SAMPLING AND ANALYSIS PLAN

INVESTIGATION OF OCCURRENCES OF HEAVY METALS AND RADIONUCLIDES IN DOMESTIC ANIMALS ON THE NAVAJO NATION COVE, APACHE COUNTY, ARIZONA

COVE LIVESTOCK ASSESSMENT

Navajo Nation, Cove Chapter, Apache County, Arizona

Cooperative Grant No: 99T54301
TDD No.:

May 29, 2019

Prepared for:

United States Environmental Protection Agency Emergency Response Section, Region 9
75 Hawthorne Street
San Francisco, California

Prepared by:

Diné College
NSF/TCUP Program
1 Circle Drive Rt.12
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In Cooperation with:

Northern Arizona University
Flagstaff, Arizona

University of New Mexico
Albuquerque, New Mexico

Montana State University - Billings
Billings, Montana

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IX
75 Hawthorne Street
San Francisco, CA 94105

July 29, 2019

Perry H Charley, Director
Dine´ College – Shiprock Campus
Dine´ Environmental Institute Research & Outreach
1228 Yucca Street
PO Box 580
Shiprock, New Mexico 87420

SUBJECT: Approval of Sampling and Analysis Plan (SAP), *Investigation of Occurrences of Heavy Metals and Radionuclides in Domestic Animals on the Navajo Nation*, Cove, Apache County, Arizona, May 2019, QA Document Control Number SPFD0092QV2

Dear Mr. Charley,

The subject SAP submitted for EPA Cooperative Agreement 99T54301-0, Cove T'oh Keeh Haas Chiin Nalkaal (Cove Watershed Assessment Project), is approved. The signed SAP cover page is attached.

The SAP was reviewed as a Quality Assurance Project Plan (QAPP) using the EPA guidance document *EPA Requirements for Quality Assurance Project* Plans (EPA QA/R-5, March 2001).

If you have any questions or concerns about this review, please contact me or Joe Eidelberg at eidelberg.joseph@epa.gov or at 415-972-3809.

Sincerely,

Audrey L. Johnson, Manager
Quality Assurance Branch, LSS-3
Laboratory Services & Applied Sciences Division

Attachment

cc: Sona Chilingaryan, SFD-6-2

SAMPLING AND ANALYSIS PLAN

INVESTIGATION OF OCCURRENCES OF HEAVY METALS AND RADIONUCLIDES IN DOMESTIC ANIMALS ON THE NAVAJO NATION COVE, APACHE COUNTY, ARIZONA

COVE LIVESTOCK STUDY ASSESSMENT
Navajo Nation, Cove Chapter, Apache County, Arizona

Cooperative Grant No: 99T54301
TDD No.:

May 2019

Prepared by: _____ 8/14/2019
Perry H. Charley, Co-PI, Sr. Scientist — Date
Diné College – NSF/TCUP

Reviewed by: _____ 8/14/2019
Dr. Donald K. Robinson, PhD., PI — Date
Diné College – NSF/TCUP

Reviewed by: Johnson, AudreyL — Digitally signed by Johnson, AudreyL Date: 2019.06.19 14:03:19 -07'00' _____
Audrey L. Johnson, Manager — Date
Quality Assurance Office

Approved by: Chilingaryan, Sona — Digitally signed by Chilingaryan, Sona Date: 2019.06.24 06:26:31 -07'00' _____
Sona Chilingaryan, Manager — Date
U.S. Environmental Protection Agency, Region 9

CONTRACT LABORATORY PROGRAM
CLP RE-ANALYSIS REQUEST/APPROVAL RECORD FORM

SECTION A (TO BE COMPLETED BY THE RSCC or REGIONAL CLP COR OF THE EPA REGION REQUESTING RE-ANALYSIS)

Initiated By: Joe Eidelberg, EPA R9, 415-972-3809
Name, Affiliation, Phone Number

Case Number: 48218
SOW: ISM02.4
TAT: 7
Requested Re-Analysis Start Date: 06/12/2019

Details of Re-Analysis Request:

- Laboratory Name/Contract Number: CHEMTEX/EPW15007
- Affected Sample Number(s) and Analysis(es): MYAN77 all samples, all ICP metals except those previously reported by ICP, ie.Ca, Mg, Na, K
- Reason for Re-Analysis: Did not previously request analysis of metals by ICP
- Contract Statement of Work Citation*: Did not previously request ICP metals
- Comments: Updated re-analysis request to reference use of MA 2980. Report results from previous ICP-AES analysis and update results as described in MA 2980. Metals were previously previously reported by ICP-MS. Need routine report and processing by EXES. It is OK if lab reports Ca, Mg, Na, K.

* PROVIDE SOW CITATION THAT SUPPORTS THIS REQUEST

- RE-ANALYSIS: Billable: ☑ Not Billable: ☐

Approved By: SUSAN STURGES Digitally signed by SUSAN STURGES Date: 2019.06.12 09:20:46 -07'00' Date: 06/12/2019
Signature of Authorized RSCC or Regional CLP COR of the EPA Region Requesting Re-Analysis

---

SECTION B (TO BE COMPLETED BY SMO)

Name of SMO Contact: _____ Date: _____

Date of Laboratory Notification (Verbal): _____

Re-analysis Start Date: _____ Data Due Date: _____

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I. INTRODUCTION

The U. S. Environmental Protection Agency – Region IX (USEPA) approved Diné College to conduct the research study "Investigation of Occurrences of Heavy Metals and Radionuclides in Domestic Animals on the Navajo Nation, Cove, Apache County, Arizona" (The Livestock Study). The study will be part of Cooperative Agreement 99T54301.

The proposed project Scope of Work is a collaboration between Diné College (DC), Northern Arizona University (NAU), University of New Mexico (UNM), and Montana State University – Billings (MSUB). The research plan is to build on the preliminary study design to investigate heavy metals and radionuclides in livestock organs and tissues (Ingram Grants: NIH/NIEHS/IHS U261IHS0092-01; NIH/NIEHS P50ES026089). DC will be taking the lead role by and through its existing Cooperative Agreement (99T54301).

The presence of abandoned uranium mines in many Diné communities has caused concern about exposure to heavy metals from abandoned mine waste. While previous research demonstrated greater risk for developing chronic diseases when people are exposed to abandoned U mine waste (Hund et al 2015), there remains limited work addressing the role of animal tissue as a point of exposure. This is a critical gap to address because certain locally raised animal tissue, such as mutton meat and organs, is a traditional food source for the Diné people. Assessing the accumulation of heavy metals in animal tissues will inform efforts assessing human metal and radionuclide exposure.

The specific aim for the proposed work is to compare metal and radionuclide concentrations in livestock grazing in mining area versus a reference area on the Navajo Reservation. We anticipate that the proposed project will provide critical preliminary data towards our long-term objective of a comprehensive understanding of environmental uranium exposure and health risks among the Diné. In addition to uranium, radium will be investigated as it has not been studied in past livestock research on Navajo.

This Quality Assurance Project Plan (QAPP) describes the project and data use objectives, data collection rationale, data quality assurance (QA) goals, and requirements for sampling and analysis activities. It also defines the sampling and data collection methods that will be used for this project. This QAPP is intended to accurately reflect the planned data-gathering activities for this task; however, site conditions, budget, and additional USEPA direction may warrant modifications. All significant changes will be documented in site records.

The specific field sampling and chemical analysis information in this SAP was prepared according to the following EPA documents: *EPA Requirements for Quality Assurance Project Plans, EPA QA/R 5, EPA/240/B 01/003 (EPA 2001b); Guidance on Systematic Planning Using the Data Quality Objectives Process, EPA QA/G 4, EPA/240/B-06/001 (EPA 2006); Guidance on Choosing a Sampling Design for Environmental Data Collection, EPA QA/G 5S, EPA/240/R02/005 (EPA 2002a); and Uniform Federal Policy for Implementing Environmental Quality System, EPA/505/F-03/001 (EPA 2005).*

II. PROJECT ORGANIZATION

The following is a list of project personnel and their responsibilities.

1. Key Personnel: Diné College

Diné College's Grant Principal Investigator – The Grant PI is Dr. Donald K. Robinson, who will be the primary project decision maker and will assure the project is proceeding with the Administrative and Programmatic Conditions of the grant, coordination of all preliminary and final reporting and fiscal matters.

Diné College's Onsite Coordinator - The Onsite Coordinator is Perry H. Charley, who will assume the primary field and onsite decision-maker and will coordinate the specific tasks of the Scope of Work with its partners, ensure that the project goals and samplings are proceeding on schedule and within the scope of the QAPP. Additional duties include coordination of required preliminary and final reporting, coordination and communication with the U.S. Environmental Protection Agency (USEPA), University of New Mexico, Northern Arizona University, Montana State University – Billings, the Navajo Nation and community livestock owners and local chapter governments.
Diné College's Environmental Specialist – The Environmental Specialist is Neilroy Singer. He will assist the Onsite Coordinator on all phases of project planning, scheduling performance of tasks of the project. He will also be primarily responsible to hire and provide mentoring of student interns for the project.

2. Key Personnel – Northern Arizona University

Jani C. Ingram, PhD (Navajo), as NAU's Project Lead, will oversee the entire project. She will direct the field and laboratory work as coordinate livestock collection with the Navajo community members. She will work with Mr. Charley from Diné College and Dr. Johnnye Lewis from University of New Mexico in coordinating efforts on the project. She will also train the graduate and undergraduate students in all procedures. Dr. Ingram will devote 0.5 summer months per year to this project. NAU is responsible for the chemical analytical work associated with the environmental samples collected (including soil, water, plants, animal tissue) by definitive analytical methodologies in the NAU analysis laboratories as well as the overseeing the analyses performed by the University of Iowa. NAU is responsible for data validation of laboratory-generated data.

