody (COC) procedures, laboratory analyses of NORM and water quality constituents and general guidance on QA practices.



**Figure 2.** Decay chain of <sup>232</sup>Th. Decay modes are alpha = α and beta = β. Abbreviations for time units as follows: a=year, d=day, h=hour, min=minute and μs=10<sup>-6</sup>seconds. Modified from IAEA, 2003.

## 2. Sampling Sites

### 2.1 Background

The sampling locations associated with oil and gas drilling and production will be located in many areas of the State of Colorado. This project will attempt to collect aqueous samples from throughout the state with an emphasis on basins and formations from which relatively larger volumes of aqueous E&P waste are produced as documented in the COGCC production database since 1999. Sampling of natural gas and produced water for analysis of <sup>222</sup>Rn will be concentrated in eastern Colorado to ease logistics of sample delivery to the lab in a timely manner. Source water and flowback samples will be collected opportunistically in areas where wells are being completed at the time of sampling.

### 2.2 Produced Water Characterization

Table 1 lists the primary NORM analytes (or constituents) of concern for aqueous E&P waste characterization. These analytes include the longer-lived radionuclides present in the uranium



and thorium decay chains, as well as  $^{40}\text{K}$  and  $^{235}\text{U}$ , a member of the third natural decay series, the actinium chain<sup>1</sup>.

The primary decay mechanisms of the most abundant U and Th isotopes and their progeny are by alpha or beta emission as shown in Figures 1 and 2. Therefore, a general characterization of NORM constituent activities in aqueous samples will start with measurement of gross alpha and gross beta activity. Though the measurement of gross alpha and gross beta activity does not provide identification of the alpha and beta emitters, it can provide useful indications of overall level of radioactivity in samples. For this study the gross alpha and gross beta analyses are considered as screening techniques that may be subject to bias due to the relatively complex matrices of produced water samples in comparison to the drinking water samples for which the gross alpha and gross beta analytical protocols were developed.

Isotopic determinations of several key radionuclides of concern in aqueous samples will be performed following chemical separation from the matrix. These include thorium decay chain members  $^{228}\text{Ra}$  and  $^{224}\text{Ra}$ , and uranium decay chain members  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ .  $^{222}\text{Rn}$  will be analyzed directly in gas samples by transfer to a scintillation cell with alpha emissions measured.  $^{222}\text{Rn}$  in water samples will be analyzed by mixing with liquid scintillation cocktail in a vial with alpha emissions subsequently measured. If aqueous concentrations of Th exceed a specified threshold (3 micrograms per liter [ $\mu\text{g/l}$ ]) in individual samples, then those aqueous samples will also be analyzed for isotopic activities of  $^{228}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$  using chemical separation followed by alpha spectrometry. If aqueous concentrations of U exceed the specified threshold (3  $\mu\text{g/l}$ ) in individual samples, then those aqueous samples will also be analyzed for isotopic activities of  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  using chemical separation followed by alpha spectrometry.

Gamma spectroscopic analysis of aqueous samples will be performed to identify and quantify gamma-emitting radionuclides using specific libraries that include members of thorium and uranium decay chains, as well as  $^{235}\text{U}$  and  $^{40}\text{K}$ . The thorium decay chain radionuclides include  $^{208}\text{Tl}$ ,  $^{212}\text{Pb}$ ,  $^{212}\text{Bi}$  and  $^{228}\text{Ra}/\text{Ac}$ . Uranium decay chain radionuclides include  $^{214}\text{Bi}$ ,  $^{214}\text{Pb}$ ,  $^{234\text{m}}\text{Pa}$ ,  $^{234}\text{Th}$  and  $^{226}\text{Ra}$ . Although it contributes only modestly to the overall activity of NORM mixtures,  $^{235}\text{U}$ , the head of the third natural decay chain, the actinium chain, emits an intense gamma ray. Please note that  $^{137}\text{Cs}$  is not expected in samples but rather it is included as a reference nuclide against which relative detection capability is assessed. The presence of  $^{235}\text{U}$  in samples can interfere with the analysis of  $^{226}\text{Ra}$  by gamma spectroscopy due to the near coincidence in their gamma ray energies. The lab will report time of analysis activity for gross alpha and gross beta which are to be prepared and counted within four days of collection. The Other radiochemistry data to be provided by ALS will be automatically decay corrected to time and date of collection by software in use at the lab.

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<sup>1</sup> This SAP concentrates analytical efforts on characterization of activity from the uranium and thorium decay chains.  $^{238}\text{U}$  and  $^{235}\text{U}$  in uranium of natural origin are found globally with a fixed mass ratio of about 138:1 and a fixed activity ratio of about 22:1. For this reason, the  $^{235}\text{U}$  decay chain (actinium chain) contributes only nominally to the overall radioactivity of NORM mixtures.

Several gamma spectrometry in water analytes that are routinely requested by customers and performed by laboratories may produce unreliable results. They are being requested here to allow assessment of data quality relative to definitive isotope specific tests. They include:

- $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{235}\text{U}$  – Due to relatively low sensitivity by gamma spectrometry, results for these radionuclides may show very high uncertainty until they are present in high concentration. Isotopic determinations of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{235}\text{U}$  (if performed) will be considered to be the definitive results and the gamma spectrometry measurements as supporting data.
- $^{226}\text{Ra}$  – Determinations for  $^{226}\text{Ra}$  by gamma spectroscopy are not specific for this radionuclide and may exhibit high errors in precision and accuracy due to spectral interferences. Results will be used only as qualitative indicators of the possible presence of  $^{226}\text{Ra}$  in samples, and a more definitive isotope specific testing for  $^{226}\text{Ra}$  will be performed on all samples.
- $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  – These two isotopes are frequently used as indicators of  $^{222}\text{Rn}$  in samples. These results are unreliable since water samples for gamma analysis are generally not managed to protect against loss of radon during sampling, transport, storage, preparation and analysis.

General water quality parameters such as metals, pH, TDS and anions will be analyzed in all aqueous samples as described in more detail in Table 1. Isotopic composition analysis of stable isotopes of water will be performed on all aqueous samples. Analysis of tritium ( $^3\text{H}$ ) and carbon-14 ( $^{14}\text{C}$ ) will be performed on approximately 10 aqueous samples including produced water, source water and flowback. We hypothesize that much of the water produced to the surface from wells drilled and completed in the Niobrara and Codell Formations is not native formation water but comes from the water used in hydraulic fracture well completions. The levels of activities of these relatively short lived non-NORM radioactive analytes can be used to help evaluate this hypothesis.

### **3. Scope and Objectives**

The primary objective of this study is to investigate the occurrence and concentrations of NORM in aqueous wastes derived from E&P activities in Colorado. Information on volumes of aqueous wastes from the COGCC production report database in conjunction with the analytical data levels of radioactivity will inform staff, other agencies, operators and the public to better understand potential risks from management of these aqueous E&P wastes as regulated by COGCC under its 900-series rules.