Andee Lister (Navajo), a doctoral graduate student in Earth Sciences and Environmental Sustainability will assist on the project. Ms. Lister will devote 40 hours per week during the summer 2019 and 2020 as well as up to 20 hours per week during the academic year. This project will be the focus of Ms. Lister's doctoral work.

Tasha Nez (Navajo), a masters graduate student in Environmental Science and Policy will assist on the project. Ms. Nez will devote 40 hours per week during the summer 2019 and 2020 as well as up to 20 hours per week during the academic year. This project will be the focus of Ms. Nez's thesis research.

3. Key Personnel: University of New Mexico

Dr. Johnnye Lewis, CEHP Director, Role on Project – Principle Investigator
Dr. Lewis is a toxicologist who has worked on uranium mine waste exposure and health risk for more than 25 years as a consultant to DOE, and as an academic researcher serving as PI to studies of

toxicity to Navajo populations spanning three generations. She currently is the PI for multiple multi-site transdisciplinary Center level studies of health impacts to tribal populations from exposures to mine waste. She will bring her expertise on toxicology, integration of multidisciplinary approaches, and modeling to the integration and leadership of this effort. She will bring her diverse expertise to the team in integrating the results of the geospatial tracking and the biomonitoring data into the development of an exposure model that can both inform the concerns of the Cove community and help to generalize the findings to other communities.

Dr. Yan Lin, Project Role: Co-Investigator
Dr. Yan Lin is an assistant professor in the Department of Geography and Environmental Studies at the University of New Mexico. Her research focuses on the development of GIS and spatial analysis methods and their applications in order to gain a better understanding of relationships among human health, the society, and the environment. Dr. Lin will be responsible for the spatial-temporal analysis of GPS data to model animal movement patterns. She will work closely with Dr. Hoover on the geospatial assessment of animal movement.

Dr. Melissa Gonzales, Project Role: Co-Investigator
Dr. Gonzales is an Associate Professor, Division of Epidemiology, Biostatistics and Preventive Medicine, Department of Internal Medicine. Her research is broadly interested in epidemiology to shape policy decisions and evidence-based interventions by reducing uncertainty in population-level exposures to environmental pollutants, key risk factors and targets for intervention. Dr. Gonzales' project responsibilities include assessing exposure information, research translation, and helping researchers interface with communities and federal agencies.

4. **Key Personnel: Montana State University - Billings**

Dr. Joseph Hoover, Role on Project: Principle Investigator
Dr. Hoover is currently a Research Assistant Professor at UNM. He will move to MSUB this Fall and holds the position of Assistant Professor of GIS and Geography. He holds a PhD in geography from the University of Denver (received in 2014). He specializes in geospatial applications to environmental health and water resource issues. He is familiar with statistical analysis of environmental data, and has experience using GPS technology for environmental research and geovisualization. His project responsibilities include managing the data collection and analysis of GPS information; supervising undergraduate students at MSUB and co-mentoring graduate students at UNM in the management, analysis and geovisualization of animal movements; compilation and presentation of GPS information to community and funding agency stakeholders as well as budgeting, reporting, and IACUC compliance.

UNM and MSU-B is responsible for all spatial-temporal analysis of GPS data. Both University partners are responsible for field data analysis and data validation.

5. **Distribution List**

Copies of the QAPP will be distributed to the following persons and organizations:

1. Sona Chilingaryan, USEPA Region 9 FOSC
2. USEPA QA Office

3. Dine College Project Files
4. Northern Arizona University
5. University of New Mexico
6. Montana State University - Billings

III. STATEMENT OF THE SPECIFIC PROBLEM

A total of 50 abandoned uranium mines (AUMs) are located within the Cove Wash watershed. Twenty-six of the AUMs were historically operated by Kerr McGee, which became Tronox. Previous studies have identified uranium and other constituents of concerns (COCs), including arsenic and molybdenum, within surface water, groundwater, and sediments (Lameman-Austin 2012, NNEPA 2014). Previous gamma screenings conducted in 2008 by US EPA Contractors have identified elevated levels in the abandoned uranium mine waste throughout the watershed. Due to the large number of abandoned uranium mines (AUMs) present within the Cove Wash watershed, it is not clear which AUMs are contributing to the elevated concentrations of COCs.
While previous research demonstrated greater risk for developing chronic diseases when people are exposed to abandoned U mine waste (Hund et al 2015), there remains limited work addressing the role of animal tissue as a point of exposure. This is a critical gap to address because certain locally raised animal tissue, such as mutton meat and organs, is a traditional food source for the Diné people. Assessing the accumulation of heavy metals in animal tissues will inform efforts assessing human metal and radionuclide exposure.

For members of the Cove Community (Cove Chapter, Navajo Nation) there remain unanswered questions about human exposure to uranium by consuming organs and meat from animals that grazed in a watershed with abandoned uranium mines and waste. Members of the Cove Community, located in the Lukachukai Mountains, have requested a study investigating the accumulation of uranium in animal tissue because there remain 50 abandoned uranium mines in the watershed. In response to this request collaborating researchers from Dine' College, Northern Arizona University and University of New Mexico will investigate human exposure to uranium via usage of animal meat and organs that are part of a traditional Navajo diet

IV. SITE BACKGROUND

1. Site Location and Description

The Site consists of the Cove Wash watershed, which includes 50 of the 70 AUMs within the Lukachukai Mountains. The Cove Wash watershed is located within the Navajo Nation and extends at the highest elevations in the Lukachukai Mountains and downstream to Cove, Arizona. The watershed contains

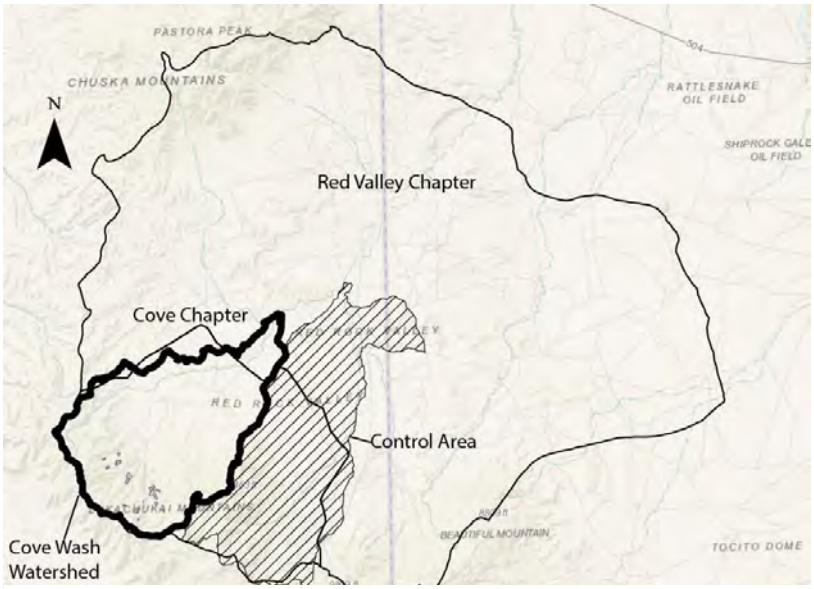

Figure Caption. Boundaries of Cove and Red Valley Chapters with the study area (Cove Wash Watershed) outlined as well as the reference area (hatched polygon).

approximately 52 miles of tributaries and is defined by the U.S. Geological Survey (USGS) as Hydrologic Unit Code 140801050903. Annual precipitation averages 12 to 16 inches throughout the study and control areas. The Cove Wash watershed is not a known drinking water source, but may have been historically used by residents before drinking water was provided by a municipal source 20 years ago. However, it is not entirely clear if residents are not currently using surface water and/or groundwater wells for drinking water (Lameman-Austin 2012, NNEPA 2014). Additionally, the Cove Wash watershed is used extensively for drinking water for grazing livestock. Livestock is dependent on surface water and groundwater for drinking.

2. Site History

During World War II, the Army Corps of Engineers formed the Manhattan Engineer District (MED) for the development of atomic weapons and acquisition of raw materials for the production of weapons. The Murray Hill Area of MED was established on June 15, 1943 for the major purpose of the exploration and development of raw materials on which the entire Manhattan Project was dependent. Determination and evaluation of the uranium resources of the world was first undertaken, and the program was later expanded to include thorium ores. Union Mines Development Corporation (UMDC), a subsidiary of Union Carbide and Carbon Corporation, was contracted to carry out the work (contract, No. W-7405, effective May 11, 1943). On the Colorado Plateau, UMDC's geologic investigations were limited to the Salt Wash Member of the Morrison Formation, and the Entrada and Glen Canyon Sandstones in the areas of roscoelite deposits.

UMDC geologists began work on the Navajo Indian Reservation on July 28, 1943 (Chenoweth, 1988). They were to make a reconnaissance of the Salt Wash Member of the Morrison Formation in the area of the Curran Brothers and Wade lease. All known outcrops of uranium-vanadium minerals were described and plotted on maps. Geologic studies and resource estimates on Cove Mesa were done by Alfred H. Coleman and John W. Harshbarger.

Uranium outcrops were discovered within the Cove area during this period. In the late 1940s Dan Phillips obtained a 528-acre lease and Koley Black obtained a 640-acre lease. Mr. Phillips and Mr. Black assigned a 75% interest in their leases to F.A. Sutton, Inc. Uranium and vanadium ore shipments from the watershed began in 1950 (NNEPA 2004). The mine sites were situated along mesas throughout the watershed. Uranium and vanadium mining ceased in the 1960s and the mine sites were abandoned. The Navajo Nation Abandoned Mined Lands Reclamation Department (NNAMLRD) reclaimed AUMs in the 1990s under the authority of the 1977 Surface Mine Control and Reclamation Act (SMRCA) , which prioritizes mine reclamation based on physical hazards ranking scheme. As the result, inaccessible mine waste (Priority 3 designation under SMCRA) remains present throughout the watershed.

3. Threatened and Endangered Protective Measures

The U.S. Fish and Wildlife Service reviewed the Biological Assessment Report for the Cove Wash Radiological Survey and concurred with the EPA's determination that planned sampling activities may affect, but not adversely affect the Mexican Spotted Owl, Navajo sedge and Zuni fleabane (EPA 2014; USFWS 2014). The following describes protective measure that will be conducted to minimize impacts from the sampling teams to the threatened and endangered species.

The canyon areas of the Cove Wash watershed are suitable nesting habitats for the Mexican spotted owl from spring to summer. Care should be taken during field activities in the canyons to ensure that

MSO nests are avoided. In the event MSO nests are observed during livestock study activities, sampling team members will be notified and the time to pass the nesting areas will be kept to a minimum and personal will not linger or disturb the MSO if they are encountered.
Wet or moist sediments and soil along the Cove Wash watershed provide aquatic habitats for plants including the Navajo sedge. Upland Areas along mine roads in the watershed may be habitat for the Zuni fleabane. The sampling team members will avoid trampling on vegetation while traversing the streams and upland areas. Sediment samples will be collected at locations that will not impact vegetation.

4. Previous Investigations

In 1999, the EPA collected surface water and groundwater samples within the Cove Wash watershed and analyzed the samples for metals and radionuclides. Uranium and other metals exceeded EPA Maximum Contaminant Levels (MCLs) for drinking water in some samples collected during the investigation. Of the 21 water samples collected, 12 water samples contained COCs in exceedance of EPA MCLs for at least one COC, including arsenic, uranium, selenium, and vanadium (Lameman-Austin 2012).

In 2008, WESTON conducted AUM screenings throughout the Lukachukai Mountains, including AUMs located within the Cove Wash watershed. The AUM screenings consisted of gamma radiation screenings in the vicinity of a majority of AUMs in the watershed. Gamma readings two to three times background were detected at multiple AUMs during the 2008 AUM screenings.
In 2011, Terri Lameman-Austin conducted a study of the uranium distribution throughout the Cove Wash watershed as part of a Master's Degree fulfillment requirement with the assistance of the USGS. A total of seven surface water, three groundwater, and 26 sediment, rock, and soil samples were collected and analyzed for metals, including uranium and other trace metals. Uranium concentrations exceeded the EPA MCL of 30 micrograms per liter (µg/L) in all surface water samples collected during the study. Arsenic was detected in one surface water sample collected within the Cove Wash watershed above the EPA MCL of 10 µg/L. Uranium was detected above the MCL in one well sample (Ellison Well).

Surface water and groundwater samples were also analyzed for major cations and anions, alkalinity, and stable oxygen isotopes (16O and 18O) in order to determine the ratio of 18O/16O (δ18O). As 16O has a lower vapor pressure that 18O, the δ18O results can be used to determine additional information about surface water sources and the study report recommends that future investigations analyze water samples for δ18O. The study report also noted that uranium isotope (234U and 238U) concentrations in water samples can be used to evaluate groundwater residence times. Selected samples will be analyzed for stable oxygen isotopes. All water samples collected during this watershed assessment will be submitted for uranium isotope analysis, 234U and 238U. The isotope ratio information will be useful for identifying the water source (Campbell, 2014).

The NNEPA completed a Surface Water Quality Assessment Report (Integrated 305(b) Report (pending revision) and 303(d) Listing) in 2014 (NNEPA 2014). The report summarized water quality sampling events conducted at two locations downgradient of historical mining activity in the Cove Wash watershed. Data used for the assessment were from a 2001 sampling event for one sampling location, and from 2011 and 2012 for the second sampling location. The NNEPA

compared concentrations of COCs found at the two locations to Navajo Nation Surface Water Quality Standards (NNSWQS) adopted by the Navajo Nation in 2013 and pending approval by the EPA. Sampling results for the surface water location sample results in 2001 did not meet NNSWQS standards for gross alpha radioactivity, chloride, and selenium. Sampling results for the surface water samples in 2011 and 2012 did not meet NNSWQS standards for gross alpha radioactivity, aluminum, and dissolved oxygen. The assessment recommended that the Cove Wash watershed be designated as impaired per the U.S. Clean Water Act Sections 305(b) and 303(d). The assessment also recommends that a total maximum daily load for gross alpha radioactivity be developed for the Cove Wash watershed. Current Navajo Nation Surface Water Quaity Standards can be accessed here: https://www.epa.gov/sites/production/files/2014-12/documents/navajo-tribe.pdf.

V. PROJECT OBJECTIVES

1. Data Use Objectives

The presence of abandoned uranium mines in many Diné communities has caused concern about exposure to heavy metals from abandoned mine waste. While previous research demonstrated greater risk for developing chronic diseases when people are exposed to abandoned U mine waste (Hund et al 2015), there remains limited work addressing the role of animal tissue as a point of exposure. This is a critical gap to address because certain locally raised animal tissue, such as mutton meat and organs, is a traditional food source for the Diné people. Assessing the accumulation of heavy metals in animal tissues will inform efforts assessing human metal and radionuclide exposure.

Previous work investigating the accumulation of uranium and other radioactive chemicals in animal tissue identified significantly higher concentrations in cattle from mining areas (Lapham 1989). This work however, did not account for animal movements throughout a contaminated area. Grazing animals may move throughout the Cove Wash Watershed suggesting various points of exposure with different duration and intensity. This limitation affects the interpretation of animal exposure, which in turns limits interpretation of results with respect to human exposure, remediation priority, and risk reduction because the relevant exposure sources are unidentifiable.

Specific Aims:

1) Compare uranium levels in tissues and organs from livestock grazing in mining versus non-mining areas on Diné Lands, and,
2) Determine environmental exposure to the livestock utilizing the GPS tracking information.

2. Project Tasks and Sampling Objectives

The University of New Mexico (UNM) and Montana State University – Billings (MSUB) will conduct a targeted investigation of Bos taurus (cattle), Ovis aries (sheep), and Capra aegagrus hircus (goat) movement and grazing patterns is necessary to inform risk analysis for human exposure to metals and radionuclides from consumption (or other uses) of animal tissue. This phase of the Livestock Study will use geospatial technology to determine the frequency and duration of livestock grazing in proximity to abandoned mines and waste.

This component of the Cove Livestock Study under UNM and MSUB will address two questions:

1. What is the frequency and duration of livestock grazing in proximity to abandoned mines and waste?
2. What environmental and land cover factors are associated with metal uptake in livestock organs and tissue?

Addressing these questions enables us to quantify and model livestock grazing on or near abandoned mine waste, better interpret inter-animal chemical uptake in animal tissue, calculate more accurate chemical transfer rates from animal tissue to humans, and inform a broader risk assessment of human exposure to metals and radionuclides in the Cove Wash Watershed.
Northern Arizona University (NAU) will use the collected data and livestock grazing patterns to:

1. Compare uranium levels in tissues and organs from livestock grazing in mining versus non-mining areas on Navajo Lands. Do livestock raised in an area of uranium contamination accumulate significantly higher tissue levels of uranium, compared to livestock from a control area?
2. Compare the uranium levels in environmental samples (soil, plants, water) collected in the grazing areas from the mining versus non-mining areas on Navajo Lands. Are the animals grazing in mining areas exposed to higher levels of uranium compared to animals grazing in non-mining areas? If so, what factors contribute the most (i.e. water, plants, etc.)?

A "control site" is selected at Red Valley, Arizona and shows no mining in the area, has similar topography, vegetation and other environmental and pastoral conditions. (see figure in Section IV. 1). Cove and Red Valley was chosen as the new collection sites because the community members have expressed interest in this study and both communities have significant uranium contamination issues due to abandoned uranium mines.

Diné College staff and Interns will take the lead on gaining approval from these communities and identifying community members to participate in the livestock collection. The Project team (DC, UNM, NAU, and MSUB) will collect samples from sheep, cattle, and goats in the Cove and Red Valley areas. Livestock organs and tissues from five sheep, five goats and five cows from Cove as well as the same number of samples from nearby Red Valley where there are no abandoned mines. We will identify community members to work with us on the livestock sample collection.

3. Environmental Screening Levels

Initially, three areas in Red Valley were sampled for water, soil, and plants to obtain preliminary information on uranium levels in the control area. Additional sampling will be performed after we collect surveillance information on animals in the control area. Three to four samples were collected of each, water, soil, and plants. These sites were chosen based on interactions with the community. Future environmental sampling will be collected within the grazing areas of the animals after monitoring has been initiated. Water sources used by the animals will be sampled along with grazing areas in which the animals grazing the majority of the time as indicated by the monitoring. The soil and plant samples collected in the grazing areas will be restricted to a total of 50 samples each due to funding limitations. At all sampling sites, the GPS coordinates will be recorded using a Garmin GPS handheld unit and recorded. Photos of the site will be taken with phone cameras and site characteristics recorded to catalog the field work.