A limited study of the activities present in produced natural gas of one radon isotope ( $^{222}\text{Rn}$ ) is included in this SAP. Analysis of natural gas and produced water samples from the same wells will aid in understanding of partitioning of radon between water and gas phases.

**Table 1.** Analytes, matrices, methods and projected number of samples

Analyte(s)	Matrix	Method(s)	Projected # of samples
gross alpha	produced water	E900.0 as modified in ALS SOP 702r20 and 724r12 (coprecipitation preparation)	50
gross beta	produced water	E900.0 as modified in ALS SOP 702r20 and 724r12	
$^{234}\text{U}$ , $^{235}\text{U}$ , $^{238}\text{U}$	produced water	DOE-U-02 as modified in ALS SOP 776r14, 778r14 and 714r13 (if total U>3µg/l)	10
$^{228}\text{Th}$ , $^{230}\text{Th}$ , $^{232}\text{Th}$	produced water	ASTM D3972 as modified in ALS SOP 776r14, 777r12 and 714r13 (if total Th>3µg/l)	10
$^{210}\text{Pb}$	produced water	ALS SOP 704	50
$^{210}\text{Po}$	produced water	ASTM D3972 as modified in ALS SOP 711r10 and 714r13	50
$^{222}\text{Rn}$	produced water	SM 7500-Rn B as modified in ALS SOP 799r5 and 704r11	25
$^{222}\text{Rn}$	natural gas	E903.1 as modified in ALS SOP 783r12	10
$^{224}\text{Ra}$ and $^{226}\text{Ra}$	produced water	E903.0 as modified in ALS SOP 701	50
$^{228}\text{Ra}$	produced water	E904.0 as modified in ALS SOP 749r3 and 724r12	50
gamma emitters $^{40}\text{K}$ , $^{137}\text{Cs}$ , $^{208}\text{Tl}$ , $^{212}\text{Pb}$ , $^{212}\text{Bi}$ , $^{214}\text{Pb}$ , $^{214}\text{Bi}$ , $^{226}\text{Ra}$ , $^{235}\text{U}$ , $^{228}\text{Ac}$ , $^{228}\text{Ra}$ , $^{234\text{m}}\text{Pa}$ $^{234}\text{Th}$	produced water	E901.1 as modified in ALS SOP 739r12 and 713r14	50
$^3\text{H}$	produced water	SOP -electrolytic enrichment and GPC of $\text{H}_2$ gas	10
$^{14}\text{C}$ of dissolved inorganic carbon (DIC)	produced water	SOP –accelerator mass spectrometry (AMS)	10
total metals B, Be, Ca, Cr, Fe, K, Li, Mg, Na, Ni, P, S, Si, V	produced water	SW3010A/SW6010B	50
total metals Al, Ag, As, Ba, Cd, Co, Cu, Mo, Mn, Na, Pb, Se, Sr, Th, Tl, U, Zn		SW3010A/SW6020A	50
dissolved metals Ba, Ca, Fe, K, Mg, Na, Si, Sr	produced water	SW3005A/SW6010B	50
pH	produced water	SW9040	50
specific conductance	produced water	SM2510 B	50
alkalinity (total, bicarbonate and carbonate) as $\text{CaCO}_3$ )	produced water	SM2320B	50
total suspended solids	produced water	SM2540 D	50
total dissolved solids	produced water	SM2540 C	50
Anions Br, Cl, F, $\text{SO}_4^{4-}$	produced water	SW9056	50
$\delta^{18}\text{O}$ & $\delta\text{D}$ of $\text{H}_2\text{O}$	produced water	laboratory SOP	50
$\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC)	produced water	laboratory SOP	50

Sampling performed for this NORM study will consist of:

- Sampling of aqueous and gaseous media for radiological and inorganic laboratory analyses to be performed at specialized commercial and research laboratories.

This section summarizes the scope and objectives of these survey activities; detailed descriptions of sampling procedures and documentation requirements are presented in Sections 4 and 5, respectively.

### 3.1 Field Sampling Activities

Field sampling will consist of collecting samples of primarily aqueous media (with a limited number of gaseous samples) from oil and gas production facilities for analysis at laboratories. The following types of field samples will be collected for the purposes identified:

- Produced water samples, which may include flowback for laboratory analysis
- Source water samples for laboratory analysis
- Natural gas samples for laboratory analysis

Laboratory analyses of aqueous samples will include the following parameters as specified in Table 1:

- gross alpha and beta
- gamma spectroscopy to identify radionuclides present
- alpha spectroscopy for uranium ( $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{234}\text{U}$ ), thorium ( $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$ ),
- alpha scintillation for  $^{222}\text{Rn}$
- $^{224}\text{Ra}$  and  $^{226}\text{Ra}$  by alpha spectroscopy following chemical separation
- $^{228}\text{Ra}$  by gas flow proportional counting beta analysis of its short-lived progeny ( $^{228}\text{Ac}$ ) following chemical separation
- alpha spectroscopy following chemical separation of  $^{210}\text{Po}$
- liquid scintillation spectrometry following chemical separation of  $^{210}\text{Pb}$
- metals analysis (total) of U and Th by mass spectrometry

Table 2 lists requested minimum detectable concentrations for the analytes and methods listed previously in Table 1. The requested minimum detectable concentrations are based on an assumption of TDS concentrations in the aqueous samples of approximately 15,000 mg/l. Some samples may have TDS of greater than this level, and the requested detection limits may not be achievable in that case. Volumes of sample required for analysis, types of containers utilized, sample preservation techniques and laboratory holding times are summarized in Table 3. Specific sampling parameters, laboratory analytical methods and numbers of samples are discussed further in Section 6.

## **4. Field Sampling Activities**

### **4.1 Aqueous Sample Type and Location**

Grab samples will be opportunistically collected from wells or their production facilities from locations outlined below and based on criteria discussed previously:

- produced water directly from well or from phase separators
- produced water from storage vessels (such as produced water tanks)

### **4.2 Sampling Methods for Aqueous Samples**

A representative grab sample will be collected from the appropriate pipe, tank or outlet directly into the sample containers using available piping and valves. If necessary, a disposable bailer or bucket may also be used to collect the sample, and the contents of the bailer added directly to sample containers. Descriptions of sampling best practices are provided to samplers along with example COC's. Samples will be placed into certified clean, laboratory-supplied containers immediately following collection, and caps and labels promptly affixed to the sample containers. The samples will be transported via overnight delivery service or brought directly to the lab under COC control for transfer of custody of the lab. Some samples will have to be shipped by the main laboratory (ALS – Fort Collins) to more specialized laboratories, and COC procedures will be used as above. Table 3 identifies container types to be used for collection of these samples. Upon receipt, the lab will check pH of containers with HNO<sub>3</sub> preservation and will re-acidify if pH >2 is measured. Samples that are acidified at the lab will be stored for a minimum of 18 hours before further processing takes place per the laboratory's Standard Operating Procedure (SOP). The majority of analyses specified in this SAP will be performed on the samples as collected (without filtration) to better mimic the E&P wastes as they reach the surface where spills and releases of the waste fluid containing sediment and particles may occur.

### **4.3 Sampling Equipment Decontamination Procedures**

Disposable sampling equipment will be used wherever possible to minimize decontamination requirements. If reusable equipment is used, such equipment will be decontaminated both prior to sampling in the field and between uses, as appropriate. The following decontamination steps will be performed for reusable equipment, in the following order as necessary:

- potable water rinse (X3)
- wash with laboratory-grade detergent (Alconox® or equivalent)
- deionized water rinse (X3)
- air dry
- rinse blanks at a frequency of 1 in 20 uses

## **5. Documentation**

### **5.1 Field Documentation**

Information pertinent to field activities will be recorded on field sampling sheets. Sufficient information will be recorded in the sheets to permit reconstruction of site sampling activities. Information recorded on official project documents (e.g., checklist or sampling forms, COCs, etc.) will not be repeated except in summary form or cross-reference notation where determined necessary. Field data sheets will be kept in the possession of the appropriate field personnel, or in a secure place when not being utilized during field work. Entries recorded on forms will be made in blue or black waterproof ink and may include, but not be limited to, the following information:

- sampler name(s) and initials, date, and times of arrival at and departure from the site
- description of the sampling activities
- sample collection method and number/volume of sample(s) collected
- photographs of facility from which grab samples collected
- information regarding activity changes and scheduling modifications
- field observations and weather conditions
- global positioning system (GPS) coordinates of spot where each sample was collected

Additionally, the sampler(s) will record any other pertinent data, such as operator representatives on site at time of sampling, during each sample event. The sampler will also record any pertinent observations such as current activities at well if not in routine production. Field data sheets or forms may be used to record field information in addition to the use of log books.

### **5.2 Sample Documentation**

#### **5.2.1 Sample Numbering System**

A unique sample numbering scheme based on COGCC facility numbers will be used to identify each sample collected. This is necessary so that data can be added electronically to the COGCC environmental database. The main purpose of this numbering scheme is to provide a tracking system for the retrieval of analytical and field data on each sample from storage in the database and document management system. Sample identification numbers will be recorded on sample labels or tags, field data sheets and/or notebooks, COC records and all other applicable documentation used during the project.

#### **5.2.2 Sample Labels**

Labels will be affixed to all sample containers during sampling activities. Information will be recorded on each sample container label using waterproof inks at the time of sample collection. The information to be recorded on the labels will be as follows:

- sample identification number

- sample type (grab or composite)
- site name and area/location number
- analysis to be performed
- type of chemical preservative present in container
- date and time of sample collection
- name or more typically the initials of the sampler

### **5.2.3 Chain-of-Custody Records**

COC procedures implemented for the project will provide documentation of the handling of each sample from the time of collection until completion of laboratory analysis. The COC form serves as a legal record of possession and transfer of samples.

Custody will be documented throughout the project field sampling activities by a COC form initiated each day during which samples are collected. The form will accompany the samples from the sampling site to the laboratory and a copy of the COC will be returned to the project coordinator at COGCC with the final analytical report. Personnel with sample custody responsibilities will be required to sign, date and note the time on a form when relinquishing samples from their immediate custody (except in the case where samples are placed into designated secure areas for temporary storage prior to shipment). Bills of lading or air bills will be used as custody documentation during times when the samples are being shipped from the site to the laboratory and will be retained as part of the permanent sample custody documentation. COC forms will be used to document who collected samples, when the samples were collected, how samples were preserved and what analyses are required for all samples collected. Laboratory-specific internal custody tracking at the lab is necessary once the sample has been received by the laboratory. The internal tracking should follow the SOP developed specifically for this purpose by the lab. Handwritten or electronic tracking of internal transfer at the lab or similar procedures specified in the lab's SOP is required.

The individual responsible for shipping the samples from the field to the laboratory will complete any fields not completed at the time of sampling including the date and time and manner of transport or shipment. This individual will also inspect the form for completeness and accuracy. After the form has been inspected and determined to be satisfactorily completed, the responsible individual will sign, date, and note the time of transfer on the form. The COC form will be placed in a sealable plastic bag and placed inside the cooler used for sample transport after the field copy of the form has been detached or a copy made and saved. The field copy of the COC form will be stored electronically with the project files.

Custody seals will also be placed on each cooler used for sample transport by commercial courier. These seals will consist of a tamper-proof adhesive material placed across the lid and body of the coolers. Custody seals will be used to ensure that no sample tampering occurs between the time the samples are placed into the coolers and the time the coolers are opened for receipt and subsequent analysis at the laboratory. Cooler custody seals will be signed and dated by the individual responsible for completing the COC form contained within the cooler. If samples remain in custody of COGCC staff and are delivered by them to the laboratory, then custody seals are not necessary.

### **5.2.4 Cooler Receipt and Condition of Samples upon Receipt Form**

The condition of shipping coolers and enclosed sample containers will be documented upon receipt at the analytical laboratory. This documentation will be accomplished using a cooler receipt checklist utilized by the laboratory. Each laboratory receiving samples will document the receipt of samples by accepting custody of the samples from the approved shipping company. In addition, the laboratory will document the condition of the environmental samples upon receipt. Temperature upon receipt for sample types with preservation at 4° Celsius (C) (Table 3) will be recorded using the laboratory-specific SOP for this process. Samples in Table 3 for which preservation is by acidification with HNO<sub>3</sub> to pH <2 will have the pH checked (using pH paper) and recorded as specified in the laboratory SOP. Adjustment of pH at the lab when necessary may be performed and this information recorded on the receipt form as specified in the laboratory SOP.

### **5.2.5 Documentation Procedures**

The tracking procedure to be used for documentation of all samples collected during the project will involve the following steps:

- collect and place samples into laboratory sample containers
- complete sample container label information
- complete sample documentation information in the field notes
- complete project and sampling information sections of the COC form(s)
- complete the air bill for the cooler to be shipped to laboratory, if applicable
- perform a completeness and accuracy check of the COC form(s)
- complete sample relinquishment section of form(s) and place the form(s) into cooler
- pack cooler with ice, as needed, for samples requiring preservation to 4°C as listed in Table 3
- place COC seals on the exterior of the cooler
- package and transport or ship the cooler to the laboratory

The following steps will be made upon receipt of the cooler at the subcontract laboratory:

- inspect contents and status upon receipt
- complete requested analyses
- transmit a copy of the original COC form(s) with final analytical results from laboratory

### **5.2.6 Corrections to Documentation**

Original information and data in field notes, on sample labels, on COC forms and on any other project-related documentation will be recorded in blue or black waterproof ink and in a completely legible manner. Errors made on any record document will be corrected by crossing out the error and entering the correct information or data. An error discovered on a document will be corrected by the individual responsible for the entry, as possible. Erroneous information or data will be corrected in a manner that will not obliterate the original entry, and corrections will be initialed and dated by the individual responsible for the entry.