At each site, livestock water will be collected in a 500mL HDPE VWR trace clean wide mouth packer. Then, two 250mL HDPE VWR trace clean wide mouth packers will be filled with filtered water using WHATMAN 0.45µm PVDF w/PP filters and NORM-JET 30mL LUER-LOCK PP/PE syringes. Only one of the 250mL packers was acidified with concentrated VWR Aristar Ultra nitric acid to a pH less than 2, immediately after filtration. Next the water's temperature, pH, conductivity, total dissolved solids, and salinity will be collected via the Multi-Parameter PCSTestr^{TM} 35 with an Orion 325A conductivity and pH meter. The pH meters will be calibrated at each site by using a two-point calibration between a pH 7 and pH 10 buffers in the field. The conductivity probe will be calibrated with an Orion 1413µS/cm conductivity standard. All of the water samples will be put in a cooler on ice during the day-long collection following the USGS water sampling guide (Wilde 2011). At NAU, the water samples will be stored in a 40°F refrigerator for future analysis.

The soil samples will be collected as "grab samples" from the top 5 cm of soil. Five grab samples will be collected within a 10 x 10 foot area at each site to determine heterogeneity of the area. The grab samples consisted of a scoop of soil being placed into new Whirl-Pak bag. All soil samples were stored upright and transported back to the laboratory (Asselin 2015). In the same area the soil samples are collected, plant samples will be collected in a similar manner. These plants will be collected through guidance from the animal surveillance information and the ranchers themselves. A shovel will be used to dig underneath the plant roots and loosen the plant from the soil. Additionally, soil samples will be collected at the base of the plant to provide information about the soil composition. Once the plant is free from the ground, the entire plant is saran wrapped. Five plant samples will be collected from the 10 x 10 foot area. Plants will be placed upright in the vehicle and transported back to NAU for segmentation. The plants are placed on clean butcher paper and allowed to dry for one week after collection to avoid microbial growth. Once dried, the plants growing together in the same root ball are separated from the other plant parts by pulling them apart into individual sections. The roots require an extra step of washing to remove excess soil with nanopure water. Next, each section is placed in coffee grinders to homogenize the sample. Coffee grinders were cleaned between each sample with a Citranox soap washing and multiple nanopure water rinses. The blended samples were placed onto paper plates to continue to dry out for 48 hours, and then placed in clean Whirl-Pak bags for storage until analysis (Froyum 2019).

Quality assurance is applied in the following procedure. The sampling containers for the water samples will be rinsed three times with the livestock water before filling. The bottles used for filtered water are trace clean and unopened prior to sampling. As a validation for statistics, all water samples will be analyzed in triplicate from each site. In between collection of soil and plant samples, shovels are rinsed with DI water and wiped off with ReliOn sterile alcohol swabs. Soil samples are collected in Whirl-Pak bags; plant samples are wrapped in Saran wrap. Both the soil and plant samples are collected in quintuplicate at each site.

4. Data Quality Objectives (DQO)

The DQO process, as set forth in the EPA Guidance on Systematic Planning Using the Data Quality Objectives Process (EPA/240/B-06/001) (EPA 2006), was followed to establish the DQOs for this project. The DQOs and the outputs for this project are included in Appendix A.

GPS Data Quality Objectives.

The livestock movement in the watershed will be tracked using Lotek 330, 360, or 420 animal GPS collars. The collars will collect latitude, longitude, air temperature, collection duration (in seconds), and dilution of precision (DOP) every 15 minutes. The collars are expected to have positional

accuracy <10 meters, which is consistent with Tier 3 described in the EPA National Geospatial Data Policy.

Receiver Performance Criteria.
For each data collection point, the number of visible satellites, PDOP value, and duration of collection will be recorded.

Statistical Quality Control Check.
Post-processing of the GPS data will be accomplished using the vendor's software package, R, and ESRI ArcGIS operating on a local workstation. Because the GPS data will have a space-time structure, data quality will be evaluated to identify points that are more than 10 meters from adjacent points. Points with a high PDOP (values >6) or low satellite visibility (fewer than 4) will be identified and reviewed.

5. Data Quality Indicators (DQI)

Measurement Quality Objectives are criteria established to assess the viability and usability of data. These are based on both field and laboratory protocols that examine whether the DQIs meet the established criteria for this project. DQI goals for this project were developed using the guidelines provided in *EPA Guidance for Quality Assurance Project Plans,* EPA QA/G-5 (EPA 2002b).
All sampling will be guided by procedures detailed in Sections 4.0 and 6.0 as well as Standard Operating Procedures (SOPs) to ensure representativeness of sampling results. Tables 3-1 and 3-2. Approved EPA methods and standard reporting limits will be used. All data not rejected will be considered complete.

Table 3-1 Screening Levels and DQI Goals for Surface Water and Groundwater

Analyte	Screening Level*	Reporting Limit (µg/L)	Accuracy (Percent Recovery for LCS)	Precision (RPD for MSD and duplicates)	Percent Complete
Arsenic	10 µg/L	10 µg/L	75-100	≤ 35%	≥90
Selenium	5 µg/L	5 µg/L	75-100	≤ 35%	≥90
Uranium	30 µg/L	1 µg/L	75-100	≤ 35%	≥90
Uranium-238	30 pCi/L	1 pCi/L	75-100	≤ 35%	
Uranium-234	30 pCi/L	1 pCi/L	75-100	≤ 35%	
Radium -226	5 pCi/L	1 pCi/L	75-100	≤ 35%	≥90

Notes:
* EPA Maximum Contaminant Level ≥ = greater than or equal to
≤ = less than or equal to µg/L = micrograms per liter
LCS = laboratory control sample
MS/MSD = Matrix Spike/Matrix Spike Duplicate pCi/L = picocuries per liter

RPD = relative percent difference

Table 3-2 Screening Levels and DQI Goals for Sediment

Analyte	Screening Level* (mg/kg)	Reporting Limit	Accuracy (Percent Recovery for LCS)	Precision (RPD for MS/MSD and duplicates)	Percent Complete
Arsenic	0.29	0.260mg/kg**	75-100	≤ 35%; ≤ 50% for field duplicates	≥90
Selenium	0.26	0.158mg/kg***	75-100	≤ 35%; ≤ 50% for field duplicates	≥90
Uranium	14	0.1 mg/kg	75-100	≤ 35%; ≤ 50% for field duplicates	≥90
Uranium-238					
Uranium-234					
Radium -226	Not Applicable	1 pCi/g	75-100	≤ 35%; ≤ 50% for field duplicates	≥90

Notes:
* EPA Regional Screening Level (RSL) - Protection of groundwater Soil Screening Level (mg/kg)
** The Reporting Limit for arsenic is 1 mg/kg, which exceeds the screening level. Therefore, the method detection limit will be used to evaluate arsenic concentrations in sediment.
** The Reporting Limit for selenium is 0.5 mg/kg, which exceeds the screening level. Therefore, the method detection limit will be used to evaluate arsenic concentrations in sediment.
≥ = greater than or equal to ≤ = less than or equal to
LCS = laboratory control sample mg/kg – milligrams per kilogram
MS/MSD = Matrix Spike/Matrix Spike Duplicate pCi/g = picocuries per gram
RPD = relative percent difference

VI. SCHEDULE OF FIELD ACTIVITIES

Table 3 Timeline of project implementation from October 1, 2018 to December 31, 2020

	2018	2019				2020			
Activity	**Q4**	**Q1**	**Q2**	**Q3**	**Q4**	**Q1**	**Q2**	**Q3**	**Q4**
Meet with livestock owners and identify individuals interested in GPS tracking (DC/ UNM)	X	X							
Purchase GPS units, train for data collection (DC/UNM)		X							
GPS track livestock (DC/UNM)			X	X	X				
Process and analyze GPS data (DC/UNM/MSUB)					X	X	X	X	
Meat and organ tissue collection (sheep and goat) (DC/NAU)				X					
Meat and organ tissue collection (sheep and goat) (DC/NAU)					X				
Processing meat and organ samples for analysis (DC/NAU)					X	X			
Sample analysis and interpretation (DC/NAU/ UNM/MSUB)						X	X	X	X
Limited human health risk associated with consuming animal meat and organs (DC/UNM/ NAU/MSUB)						X	X	X	X
Community engagement (DC/NAU/UNM/MSUB)	X	X	X	X	X	X	X	X	X

1. Special Training Requirements/Certifications

The Study Team will complete the NIH's online training session on Protecting Human Research Participants Online Training course. This course is for staff, interns and other field support personnel seeking to develop knowledge and skills on Human Subjects Protection issues and receive certification of completion. In addition, the Study Team will train their staff and student interns in all aspects of the livestock research, integrating Diné tradition and customs in animal use in research. The Institutional Animal Care and Use Committee (IACUC) are of central importance to the application of laws to animal research on the Navajo Nation. The study PI will ensure all personnel will follow these standards of training and will keep the Certificates of personnel completing the training. NAU Environmental Health & Safety Department has a website: https://nau.edu/nau-research/research-safety-and-compliance/environmental-health-and-safety. Also, similar UNM website link: https://srs.unm.edu/employee-safety/chemical-safety/index.html. MSUB safety policies and procedures may be accessed here: https://www.msubillings.edu/police/emergency_procedures.htm. The Dine' Environment Institute at Dine' College has the College safety policies and procedures: https://www.dinecollege.edu/wp-content/uploads/2018/04/DC-Tsaile-ERP-April-2017.pdf

Field sampling personnel have experience with all sampling hazardous waste sites while wearing appropriate personal protective equipment (PPE). At least one field sampler will be trained and familiar with Global Positioning System (GPS) data collection and applicable software. All sampling personnel must have appropriate training that complies with 29 Code of Federal Regulations 1910.120. The site-specific health and safety plan for this project is to be appended to this plan.