### **5.3 Sample Packaging and Shipping**

Sample containers destined for offsite laboratory analysis will be packaged in thermally insulated rigid-body coolers, which will be stored in a secure area during the time period between collection and shipment to the laboratory.

### **5.4 Management and Retention of Records**

Original copies of field data, field records, analytical data, training records, and other project-specific documentation will be retained by COGCC staff with images of all documents stored in the COGCC document retrieval system linked to this special project. Analytical data will also be uploaded to the COGCC Environmental database (COENV). Both documents and analytical data can be retrieved using tools available on the COGCC web pages. Laboratories will retain records as per their laboratory QA program (LQAP), but for a period of no less than 2 years.

## **6. Laboratory Analysis**

The contracted laboratories shall perform analysis of aqueous and gaseous samples for characterization as listed in Table 1. Table 2 defines the desired detection limits for laboratory analysis. Table 3 summarizes volumes of samples to be collected, containers samples are to be placed in, preservation methods and holding time requirements for each applicable media on this project. Laboratory analysis of matrix spike/matrix spike duplicate (MS/MSD), field duplicate, and QA split samples will be performed in accordance with the requirements of Section 7.

Samples will be shipped to or transported to laboratories for analyses. Those laboratory analyses will be performed in accordance with documented laboratory-specific SOPs based on published or accepted methods listed in the Methods column of Table 1. The samples will be analyzed for NORM constituents and general water quality parameters at ALS Fort Collins, as outlined in Table 1. Gas samples will be analyzed for  $^{222}\text{Rn}$  as described in Table 1. Tritium ( $^3\text{H}$ ) will be analyzed at the University of Miami RSMAS tritium laboratory. The analysis of  $^{14}\text{C}$  will be done at the University of Arizona accelerator mass spectroscopy (AMS) facility. The stable isotopes of water will be analyzed under arrangements with Dolan Integration Group and a subcontract laboratory.

**Table 2.** Requested Detection Limits

Analyte(s)	Matrix	Requested Minimum Detectable Concentrations for samples with TDS approx. 15,000mg/l
gross alpha	produced water	15pCi/l (depends on TDS)
gross beta	produced water	30pCi/l (depends on TDS)
<sup>234</sup> U, <sup>235</sup> U, <sup>238</sup> U	produced water	0.2pCi/l
<sup>228</sup> Th, <sup>230</sup> Th, <sup>232</sup> Th	produced water	0.2pCi/l
<sup>210</sup> Pb	produced water	1pCi/l
<sup>210</sup> Po	produced water	0.5pCi/l
<sup>222</sup> Rn	produced water	50pCi/l
<sup>222</sup> Rn	natural gas	1pCi/l
<sup>224</sup> Ra and <sup>226</sup> Ra	produced water	0.5pCi/l
<sup>228</sup> Ra	produced water	1pCi/l
Gamma <sup>40</sup> K, <sup>137</sup> Cs, <sup>208</sup> Tl, <sup>212</sup> Pb, <sup>212</sup> Bi, <sup>214</sup> Pb, <sup>214</sup> Bi, <sup>226</sup> Ra, <sup>228</sup> Ra, <sup>228</sup> Ac, <sup>234m</sup> Pa <sup>234</sup> Th, <sup>235</sup> U,	produced water	<sup>137</sup> Cs - 10pCi/l, <sup>40</sup> K- 200pCi/l, <sup>226</sup> Ra/ <sup>235</sup> U by 186 keV, 228Ra from <sup>228</sup> Ac decay, other analytes minimum detectable concentrations (MDCs) vary
<sup>3</sup> H	produced water	0.32pCi/l
<sup>14</sup> C of dissolved inorganic carbon (DIC)	produced water	<48,000 years BP and/or PMC
total metals B, Be, Ca, Cr, Fe, K, Li, Mg, Na, Ni, P, S, Si, V	produced water	varies by element and matrix
total metals Al, Ag, As, Ba, Cd, Co, Cu, Mo, Mn, Na, Pb, Se, Sr, Th, Tl, U, Zn		U -1µg/l, Th - 2µg/l others vary by element and matrix
dissolved metals Ba, Ca, Fe, K, Mg, Na, Si, Sr		varies by element and matrix
pH	produced water	0.1 SU
specific conductance	produced water	50µmhos/cm
alkalinity (total, bicarbonate and carbonate alkalinity as CaCO <sub>3</sub> )	produced water	20mg/l
total suspended solids	produced water	20mg/l
total dissolved solids	produced water	20mg/l
Anions Br, Cl, F, SO <sub>4</sub>	produced water	10, 10, 10 and 50mg/l respectively
δ <sup>18</sup> O & δD of H <sub>2</sub> O	produced water	NA
δ <sup>13</sup> C of dissolved inorganic carbon (DIC)	produced water	NA

<b>Table 3. Sample volumes, containers, preservatives and holding times</b>					
<b>Analyte(s)</b>	<b>Matrix</b>	<b>Volume</b>	<b>Container</b>	<b>Preservative</b>	<b>Holding Time</b>
gross alpha	produced water	1l	LDPE cubitainer	pH<2 with HNO <sub>3</sub>	≤4 days to count
gross beta	produced water				
<sup>234</sup> U, <sup>235</sup> U, <sup>238</sup> U	produced water	1l		pH<2 with HNO <sub>3</sub>	NA
<sup>228</sup> Th, <sup>230</sup> Th, <sup>232</sup> Th	produced water	1l		pH<2 with HNO <sub>3</sub>	
<sup>210</sup> Pb	produced water	1l		pH<2 with HNO <sub>3</sub>	
<sup>210</sup> Po	produced water	1l		pH<2 with HNO <sub>3</sub>	
<sup>222</sup> Rn	produced water	3x40ml	glass VOA vial with PTFE/ silicone septa	none	as soon as practical
<sup>222</sup> Rn	natural gas	2x500ml	Tedlar bag	none	as soon as practical
<sup>224</sup> Ra and <sup>226</sup> Ra	produced water	1l	LDPE cubitainer	pH<2 with HNO <sub>3</sub>	≤4 days to count <sup>224</sup> Ra
<sup>228</sup> Ra	produced water	1l		pH<2 with HNO <sub>3</sub>	NA
gamma emitters <sup>40</sup> K, <sup>137</sup> Cs, <sup>208</sup> Tl, <sup>212</sup> Pb, <sup>212</sup> Bi, <sup>214</sup> Pb, <sup>214</sup> Bi, <sup>226</sup> Ra/ <sup>235</sup> U, <sup>228</sup> Ac/ <sup>228</sup> Ra, <sup>234m</sup> Pa and <sup>234</sup> Th	produced water	1l		pH<2 with HNO <sub>3</sub>	
<sup>3</sup> H	produced water	1l	HDPE	none	NA
<sup>14</sup> C of dissolved inorganic carbon (DIC)	produced water	2 X 0.5l	HDPE	none	NA
total metals B, Be, Ca, Cr, Fe, K, Li, Mg, Na, Ni, P, S, Si, V	produced water	250ml	HDPE	pH<2 with HNO <sub>3</sub>	180 days
total metals Al, Ag, As, Ba, Cd, Co, Cu, Mo, Mn, Na, Pb, Se, Sr, Th, Tl, U, Zn					
dissolved metals Ba, Ca, Fe, K, Mg, Na, Si, Sr	produced water	250ml		filter and preserve at lab	
pH	produced water	1l	HDPE	4C	as soon as practical
specific conductance	produced water				30 days
alkalinity (total, bicarbonate and carbonate alkalinity as CaCO <sub>3</sub> )	produced water				
total suspended solids	produced water				
total dissolved solids	produced water				
Anions Br, Cl, F, SO <sub>4</sub>	produced water				
δ <sup>18</sup> O & δD of H <sub>2</sub> O	produced water	40ml	glass	none	NA
δ <sup>13</sup> C of dissolved inorganic carbon (DIC)	produced water	40ml	glass		

## **7. Quality Assurance**

The data generated from this SAP must be technically sound and supported by defined and verified limits of confidence. Therefore, the objective of this QA section of the SAP is to ensure the generation of accurate, precise, representative and complete data.

This section provides additional details of the laboratory analytical methods, the quality control (QC) of laboratory equipment, and the QC program including establishing reference background samples where appropriate, blank analyses, duplicate analyses and matrix spike analyses, where possible and applicable. The data collection procedures and data evaluation processes, which will ensure that appropriate levels of data quality are obtained, are also described.

Many of the practices essential to QA, such as use of field notes and forms, sample identification, COC, packaging, shipping and management of records have already been described in prior sections and are not repeated here.

### **7.1 Data Quality Levels**

Four analytical data quality levels (DQL) may be useful to accomplish the objectives of investigations of this type. These levels as modified for this study are as follows:

- Level 1: field screening or analysis using portable instruments, calibrated and operated per manufacturer's instructions
- Level 2: field analysis using portable instruments, calibrated to specific compounds
- Level 3: general characterization procedures including analysis of stable isotopes of water and carbon (DIC),  $^{14}\text{C}$  in DIC analysis and tritium in water analysis by laboratory standard operating procedures and methods with final results provided
- Level 4: full record of digestions, cleanups, separations, analytical calibrations, standards used, et cetera, such that a knowledgeable individual could re-calculate individual results when provided with SOPs and other appropriate documentation from the lab to allow data validation if third party validation occurs

The following sections describe the use of the analytical procedural levels for the project.

#### **7.1.1 Field Screening Methods - Level 1 and Field Analysis – Level 2**

No radiometric field screening or field analysis will be performed as part of the sampling process.

#### **7.1.2 Laboratory Methods – Level 3**

Analysis of tritium in water,  $^{14}\text{C}$  in DIC and analysis of stable isotopes of oxygen and hydrogen in water and carbon in dissolved inorganic carbon are for general characterization using laboratory standard operating procedures for relative abundance

determination relative to international reference materials. Basic analytical summary reports will be provided by the labs.

### 7.1.3 Laboratory Methods - Level 4

Level 4 analytical procedures provide precise, accurate, and defensible data for the intended data uses. Level 4 data provide enough information such that an independent reviewer can validate or recalculate the analytical data reported by the laboratories.

## 7.2 Quality Control Parameters

The exact quantitative criteria used to evaluate data quality from the laboratory's precision and accuracy perspective for the aqueous and solid sampling media will be presented in the selected LQAP and in many more-detailed SOPs developed within that quality program. The following is a description of terms that typically appear in a laboratory's QAP.

**Reference:** The reference identification number of the U.S. Environmental Protection Agency (EPA) or other standard analytical methodology. Organizations that develop analytical methods by consensus include ASTM and the Standard Methods Committee (APHA, 2012). Each analytical procedure at a laboratory should have a SOP developed by the lab which documents any modifications to the published methods including how those modifications have been validated.

**Precision:** A measure of the mutual agreement among individual measurements of the same property under prescribed similar conditions. Precision is evaluated based on the duplicate error ratio (DER) between duplicate matrix spike (MS) results or duplicate sample results, as appropriate. The 2 sigma DER limits are parameter- and method-specific; MS/MSD or DER QC limits will be presented in the laboratory QAP or associated SOPs. Laboratory duplicate sample DER limits are typically where  $>2.13$  is out of control and  $>1.42$  but  $<2.13$  are in warning range. Field duplicates are also evaluated by calculating the relative percent difference (RPD) or DER between field duplicate sample results. However, evaluations of field duplicate DERs are used as advisory determinations since numerous factors in sampling and analysis may cause variances between field duplicate results.

**Accuracy:** The degree of agreement of a measurement with an accepted reference or true value. Accuracy is evaluated based on the percent recovery of spiked samples. The MS recoveries for inorganic and most conventional parameters are typically in the range of 75-125% or tighter. Chemical and/or isotopic tracer recovery will be evaluated for tests such as determination of lead, polonium, radium, uranium and thorium isotopes that undergo extraction and separation processes using laboratory-specific criteria.

**Completeness:** A measure of the amount of valid data obtained from a measurement system compared to the amount expected to be obtained under normal conditions. The method of calculation for percent completeness is defined in Section 7.9. Completeness can be evaluated in two ways: 1) by comparing the number of samples actually collected to the expected number of samples to be collected; and 2) by comparing the number of valid analyses received from the laboratory to the number of actual samples collected. The results of any Level 3 analyses to be

performed are typically used for characterization studies and as such will have a minimum completeness of 95 percent for both evaluations of completeness.

Exact QA/QC criteria the laboratory will use to evaluate its data's precision and accuracy will be provided following selection of the analytical laboratory, if the criteria are not method-specific.

### **7.3 Calibration Procedures and Frequency**

All laboratory analytical equipment must be calibrated before use to ensure proper operating capability. Laboratory instrument calibration procedures are presented in the LQAP and in process-specific SOPs. Frequency of instrumental calibration at laboratories must follow method and internal lab requirements and acceptance criteria before samples can be analyzed. Field calibration procedures and frequencies should be followed in accordance with the manufacturer's specifications. Field operational checks must be completed each day at a minimum.