VII. SAMPLING RATIONALE AND DESIGN

The Project Team met with the Cove Community, reviewed available site information, reviewed Traditional Ecological Knowledge (Diné customs, traditions and values) and frequently met with USEPA to determine a specific livestock study design. The following sections describe the specific sampling designs that will be implemented during this livestock study.

1. Rationale For Livestock Study

The project team will investigate the relationship between animal movement patterns and habitat type by overlaying individual animal paths with a land use layer and calculating the fraction of grazing time animals spend on each vegetation type (e.g., forest, grasslands, shrubland, herbaceous, or water). A multiple linear regression model will be developed to identify variables that predict tissue metal concentrations for each animal and livestock type. The study area will be subdivided into a grid (30-meter resolution) to examine associations between the total number of grazing records per grid cell (the dependent variable) and environmental variables in each grid (Putfarken et al., 2008). These variables may include the fraction of each vegetation type, percent canopy cover, distance to water source or distance to abandoned uranium mine or waste.

2. Selecting Animals for GPS Tracking

Working with Chapter grazing officials, we will recruit four to five cattle owners for study participation and we will work with the livestock owners to select and collar animals.

- Each livestock owner select fully-grown, non-pregnant female cattle for collaring
- 10 cows, 10 sheep, and 10 goats will be collared in the study area and the same number of livestock in the control area
- Dine College staff and UNM/MSUB team members would assist the owner with collar installation.
- To minimize risk of swelling and account for animal weight gain during the grazing period owners should be able to slide one to two fingers between the collars after fitting. A tight (but not too tight) fit is critical for minimizing discomfort to the animal
- Attaching each collar should be accomplished in no more than 2-3 minutes per animal.

We selected 5 as our sample size for cattle, sheep, and goats because the NAU researchers indicated that this is the minimum number of animals needs to detect a mean difference in tissue metal concentration between groups with 80% power.

3. Selecting Animals For Tissue Analysis

Tissue samples would be collected from GPS tracked livestock. From the study area and control area, five of each livestock (sheep, goat, cattle) will be butchered by community members and sampled by researchers from Northern Arizona University. Additionally, each of the tracked goats and sheep would be butchered by community members and tissue samples collected for analysis by NAU researchers. All of the livestock will be euthanized using the Navajo butchering technique. For

example, the procedure for the Navajo butchering of sheep begins with tying the sheep's leg together so the animal will not get up and run off or hurt someone with their hooves. A piece of log is also place underneath the neck. The log is for the head to hang while the sheep's blood drain after the throat has been cut. A person then proceeds to cut close to the jaw bone for slitting the throat. A sharp knife is used to cut the throat. The knife is sharpened before use. Knives have always been used in cutting of the sheep throat in Navajo tradition. This is out of respect to the animal. The throat, main artery, and the spinal cord are cut. The spinal cord is cut between the C1 and C2 backbone. The blood is also collected with a bowl during this process. The blood is used to make blood sausage using the stomach. Nothing happens until the sheep is completely dead before the dissecting begins. This process takes about 4-5 minutes before the sheep is completely dead. Once the sheep is completely dead, the head is cut-off. The sheep is then skinned and the extremities are broken at the joints. The sheep is then hung upside down by the Achilles tendon. The breast bone is then broken and cut vertically down to the lower abdominal. The stomach and intestines are taken out. The lungs, heart, esophagus, liver, kidneys, spleen, and gallbladder are taken out too. The arms, legs, ribs, spine are then all separated. Typically this procedure is done outside. Multiple organs will be collected from each sheep; upon collection, the samples (organs, tissues, and body parts) will be placed in gallon sized freezer bags, placed in an ice chest, and transferred back to NAU. (Lister 2018).

4. Tissue Analysis

The day after collection and storage, the tissues and organs will be sliced thinly, air dried for two weeks, powered to a sawdust-like consistency with a standard kitchen coffee grinder, and combined/homogenized in one bag. Each individual organ and tissue sample will be put into one bag and homogenized for sample preparation and bulk analysis. The next step is to dry ash the organ or tissue, then acid digest the ashed sample. This will be accomplished by weighing and transferring the sample into a 50 mL centrifuge tube, acidify with 25 mL of 25% HNO_3, place in 80 °C Thermo VWR 1350 oven overnight, filter with 50 mL syringe and a 0.45 mm filter, and dilute with nanopure water (18.2 MΩ·cm) to 50 mL (Lister 2018). Once tissue samples are acid digested by NAU researchers then animal tissue would be analyzed for arsenic, selenium, and uranium using ICP-Mass Spectrometry to analyze tissue samples for. This analysis would be limited to acid digested samples of bone, muscle, kidney, and liver. The analysis would be completed for these four organs from all 30 butchered animals (15 from the Cove Wash Watershed and 15 from the Control area). If non-dedicated sampling equipment is used to collect tissue/organ samples at the site, a rinsate blank will be collected at a rate of one per day to evaluate decontamination procedures. The rinsate blank will be collected by pouring deionized water over the decontaminated sample collection device (e.g., stainless steel butchering knife) and capturing the water in the specified sample container. Five animals per groups is sufficient to detect a 2.9 standard deviation difference in the mean values with 80% statistical power, even after adjusting for multiple comparisons. The lab costs would include any dilution and instrument calibration needed to analyze the samples. It would also include quality control measures and data reporting once samples are analyzed. The elemental concentrations of the tissue samples will be determined using inductively coupled plasma mass spectrometry (ICP-MS). The sample concentrations and extraction efficiencies will be determined from the highest abundant isotope and compare to an internal standard collected using an Thermo X-Series II ICP-MS with an APEX introduction system, equipped with a self-respiration concentric MicroFlow PFA-ST nebulizer, argon gas flow rate was set at 11.9, auxiliary flow of 0.70, and nebulizer flow at 0.83 L/min.

5. Livestock Water and Soil Sampling

The team will determine number of livestock water samples, including background samples, that will be collected from the control area near Red Valley Chapter. The sampling locations are meant to delineate potential sources of COCs to the control area. It is likely that many sampling locations will not contain water during the sampling event. In the case that water is not present, sediment samples will still be collected at each sampling location if possible.

A sample volume of approximately 500 ml will be collected at each surface water location. Approximately 250 ml of surface water will be filtered using 0.45 micrometer filter before analysis. The samples may be filtered on site, or by the laboratory. As the criteria to which these results will be compared are the EPA's drinking water standards, all mud and other material must be removed before analysis. Otherwise, entrained mud and sediments which contain uranium and radium will influence the analytical result of the water. Approximately 250 ml of collected surface water will be submitted for all analyses without filtering in order to determine total concentrations of COCs. The suite of metals to be analyzed in each surface water sample includes a modified Target Analyte List (TAL) metals (including arsenic, selenium, and uranium.

VIII. FIELD ANALYSIS

1. Water Quality Measurements

Field measurements will be collected at each surface water sampling location including pH, temperature, conductivity, oxidation-reduction potential, and turbidity. Flow measurements will be collected at each surface water sampling location where flow is fast enough to measure. Flow will be measured using a Marsh McBirney Flo-Mate 2000. Visual observation of each surface water sample will be recorded.

IX. LABORATORY ANALYSIS

1. Livestock Water and Groundwater Analyses

Surface water samples will be analyzed for trace elements at Northern Arizona University. The water is acidified to preserve the dissolved solids in the field and brought back to lab. To check the preservation of the water, samples were checked one week after collection for a pH less than 2 and all samples were acidified properly in the field. No further digestion or preparation was required for the water until the day of analysis External and internal calibration techniques will be paired together to accurately determine the concentrations of the analytes of interest. The external calibration allows for comparison of the instrument signal from known concentrations of analyte to instrument signal from the samples with unknown concentrations of analyte. Usage of internal standardization is to correct for instrument drift and matrix effects during the data collection. For the water analysis, multi-element calibration standards will be prepared containing 0, 0.1, 0.5, 1.0, 2.0 and 5.0 µg/L of the analytes with an internal standard of 1.0µg/L. Both the calibration standards and the diluted samples contained equal amounts of the internal standard. Calibration standards are used to produce calibration curves for each analyte. The instrument signal for the analyte of interest and the internal standard is given in the form of counts per second (CPS). The CPS of the analyte of interest is divided by the CPS of the internal analyte. This produces a ratio that accounts for the signal of the external standard to the internal standard produced during instrument drift. The known concentration on the x-axis of the external standards are plotted on a scatter plot versus the ratio on the y-axis. After the least's squares best fit line (as determined by the Excel software) is applied to the scatter plot, the resulting linear equations is used to calculate the concentration in µg/L for each sample.

For each analysis, the instrument is switched from vacuum to operation mode. Once operating, the instrument is warmed-up by pumping water for 15 minutes, followed by 30 minutes in 2% HNO_3. This warm-up time allows for the determination of contamination in the nitric acid prior to analysis. It additionally provides time for the instrument parameters to be optimized, maximizing analyte signal and increase stability of readings at the detector. To maintain stability of reading approximately 100 sweeps of three replicates are processed at the detector per sample.

Once the tuning is complete, the calibration standards are analyzed first including a reagent blank, followed by the National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 1640a for trace elements in natural water, and then the diluted unknown samples. The SRM 1640a is used to check the validity of the calibration curves and the consistently in sample preparation prior to analysis. After every 15-20 unknown samples, a check standard is analyzed to check instrument signal.

Sample containers, preservatives, holding times, and estimated number of soil confirmation and QC samples are summarized in Table 5-1.

To provide QC for the analytical program, the following measures will be utilized:

1. Duplicate samples will be collected from 10 percent of the soil sampling locations or one per sample design group. Duplicate soil samples will be collected as a 50/50 split of the sample after collection and homogenization.
2. If non-dedicated sampling equipment is used to collect soil samples at the site, a rinsate blank will be collected at a rate of one per day to evaluate decontamination procedures. The rinsate blank will be collected by pouring deionized water over the decontaminated sample collection device (e.g., trowel or hand auger) and capturing the water in the specified sample container.
3.