### **7.4 Preparation of Standards**

A calibration standard is prepared by the appropriate dilution of a pure substance or known concentration/activity reference material, the purity of which is traceable to National Institute of Standards (NIST) or from vendors who can document traceability of the standards preparation comparable to NIST standard reference materials. Because of the high sensitivity of many analytical instruments, the calibration standard is typically prepared by serial dilution of a pure substance by a commercial vendor using weights and measures traceable to NIST. In order to provide standard solutions at sufficiently low concentrations, a minuscule amount of the pure substance would be required, the measurement of which is subject to extreme error. Thus, it is preferable to deal with potential dilution errors, rather than with the potentially larger error associated with the measurement of a very small amount of a pure substance.

The initial standard is typically obtained either as a pure material or as a prepared certified solution of a given concentration or activity of the pure compound or compounds. In preparing the stock solution of the calibration standard, great care must be exercised in measuring weights and volumes as accurately as possible, since all of the analyses following the calibration will be based on the accuracy of the calibration, and the accuracy of the analytical data is dependent on the calibration curve. It is the analyst's responsibility to assure that all standards used are within the standard solution holding time, and to prepare fresh standard solutions whenever necessary. In preparing working solutions, or using working solutions, the analyst must check for signs of deterioration of the standard, such as cloudiness, precipitation or discoloration. The standard must also be periodically compared with previous runs of standards, and with independently prepared standards to assure that response factors fall within a historically accepted range.

### **7.5 Data Evaluation and Validation**

Data are typically validated by the field personnel and laboratory personnel. First, during the field operations, field measures will be validated at the time of collection by the field sampler by verifying the use of SOPs for the sampling effort and using field QC checks. Second,

laboratory analytical results will be validated by the Laboratory Department Manager or the analyst who is the specific analytical task leader.

### **7.5.1 Laboratory Data Validation**

The individual Laboratory Department Managers or their designees shall validate all laboratory data prior to reporting. The following typical QA/QC reviews and/or procedures shall be used:

- Standard calibrations are prepared prior to sample analysis
- Acceptance criteria for calibrations as defined in the method or SOP are within the acceptable range
- Standard reference materials are analyzed at the proper frequencies and acceptable results are obtained
- Verification or checks of calibrations and instrument stability, as required by the method or SOP, are at the proper frequencies and acceptable results are obtained
- Method QC samples (e.g., reagent blanks, laboratory control samples, duplicates and matrix spikes) are analyzed at the proper frequency and acceptable results are obtained
- Precision requirements of this plan are met
- Accuracy requirements of this plan are met
- Completeness requirements of this plan are met
- Samples are analyzed within the proper sample holding times
- All calculations are verified as correct
- Proper units are reported
- Proper methodologies are used

In addition to this review of analytical results and project-specific precision, accuracy, and completeness requirements, the QA officer should perform unannounced audits of report forms and other data sheets as well as regular reviews of instrument logs, performance test results and analysts' performance.

In the event that any review of analytical results or internal QA/QC checks indicate problems, immediate corrective actions must be taken and all data collected before the previous approved QC audits must be reviewed for validity. Specific laboratory procedures for validation of the analytical data generated are described in the LQAP and associated SOPs.

### **7.5.2 Data Validation**

The laboratory will provide DQL Level 4 data packages for radiochemistry and general metals and inorganic analytical procedures.

## **7.6 Data Reporting**

After the data have been validated internally by the laboratory, all of the results are electronically or manually entered into the laboratory's data management system where they are stored prior to reporting. When all analyses are completed, the Laboratory Director (or a

designee) will issue a final data report including a descriptive case narrative. The Laboratory Director will then issue the report to the data user.

The data reports generated for this project should contain all pertinent information for the data user to determine the applicability and usability of the data for its intended purposes. For this reason, a specified and uniform data reporting format will be implemented. The following criteria and information must be supplied, at a minimum, for data reports generated for this project:

- A descriptive case narrative identifying any problems encountered during internal data validation (as described above)
- Completed and legible COCs for all analyses contained within each submitted data package
- A lab sample chronicle indicating which analyses were requested and performed for the samples contained in the data package
- A summary of the laboratory sample identifications and the correlating field sample identifications
- A summary of all applicable analytical results, uncertainties, MDCs reported in unambiguous fashion, with the correct number of significant figures, appropriate reporting units
- Complete sample identifications, sample dilutions (if necessary), and individual sample analysis dates included in the individual sample reporting results

#### **7.6.1 Level 4 Reporting**

The following summary forms and raw data deliverable requirements will apply for Data Quality Level 4.

The following forms are required to be made available for all inorganic analyses and radiochemistry analyses using gamma spectroscopy, alpha spectroscopy, liquid scintillation and gas flow proportional counting methods:

- Narrative and sample identification cross-reference
- Copies of COC documentation
- Laboratory chronicle
- Method summaries and references
- Laboratory control sample (LCS )summary and results
- MS/MSD summary or any lab duplicate
- QC Check Sample summary
- Method blank summary and results
- Instrument performance check summary
- Instrument set up and calibration summary
- Continuing calibration check summary for all constituents of interest where utilized

Note that a Level 4 data package should also include raw data, background data, calibration data, sample analysis data, and standards and tracer data, such that a knowledgeable scientist



can recalculate/verify results. It will also include copies of spectral data for gamma spectrometry, or spectral plots for alpha and liquid scintillation spectrometry.

## **7.7 Quality Control Procedures**

QC procedures and checks are used to verify the accuracy and reproducibility of investigation data. Field QC checks are used to identify potential problems with sampling procedures, such as the inconsistent use of sampling SOPs or field-introduced sample contamination and/or problems with sample homogeneity or representativeness. Laboratory QC checks are used to identify potential problems with analytical procedures such as the misapplication of required analytical methodologies or other laboratory-related problems which could result in inaccurate or imprecise data reported. The laboratory QC checks and procedures presented in this section are required for most of the applicable methods, but the frequency of the QC checks should follow procedures outlined in the LQAP and associated SOPs.

### **7.7.1 Field QC**

To check the quality of data from field sampling efforts, field duplicate samples will be collected for analysis at a blind duplicate frequency of 1 per 10 samples. These samples will be treated as separate samples for identification, logging and shipping. Analytical results on duplicates will be reported with the appropriate field sample data.

### **7.7.2 Internal Laboratory QC Checks**

The QC check frequencies and requirements specified in the following sections is a general description only. The laboratory will follow the internal QC checks specified in its LQAP and associated SOPs for each analysis type employed. However, these QC checks at a minimum must meet the requirements specified in the respective U.S. EPA analytical methods, or absent external requirements, as defined in the LQAP and SOPs. These should be statistically or tolerance based as described in many reference methods.

The following internal laboratory QC checks are performed for most analyses, whenever applicable, to ensure the measurement systems are under control:

- initial and continuing calibrations
- preparation/method blanks
- MS/MSD or matrix spike and LCS or laboratory duplicate (DUP) analysis, as appropriate

Additional internal laboratory QC checks are typically performed for most analyses, as required by the associated analytical method. Only the most common QC checks are generally described below.

#### **7.7.2.1 Initial and Continuing Calibration, Calibration Verification, Instrument Performance Checks and Instrument Background Measurements**

Each measurement system must be calibrated and the calibration verified prior to use and while in use (for many inorganic and organic methods). Instruments must be recalibrated

according to the requirements specified in the LQAP and SOPs or in methods on which the SOPs are based.

Instrument Performance Checks must be performed at the frequency specified in the LQAP and SOPs. Performance Check results must be evaluated in real time (e.g., compare results to acceptance criteria, monitor control charts for unacceptable trends) and must document ongoing instrument stability from the time of the initial calibration of the instrument through completion of the analysis. An initial calibration will be performed and/or confirmed prior to the sample analyses. Continuing calibrations will typically be analyzed at a minimum frequency as recommended by manufacturer and as required in the LQAP and SOPs, based on reference methods specifically for inorganic analysis.

Instrument backgrounds in radiochemistry analyses must be performed at the frequency and applied to results in accordance with the LQAP and SOPs. Results of method/reagent blanks should be monitored and trended to ensure the adequacy of background measurements.

#### **7.7.2.2 Calibration Check Compounds, Reagent Blanks and Method Blanks**

Calibration check compounds and reagent blanks are analyzed periodically throughout the course of inorganic analyses, depending upon the required analysis. The exact frequencies and methods of use are presented in the LQAP or SOPs based on methods. Method blanks (MB) are material such as deionized water or clean sand carried through all aspects of the preparation and analysis along with the associated batch of samples. The frequency of MB is typically 1 with every batch of 20 or fewer samples.

### **7.8 Performance and System Audits**

Two types of audit procedures may be conducted during any environmental investigation: performance audits and system audits. These audits may be performed on the laboratory as well as field activities. A description of the laboratory's specific guidance for Performance and System Audits will be presented in the LQAP. General procedures for laboratory performance and system audits are presented below.

#### **7.8.1 Laboratory Performance Audits**

Laboratory performance audits are typically conducted by the Laboratory QA Officer on a routine basis. Laboratory analysts are provided a performance evaluation sample containing analytes for the parameters which they perform. These audit samples are used to identify problems in sample preparation or analytical techniques or methodologies which could lead to future analytical problems.

Additionally, the laboratory performance audits include verification of each analyst's record-keeping, proper use and understanding of procedures, and performance documentation. Corrective action will be taken for any deficiencies noted during the audit.

## 7.8.2 Laboratory System Audits

Laboratory system audits are typically conducted by the Laboratory QA Officer. These audits are used to ensure that all aspects of the LQAP are operative. This involves a thorough review of all laboratory methods performed and documentation to confirm that work is performed according to project specifications.

In some cases, outside certification agencies conduct performance and system audits to verify contract compliance or the laboratory's ability to meet certification requirements on methods of analysis and documentation. Results of these outside certification audits may be reviewed at any time as a check on the laboratory's internal auditing procedures.

## 7.9 Assessment Procedures for Data Acceptability

The following discussion describes the procedures that will be employed to evaluate the precision, accuracy, and completeness of the generated data.

### 7.9.1 Precision

Precision is a measure of agreement among individual measurements of the same property under prescribed similar conditions. Precision is assessed by calculating the RPD of replicate spike samples or replicate sample analyses according to the following equation:

$$RPD = \frac{|R_1 - R_2|}{(R_1 + R_2)/2} \times 100$$

Where:  $R_1$  = result 1  
 $R_2$  = result 2

In radiochemistry the DER is used to assess precision and is calculated computing the difference of sample and duplicate results and dividing by a function of the propagated uncertainties of the duplicate results according to the following equation:

$$DER = \frac{|S - D|}{2 * \sqrt{TPUS^2 + TPUD^2}}$$

Where:  $S$  = sample result  
 $D$  = duplicate result  
 $TPUS$  = the  $1\sigma$  total propagated uncertainty of the sample  
 $TPUD$  = the  $1\sigma$  total propagated uncertainty of the duplicate

The laboratory utilizes control limits such that DER in excess of 2 is out of control. Results outside of control limits should be evaluated. If there is no indication that homogeneity of the sample is responsible for the excursion, the sample should be recounted, or reprepared. Both the original and reprep/recount results should be reported.

## 7.9.2 Accuracy

Accuracy is a measure of the closeness of an individual measurement to the true value. Accuracy for non-radiochemistry analyses is measured by calculating the percent recovery (%R) of known levels spiked compounds in LCS and matrix spike results as follows:

### 7.9.3 Percent Recovery:

Calculation of percent recovery is illustrated below

$$\%R = \frac{[\text{spiked sample conc.} - \text{unspiked sample conc.}]}{\text{spike added}} \times 100$$

### 7.9.4 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements that should have been collected. As is specified in Section 4.2, more than one completeness check can be evaluated. It is calculated as follows:

$$\text{Completeness (\%)} = \frac{\text{number of valid samples reported}}{\text{total number of samples analyzed}}$$

### 7.9.5 Quality-Control Charts

Quality control charts can be prepared after the initial 20 analytical determinations to graphically evaluate precision and accuracy criteria. The charts are prepared by calculating the mean value of the determinations and setting control limits at  $\pm 3$  standard deviations from that mean. Standard definitions for mean and standard deviations apply and are not shown here.

The %R should be within control chart acceptance limits or ranges presented in the LQAP and associated SOPs. If the %R values are found to be outside these limits or ranges, the analytical system is examined to determine if possible problems exist.

### 7.10 Preventive Maintenance

Periodic preventive maintenance is required for equipment whose performance can affect result. Instrument manuals are kept on file for reference if equipment needs repair. Troubleshooting sections of manuals are often useful in assisting personnel in performing maintenance tasks.

#### 7.10.1 Field Equipment

Field sampling personnel will be responsible for preventive maintenance of all field equipment. All field equipment will be subject to a routine maintenance program, prior to and after each use. The routine maintenance program for each piece of equipment will be in accordance with the manufacturer's operations and maintenance manual. All equipment will be cleaned and checked for integrity before and after each use. Necessary repairs will be performed

immediately after any defects are observed and before the equipment is used again. Equipment parts with a limited life (such as batteries and some electronic components) will be periodically checked and replaced or recharged as necessary according to the manufacturer's specifications. Preventive maintenance provides for a longer useful life of the equipment and helps to ensure a successful field sampling program.

### **7.10.2 Laboratory Instruments**

All major laboratory instruments should normally be under service contract so that trained professionals are available on call to minimize instrument downtime. Alternatively, labs may have redundant capabilities to ensure continued productivity in the case that instrumentation requires maintenance.

Other preventive maintenance schedules and/or procedures for laboratory equipment are presented in the LQAP and associated SOPs.