Table 5-1. Water and Soil Sampling and Analysis Summary

Method	Elements by EPA 200.7 and 200.8	Uranium Isotopes by EPA 908.0	Ra-226 by Iowa State Hygienic Laboratory (SOP-Appendix I)
Sample Container	500-mL poly	500-mL poly	1-gallon poly
Preservation	HNO3	None	None
Analysis Holding Time	28–180 days	180 days	180 days
Estimated Number of Unique Discrete Samples	56	56	56
Estimated Number of Duplicate Samples	6	6	6

MinimumTotal Site Sample Analyses	62	62	62
Equipment Rinse Blanks (if non-dedicatedequipment is used for groundwater sampling			
Sample Container			500 milliliter plastic bottle/1-gallon poly
Preservation			HNO3 and 4 °C
Analysis Holding Time			28-180 days
Number of Samples			As needed for groundwater sampling

2. Soil Analyses

Soil samples will be prepared and analyzed at the NAU laboratory for elements and uranium. The Iowa State Hygienic Laboratory will analyze soil for radium 226 and uranium isotopes (Appendix E) . For metals, a complete digestion of soils by acid digestion using EPA method 3052 will be implemented. This method utilizes a microwave digester to assist the process. Prior to acid digestion samples will be homogenized and sifted to a 1 mm grain size. Then the samples will be milled for homogenization by tungsten ball mill. Samples will then weighed to 0.5 grams and placed in digestion vessels for the CEM Mars6 microwave digester.

A total volume of 12 mL composed of 9 mL of concentrated nitric acid and 3 mL of hydrofluoric acid is added to the digestion vessel. The digestion is run according to the EPA 3052 method for the microwave digester. Upon completion of the digestion it will be necessary to neutralize the fluorine ions free in solution of the digested samples. After completion of the digest, the microwave vessels will be opened, boric acid added, vessels will be re-sealed, and placed back in the carousel.

The vessels will be placed back in the microwave where the boric acid neutralization is assisted by the instrument. The samples will then be removed from the vessels and placed in either a 30 or 50 mL syringe attached to a 0.45 µm Wattman filter. The vessels will be rinsed out with nanopure 18.20 MΩ·cm water to quantitatively transfer the sample completely to the syringe. The samples will be filtered into ultra-clean new 50 mL centrifuge tubes. Similar sample preparation will be done on NIST Standard Reference Material 2709a (San Joaquin Soil) as a quality assurance step. Sample containers, preservatives, holding times, and estimated number of soil confirmation and quality control samples are summarized in Table 5-2.

The ICPMS analysis is carried out in the same specifications found in section IX 1 describing the water analysis, except for some minor changes are made for the soil analysis compared to the water analysis. The calibration standards concentrations are 0, 1.0, 2.0, 5.0, 10.0, and 15.0µg/L of the analyte with an internal standard of 1µg/L. Diluted unknown samples are prepared with equivalent amounts of 1µg/L of internal standard. Additionally, a digestion blank and a digested SRM 2709a are analyzed. A reagent blank is digested with each batch to determine if the digestion process introduced any contamination. The SRM 2709a results are to confirm that the digestions in each batch via the CEM Mars6 microwave digestion system are consistent and reproducible.

To provide quality control for the analytical program, the following measures will be utilized:

1. Duplicate samples will be collected from 10% of the soil sampling locations or one per sample design group. Duplicate soil samples will be collected as a 50/50 split of the sample after collection and homogenization via sieving.

X. FIELD METHODS AND PROCEDURES

1. Equipment

The equipment listed below may be utilized to obtain environmental data from the respective media according to the following sampling SOPs or their equivalent:

1. Lotek LiteTrack 330, 360 or 420 GPS animal collars. These collars are lightweight (450 grams) and have a robust design that can withstand normal wear-and-tear expected during monitoring. These collars also use differential correction for positional accuracy less than 1 meter and have sufficient internal data storage and battery life for more than 12 months of tracking (assuming GPS collection at 15-minute intervals). GPS and ancillary information are stored on-board for quick data download and retrieval so there are no on-going data transfer fees. If needed, the researchers can replace batteries and the manufacturer's warranty covers electrical and software problems. Software for programing, download, and exporting data for analysis is provided at no cost with the purchase of the collars.
2. Water samplers, if any
3. Soil Sampling equipment, if any
4. Other equipment
5. Dedicated plastic scoops
6. Dedicated plastic sample jars or sealable plastic bags
7. Non-dedicated hand auger
8. Disposable nitrile gloves

2. Equipment Maintenance

Field instrumentation for the collection of samples will be operated, maintained, and have operational checks conducted by the sampling team according to the SOPs listed in Section 6.1.1 or their equivalent. Field instrumentation utilized for health and safety purposes will be operated, maintained, and have operational checks conducted by the sampling team according to the manufacturer's instruction. Operational checks and field use data will be recorded in the instrument or field logbooks.

3. Inspection/Acceptance Requirements for Supplies and Consumables

There are no project-specific inspection/acceptance criteria for supplies and consumables. It is standard operating procedure that personnel will not use broken or defective materials; items will not be used past their expiration date; supplies and consumables will be checked against order and packing slips to verify the correct items were received; and the supplier will be notified of any missing or damaged items.

4. Field Logbooks

Field logbooks will document where, when, how, and from whom any vital project information was obtained. Logbook entries will be complete and accurate enough to permit reconstruction of field activities. Logbooks are bound with consecutively numbered pages. Each page will be dated and the time of entry noted in military time. All entries will be legible, written in ink, and signed by the individual making the entries. Language will be factual, objective, and free of personal opinions. The following information will be recorded, if applicable, during the collection of each sample:

1. Sampling location and description

2. Property sketch showing sampling, removal excavations, and in-place capping locations with measured distances
3. Sampler's and documenter's name(s)
4. Date and time sample collection, removal excavation, and in-place capping occurred
5. Type of samples, excavated, or capped material
6. Type of sampling equipment used and matrix
7. Field observations and details (e.g., rain, odors, etc.)
8. Field instrument reading Shipping arrangements (air bill numbers)
9. Receiving laboratory GPS animal collar ID

The project team members will be on site performing different duties related to sample collection, processing, and analysis. Each logbook will document the information relevant to the site radiation activity, and at a minimum will include:

1. Team members and their responsibilities
2. Time of activities
3. Deviations from sampling plans, site safety plans, and SAP procedures
4. Levels of safety protection
5. Calibration information
6. Analytical data, if any

5. Photographs

Photographs will be taken at representative sampling locations and at other areas of interest on site. They will serve to verify information entered in the field logbook. When a photograph is taken, the following information will be recorded in the appropriate field logbook or field computer tablet:

1. Time, date, location, and, if appropriate, weather conditions
2. Description of the subject photographed
3. Name of person taking the photograph

6. Electronic Sample Logging

The sampling team may utilize field management software to prepare sample labels and chain-of-custody forms. Blank sample labels and chain-of-custody forms will also be available. The following information should be entered for each sample after collection:

1. Sample name
2. Sample date and time
3. Number of Sample bottles
4. Type of Preservation Analyses

In addition to these items, the software may also be used to keep track of other information such as sample depth, field measurements, and split samples. The field team will generate chain-of-custody forms for each cooler of samples packaged and sent to a laboratory. Each chain-of-custody form will refer to the shipping method and tracking number. Printed chain-of-custody forms will be submitted to the laboratory with the samples. The use of field management software will require that the field team have access to a computer, a printer, computer paper, and labels while in the field. The field data manager will be responsible for implementing the software.

7. Mapping Equipment

Sampling points and site features will be located and documented with a GPS unit. The GPS will be used to assign precise geographic coordinates to sampling locations on the site. GPS mapping will be done by personnel trained in the use of the equipment and will be completed according to the manufacturer's instructions. Expected output from the use of GPS mapping will be site maps with sampling locations and major site features. Sampling locations and gamma survey areas will be identified on a printed aerial image or topographic map at locations of poor GPS satellite reception. GPS animal collars will be checked for function and accuracy prior to deployment. Collars will be stored according to manufacturer recommendation.

8. Chain-of-Custody Forms and QA/QC Summary Forms

A chain-of-custody form will be maintained for all samples to be submitted for analysis, from the time the sample is collected until its final deposition. Every transfer of custody must be noted and a signature affixed. Corrections on sample paperwork will be made by drawing a single line through the mistake and initialing and dating the change. The correct information will be entered above, below, or after the mistake. When samples are not under the direct control of the individual responsible for them, they must be stored in a locked container sealed with a custody seal. The chain-of-custody form must include the following:

1. Sample identification numbers
2. Identification of sample to be used for MS/MSD purposes
3. Site name
4. Sample date Number and volume of sample containers
5. Required analyses
6. Signature and name of samplers
7. Signature(s) of any individual(s) with control over samples
8. Airbill or FedEx number
9. Note(s) indicating special holding times and/or detection limits

The chain-of-custody form will be completed and sent with the samples for each laboratory and each shipment. Each sample cooler should contain a chain-of-custody form for all samples within the sample cooler.

A sample summary form will be completed for each method and each matrix of the sampling event. The sample number for all blanks, reference samples, laboratory QC samples (MS/MSDs), and duplicates will be documented on this form. This form is not sent to the laboratory. The original form will be sent to the reviewer who is validating and evaluating the data; a photocopy of the original will be made for the project file.