### **7.11 Corrective Action**

There are many laboratory functions that may require corrective action. The decision to undertake corrective action and the ensuing action must be documented so that traceability can be maintained. The laboratory shall maintain an active corrective action program. The corrective action program must, at minimum, address the following:

Corrective action procedures are divided into two subgroups: methods corrective action and systems corrective action. These corrective actions are implemented whenever system or performance audits note deficiencies or when QC procedures indicate a potential analytical problem. The point of originating the corrective action varies, depending upon the mode of detection that such action is necessary. It is generally the role of either the Laboratory QA Officer or the Laboratory Department Manager to initiate such action. Those actions that affect the quality of the data will be recorded and the record maintained by the Laboratory QA Officer. The general procedures for appropriate laboratory corrective actions and identification of potential problems are presented in the analytical LQAP and associated SOPs.

### **7.12 QA Reports to Management**

Audit reports will be provided by the Laboratory Director (or designee) as a means of tracking program performance, as applicable, or if needed. Additionally, periodic assessments of measurement data accuracy, precision, completeness and significant QA/QC problems will be performed and reported to laboratory and/or project management, if needed.

Field QA reports will not be necessary considering the expected size and length of any individual sample collection activity. Any problems noted during sampling will be immediately communicated to the COGCC staff member in charge.

The final project report prepared as a result of this SAP should address the overall degree of project conformance to specifications and the impact of any non-conformance that may affect management decisions.

The final electronic long-term storage location of the data and files will be maintained by the COGCC staff within the COGCC document storage system and within the COGCC Environmental database.

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## 9. List of Abbreviations, Acronyms and Technical Jargon

$\alpha$  – alpha decay mechanism  
a – year, annum  
<sup>228</sup>Ac – actinium-228 isotope  
Ag - silver  
Al – aluminum  
AMS – accelerator mass spectrometry  
ALS – ALS Laboratories  
ANSI – American National Standards Institute  
API – American Petroleum Institute  
As - arsenic  
ASTM – American Society for Testing and Materials  
Ar – argon  
 $\beta$  - beta decay mechanism  
B - boron  
Ba – barium  
Be – beryllium  
<sup>212</sup>Bi – bismuth-212 isotope  
<sup>214</sup>Bi – bismuth-214 isotope  
Br – bromide anion or elemental bromine  
<sup>14</sup>C – carbon-14 isotope  
°C – degree Celsius  
Ca – calcium  
CBM – coal bed methane  
Cd – cadmium  
Cl – chloride anion or elemental chlorine  
Co – cobalt  
<sup>137</sup>Cs – cesium-137 isotope  
Cu – copper  
CDPHE - Colorado Department of Public Health and Environment  
CFR – Code of Federal Regulations  
CLP – Contract Laboratory Program  
COC – chain-of-custody  
COGCC – Colorado Oil and Gas Conservation Commission  
Cr – chromium  
d – day  
 $\delta$  – delta  
D – deuterium isotope, <sup>2</sup>H isotope  
DER – duplicate error ratio  
DIC – dissolved inorganic carbon  
DOE – Department of Energy



DOT – Department of Transportation  
DQL – data quality levels  
DQO – data quality objectives  
DUP – duplicate  
E### - analytical method from EPA 900 series of methods of analysis of radioactivity  
E&P – exploration and production  
Fe – iron  
F – fluoride anion or elemental fluorine  
 $\gamma$  - gamma radiation (electromagnetic energy emitted by radionuclides)  
GPC – gas-flow proportional counting system  
GPS – global positioning system  
H - hydrogen  
 $^3\text{H}$  – tritium isotope of hydrogen  
HDPE – high-density polyethylene  
 $\text{HNO}_3$  – nitric acid  
IAEA – International Atomic Energy Agency  
K – potassium  
 $^{40}\text{K}$  – potassium-40 isotope  
Li – lithium  
LCS – laboratory control sample  
LQAP – laboratory quality assurance plan  
MB – method blank  
MDC – minimum detectable concentration  
mg/kg – milligrams per kilogram  
mg/l – milligrams per liter  
Mg – magnesium  
min - minute  
Mn – manganese  
Mo – molybdenum  
MS/MSD – matrix spike/matrix spike duplicate  
NA – not applicable  
N - nitrogen  
Na – sodium  
NIST – National Institute of Standards and Technology  
NORM - naturally occurring radioactive material  
Ni – nickel  
O- oxygen  
 $^{18}\text{O}$  – oxygen-18 isotope  
pCi/l – picoCuries per liter,  $10^{-12}$  Curies per liter or approximately 2.2 disintegrations/minute  
P- phosphorus  
 $^{234\text{m}}\text{Pa}$  – metastable protactinium-234 isotope  
Pb – lead  
 $^{210}\text{Pb}$  – lead-210 isotope

$^{212}\text{Pb}$  – lead-212 isotope  
 $^{214}\text{Pb}$  – lead-214 isotope  
 PESI – Perma-Fix Environmental Services, Inc.  
 pH – measure of acidity  
 $^{210}\text{Po}$  – polonium-210 isotope  
 PTFE – polytetrafluoroethylene  
 QA – quality assurance  
 QAP – quality assurance plan  
 QC – quality control  
 Ra – radium  
 $^{224}\text{Ra}$  – radium-224 isotope  
 $^{226}\text{Ra}$  – radium-226 isotope  
 $^{228}\text{Ra}$  – radium-228 isotope  
 Rn – radon  
 $^{222}\text{Rn}$  – radon-222 isotope  
 RPD – relative percent difference  
 S- sulfur  
 SAP – sampling and analysis plan  
 Se – selenium  
 Si – silicon  
 SM####- analytical method from Standard Methods for the Examination of Water and Wastewater  
 $\text{SO}_4$  – sulfate anion  
 SOP – standard operating procedure  
 Sr – strontium  
 STRONGER - State Review of Oil & Natural Gas Environmental Regulations  
 SU – standard unit (for pH)  
 SW#### - analytical method from SW-846  
 TDS – total dissolved solids  
 TENORM – technologically enhanced naturally occurring radioactive material  
 Th – thorium  
 $^{228}\text{Th}$  – thorium-228 isotope  
 $^{230}\text{Th}$  – thorium-230 isotope  
 $^{232}\text{Th}$  – thorium-232 isotope  
 Tl – thallium  
 $^{208}\text{Tl}$  – thallium-208 isotope  
 TPU – total propagated uncertainty  
 U.S. EPA – United States Environmental Protection Agency  
 USGS – United States Geological Survey  
 U – uranium  
 $^{234}\text{U}$  – uranium-234 isotope  
 $^{238}\text{U}$  – uranium-238 isotope  
 $^{235}\text{U}$  – uranium-235 isotope  
 V – vanadium

VOA – volatile organic analysis

Zn- zinc

% - percentage

< - less than

µg/l - micrograms per liter

µmhos/cm – micromhos per centimeter

µs – microsecond,  $10^{-6}$  seconds

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