XI. QUALITY ASSURANCE AND CONTROL (QA/QC)

QA/QC samples to be collected are described in the following subsections. QA/QC described in the following sections pertains to samples collected for laboratory analysis to obtain definitive data and do not pertain to field measurements.

1. **Equipment Blank Samples**

For non-dedicated equipment such as hand augers, to collect samples equipment rinsate blanks will be collected at a rate of one per day to evaluate field decontamination procedures. An equipment rinsate blank consists of a sample of analyte-free water passed through or over a decontaminated sampling device into a 500 milliliter plastic bottle.

2. **Assessment of Sample Variability**

Duplicate soil samples will be collected at selected sampling locations. These locations will be chosen randomly in the field and will be collected at a rate of one for every 10 field samples. The duplicate sample will be obtained by splitting the homogenized sample collected from the soil location. The duplicate sample will be placed in an 8-ounce plastic jar and labeled accordingly.

3. **Livestock GPS Quality Control**

Quality control will be achieved by assuring that collected GPS coordinates and GPS receiver performance criteria under Section V.4 are met. Statistical checks will be performed on the data during the post-processing phase and the data will be compared to known map coordinates and features in the study area using existing US geospatial project data, USGS topographic maps, or other appropriate map sources of known quality.

4. **Livestock GPS Instrument/Equipment Testing, Inspection and Maintenance Records**

Equipment testing will be accomplished by the MSUB PI and UNM research team prior to and after field use. Built-in equipment diagnostics and functionality checks will be utilized in accordance with the operation manuals. Results will be reported in pre-field use and post-field use logs. Issues will be documented and resolved with the GPS manufacturer as required.

5. **Livestock GPS Instrument Calibration and Frequency**

GPS receivers cannot be calibrated by the researcher and only by the manufacturer. Frequency of data collection will be set to every 15 minutes and manufacturer default settings will be used for other settings for optimum data accuracy.

6. **Laboratory Quality Control Samples**

Quality control is performed by doing parallel sample preparation and analysis of Standard Reference Materials as described in the sections describing analysis.

7. **Analytical and Data Package Requirements**

All field measurements and QA/QC information will be documented in logbooks, field forms, and spreadsheets, or may be directly downloaded into a database. The following intended to supersede or change requirements of each method. A copy of the chain-of-custody, sample log-in records, and a case narrative describing the analyses and methods used.

Analytical data (results) for up to three significant figures for all samples, method blanks, MS/MSD, Laboratory Control Samples (LCS), duplicates, Performance Evaluation (PE) samples, and field QC samples.

QC summary sheets/forms that summarize the following:

1. MS/MSD/LCS recovery summary

2. Method/preparation blank summary Initial and continuing calibration summary (including retention time windows)
3. Sample holding time and analytical sequence (i.e., extraction and analysis)
4. Calibration curves and correlation coefficients
5. Duplicate summary
6. Detection limit information
7. Analyst bench records describing dilution, sample weight, percent moisture (solids), sample size, sample extraction and cleanup, final extract volumes, and amount injected.
8. Standard preparation logs, including certificates of analysis for stock standards.
9. Detailed explanation of the quantitation and identification procedure used for specific analyses, giving examples of calculations from the raw data.
10. The final deliverable report will consist of sequentially numbered pages.

8. Data Management

Data collected during the removal assessment will consist of field and laboratory data. Field activities and sample information will be documented in a logbook as discussed in Section 6.1.4. Field and laboratory data including gamma radiation measurements, Ra-226 sample results, and location coordinates, will be loaded in SCRIBE. All data including logbook, complete analytical and validation data packages, photographs, and electronic data will be archived by Project Team. The laboratory data summary and validation reports will be included in the final report submitted to USEPA.

8.1 GPS Data Dictionary.

For GPS livestock movement data the MSUB PI and UNM research team will create a data dictionary. This will include the following elements:

1. GMT.Time
2. Latitude
3. Longitude
4. Altitude
5. Duration
6. Temperature
7. DOP
8. Satellites
9. Unit ID

For each GPS unit, the control file will also be stored along with GPS data. The data dictionary for the control file will include the following elements:

1. Product type
2. Product ID
3. Product status
4. Current Firmware
5. GPS Enabled
6. GPS Schedule details
7. Beacon enabled

8. Beacon frequency
9. Beacon transmit power
10. Beacon rule period
11. Fix type
12. GPS timeout
13. Total number of GPS fixes
14. Product time

8.2 Data Collection Process and Quality Checks. See Section V.4 above

8.1 Data Processing. See Section V.4 above.

8.2 Metadata Preparation.

Metadata preparation will be accomplished for livestock GPS data upon conclusion of the data processing phase. Metadata standards developed by the Federal Geographic Data Committee will be evaluated and used to develop metadata elements that will include:

1. Identification: Citation type information about the data including the title, abstract, purpose for creation, status, keywords, spatial and temporal extent.
2. Constraints: Information about data limitations
3. Data quality: Information about the processes used to evaluate positional and attribute accuracy
4. Maintenance: Information about the scope and frequency of data updates
5. Spatial representation: Information about the mechanism used to represent spatial data (i.e., raster or vector, point line or polygon)
6. Reference system: Information about the geographic datum and projection used to represent geographic position
7. Content: Information about the data entities and attributes
8. Symbology: Information about the symbols used to represent the spatial features
9. Distribution: Information about data distributors and methods for obtaining the data

9. Data Validation

All project data and quality control information will be provided to US EPA to facilitate additional validation by US EPA as needed.

10. Field Variances

As conditions in the field may vary, it may become necessary to implement minor modifications to this plan. When appropriate, the Project Team and the EPA FOSC will be notified of the modifications and a verbal approval obtained before implementing the modifications. Modifications to the original plan will be recorded in Site records and documented in the final report.

XII. ASSESSMENT OF PROJECT ACTIVITIES

1. Assessment Activities

The following assessment activities will be performed by the Project Team:

All project deliverables (SAP, Data Summaries, Data Validation Reports) will be peer-reviewed by Project team prior to submission to EPA. In time-critical situations, the peer review may be concurrent with the release of a draft document to EPA.

The Project Team will review project's QA documentation such as logbooks and chain-of-custody forms to ensure the SAP was followed and that sampling activities were adequately documented. The Project Team will document deficiencies, and the Principal Investigator will be responsible for corrective actions.

2. Evaluation of Results

The analytical chemistry results from the environmental and livestock samples will be evaluated by comparing the levels of contaminants tested in the various sample types to background levels established by USEPA and other regulatory entities. If the levels are elevated in the Cove samples compared to the regulatory backgrounds, then the Project Team will pursue additional support to develop a risk assessment with respect to contaminants of interest. Tissue results will also be evaluated in the context of the GPS data, which will include movement tracks, proximity to abandoned mine waste, and seasonal grazing patterns. Additionally, we will identify the environmental and land cover factors that are associated with livestock grazing patterns and identify what environmental and animal grazing factors are associated with metal and radionuclide accumulation in animal tissue.

3. Project Status Reports to USEPA

It is standard procedure for the Project Team PI to report to the USEPA any issues, as they occur, that arise during the course of the project that could affect data quality, data use objectives, the project objectives, or project schedules. As requested by USEPA, the Project Team will provide unvalidated data as they are received from the laboratory.

4. Reconciliation of Data with DQOs

Assessment of data quality is an ongoing activity throughout all phases of a project.

5. Final Deliverables

At the conclusion of project activities the following products and deliverables will be generated:

- Sample Analysis Plan
- Data summaries
- Data validation reports
- A report interpreting GPS animal tracks relative to abandoned uranium mines and waste as well as interpreting animal tissue results along side GPS analysis. The report will address the proposed research questions and include cartographic products of environmental and GPS data.
- A database integrating project environmental and tissue results; this will include spatial analysis results derived from GPS animal tracks.
- A metadata file for the database, as described in section 8.2

XIII. REFERENCES

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XIV. APPENDICES

Appendix A: Plutonium, Radium-226, and Uranium in Solids, The University of Iowa, State Hygienic Laboratory

THE UNIVERSITY OF IOWA

STATE HYGIENIC LABORATORY
Iowa's Environmental and Public Health Laboratory
www.shl.uiowa.edu

Plutonium, Radium-226, and Uranium in Solids

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1 Introduction

This method was created for the purpose of measuring actinides, plutonium and uranium specifically, and radium-226 in solid materials. It is adapted from four different methods from various sources, including EPA and Eichrom. The initial dissolution protocol was developed for high-silicate matrices (brick and concrete). The sodium hydroxide fusion utilized very efficiently destroys these complexes, making it ideal for the measurement of nuclides that incorporate into silicate crystal structure or form highly insoluble refractory oxides (such as plutonium). The end result of this digestion and subsequent matrix removal steps creates a sample that can be analyzed by conventional water methods.

2 Purpose, Scope and Policy

2.1 Purpose

This method cover the preparation and analysis of solid samples for uranium, plutonium, and radium-226 that require complete dissolution, high purity separation, and isotopic identification.

2.2 Scope

This method may be applied to most solid samples once sufficiently prepared and processed to destroy organic material, either via dry or wet ashing following sufficient matrix validation.

3 Definitions/Glossary

Activity - The rate of disintegration (transformation) or decay of radioactive material. The unit of activity used in the U.S.A. is the curie(Ci).

Analyte - Is “the specific component measured in a chemical analysis.

Alpha particle - A positively charged particle ejected spontaneously from the nuclei of some radioactive elements. It is identical to a helium nucleus.

Bkgd – Background

Background radiation - Radiation from cosmic sources and naturally occurring radioactive materials including radon and global fallout, as it exists in the environment.

Blank - the measured value obtained when a specified component of a sample is not present during the measurement.

Calibration - The check or correction of the accuracy of a measuring instrument.

Carrier - A non-radioactive form of an element that is being analyzed for in the method. It is used to measure the yield of the method.

Control chart - A graphical plot of test results with respect to time with limits to show when a system is in a state of statistical control.

Control Limits - The limits on a control chart beyond which it is highly improbable that a point could lie while the system remains in a state of statistical control.

Counting Error (C.E.)- An error measurement that is based on the 2 sigma value of the natural background measured by an instrument and the count time.

CPM - counts per minute the instrument detected.

Curie - The basic unit used to describe the intensity of radioactivity. The curie is equal to 37 billion disintegrations per second.

Decay (Radioactive)- The decrease in the amount of any radioactive material with the passage of time.

Detector - a material or device that is sensitive to radiation and can produce a signal response suitable for measurement.

DPM /Disintegrations per minute - The amount of radioactive particles emitted by a source. It is the known amount in pCi multiplied by 2.22 (a known and steady factor).

Duplicate measurement - a second measurement made on the same sample to assist in the evaluation of a measurement variance.

Efficiency - The percentage of total disintegration's from a source or sample an instrument is actually able to detect. It is the number of counts per minute detected, divided by the known disintegrations per minute.

EHS- University of Iowa Environmental health and safety office

OpenELIS -Environmental Laboratory Information System - The name given to the computerized system used at the State Hygienic Lab (SHL) for the entry, processing, tracking and reporting and storage of laboratory sample information.

EPA - Environmental Protection Agency

Error - The difference between the true value and the measured value.

Half-life - The time in which half the atoms of a particular radioactive substance disintegrate to another nuclear form.

IDOC - Initial Demonstration of Capability performed by a new analyst to show proficiency.

Ingrowth – a term used to refer to the increase in daughter radioactive material with the passage of time from the parent isotope.

Ions - An atom that has too many or too few electrons causing it to be chemically active.

Ionizing radiation - Any radiation capable of displacing electrons from atoms or molecules, thereby producing ions.

Isotope - One of two or more atoms with the same number of protons, but different numbers of neutrons, in their nuclei (for example Cs-134, Cs-137 are isotopes of Cesium (Cs) the numbers denoting the atomic weight.

Lab control standard - A sample or solution prepared in distilled water with a known amount of activity of a substance that is used to establish quality control of a method or calibration.

MCL- Maximum Contaminant Level is the upper limit a public water supply is allowed to expose the public to.

MDA - Minimum Detectable Activity- a calculated amount of activity that the lab is capable of detecting

Natural Uranium - Uranium as found in nature. It contains 0.7% U-235, 99.3% U-238 and a trace of U-234.

NELAC – National Environmental Laboratory Accreditation Conference or NELAP -Program

Nuclide - A general term referring to all known isotopes both stable and unstable.

Outlier - A value, which appears to deviate markedly from a group of data.

PicoCurie (pCi)- One-trillionth part of a curie (e-12).

PT- Proficiency Test

Proportional counter - An instrument in which an electronic detection system receives pulses that are proportional to the number of ions formed in a gas-filled tube by ionizing radiation.

QA - Quality Assurance - Involves all the planned and systematic actions necessary to provide adequate confidence that a facility, structure, system, or component will perform satisfactorily.

QASP – Quality Assurance Section Plan

QC - Quality control - Is included in quality assurance and is all those actions necessary to control and verify the features and characteristics of a process.

RAD or RADCHEM - SHL Radiochemistry section abbreviations.

RPO – University Iowa Radiation Protection Office

SDWA – Safe Drinking Water Act.

SOP – Standard Operating Procedure.

Standard - A substance that is used to evaluate a method or instrument that has a known value and is certified.

SHL – State Hygienic Lab

4 Sample Type and Volume (Collection, Transport, Preservation, Storage, & Security)

Samples should be collected such that they are representative of the material being sampled. Perishable samples must be preserved and delievered to the laboratory promptly . A sample amount of sample, 10 grams, is required for this analysis, but larger sample quantities will be accepted. The sample will be kept for 6 months (unless otherwise negotiated with the client) and disposed of properly or returned to the client. See RAD-QASP-001 for more information.

5 Specimen/Sample Accessioning

All samples should be assigned a unique lab number in OpenELIS and should have been preserved upon arrival in the lab. For more sample receiving info, see RAD-QASP-001 section 5.0, and section 4.0 of this procedure. Note the removal of the aliquot if a Chain of Custody form requires this type of documentation.

6 Process (Summary of Procedure or Method)

Two, dry, representative 2-gram aliquants are taken from the sample. These aliquants are fortified with appropriate tracers and ashed in a muffle furnace via gently ramping to 600°C. The ashed aliquant are then fused with sodium hydroxide at 600°C until complete dissolution is achieved.

The actinide aliquant is then purified via successive co-precipitations with calcium phosphate and iron hydroxide and lanthanum fluoride. This aliquant is then separated into uranium and plutonium fractions utilizing TEVA and UTEVA resins. The fractions are then co-precipitated with cerium fluoride to prepare the final counting source and are counted via alpha spectrometry.

The radium aliquant is first purified via succesive co-precipitations with calcium carbonate and barium sulfate. The final counting source, as barium sulfate, is counted immediately for tracer yield via gamma spectrometry. The source is then held for 2-3 weeks to allow for ingrowth of Ra-226 progeny and the decay of Ra-224, and counted via gas-flow proportional counting.

7 Safety

General good laboratory safety practices will be used. RAD-SOP 2.0 and 3.0 will be followed for safety. When working with concentrated acids, gloves, lab coat and eye protection will be used. All work should be performed in a fume hood, when feasible. Extra precautions should be taken when working with hydrofluoric acid, including a face shield and extended cuff gloves. Calcium gluconate gel is available for exposure.

8 EQUIPMENT, SUPPLIES, AND SOFT/HARDWARE, VALIDATION, XVI. AND MAINTENANCE

8.1 LARGE EQUIPMENT

8.1.1 Alpha spectrometry system – Ortec Octete Plus and Alpha Ensemble, Ortec AlphaVision 7 software

8.1.2 Gas-flow proportional counting (GPC) System – Canberra LB4200, Canberra Apex AB software

8.1.3 Muffle furnace

8.1.4 High-capacity centrifuge

8.1.5 Vacuum box system

8.1.6 Hot plates

8.1.7 Water bath

8.1.8 Heat lamps

8.1.9 Analytical balance

8.1.10 Vacuum pump

8.2 SMALL EQUIPMENT

8.2.1 Zirconium crucibles with lids, 250 mL

8.2.2 Forceps, stainless steel and Teflon

8.2.3 Serological Pipettes

8.2.4 Gelman polysulfone filter apparatus, 25 mm

8.2.5 Centrifuge bottles, 250 mL

8.2.6 Centrifuge tube racks

8.2.7 Vacuum flask, polypropylene

8.2.8 Evaporating Dish

8.2.9 Wire D loop

8.3 CONSUMABLE SUPPLIES

8.3.1 Eichrom Resolve filters, 0.1 µm, 25 mm diameter

8.3.2 Stainless steel discs, affixed with double sided tape, 1 inch

8.3.3 Petri dishes, 35 x 10 mm &

8.3.4 Stainless Steel Planchets, 2-inch ringed

8.3.5 Mechanical pipette tips

8.3.6 Centrifuge tubes, 50 mL

8.3.7 Vacuum box supports

8.3.8 Vacuum box cartridge reservoirs, 25 mL

See RAD-QASP-001 section 7.0 on equipment and the Appendix A in that manual for an equipment list. For operation of equipment see RAD-SOP 9.0.

9 Reagents Standards, and/or Media

9.1 Standards

Various standards are required for this analysis. Standards of different lot numbers and/or suppliers are utilized for calibrations and quality control. All standards utilized for absolute analysis shall be traceable to NIST. Standards are verified prior to use. See RAD QASP for more information.

9.1.1 Traceable Standards

9.1.1.1 Radium-226

9.1.1.2 Natural Uranium

9.1.1.3 Plutonium-238

9.1.1.4 Uranium-232

9.1.1.5 Plutonium-242

9.1.2 Nominal Standards

9.1.2.1 Barium-133

9.2 REAGENTS/MEDIA AND/OR CULTURES

9.2.1 Sodium hydroxide pellets.

9.2.2 Iron carrier (50 mg/mL): Dissolve 362 g of ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) in 600 mL water and dilute to 1 L with water.

9.2.3 Lanthanum carrier (1.0 mg La3+/mL): Add 3.12 g lanthanum (III) nitrate hexahydrate [$La(NO_3)_3 \cdot 6H_2O$] in 600 mL water and dilute to 1 L with water.

9.2.4 Calcium nitrate (1.25M): Dissolve 294 g of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot {}_4H_2O$) in 600 mL of water and dilute to 1 L with water.

9.2.5 Ammonium hydrogen phosphate (3.2M): Dissolve 424 g of $(NH_4)_2HPO_4$ in 600 mL of water, heat on low to medium heat on a hot plate to dissolve and dilute to 1 L with water.

9.2.6 Titanium (III) chloride solution (TiCl3), 10 wt% solution in 20–30 wt% hydrochloric acid.

9.2.7 Hydrochloric acid (1.5N): Dilute 125 mL concentrated HCl to 1 L with water.

9.2.8 Hydrochloric acid (0.01N): Dilute 0.83 mL concentrated HCl to 1 L with water.

9.2.9 Hydrofluoric acid (28M): Concentrated.

9.2.10 Nitric acid (3N)-boric acid (0.25M): Dissolve 15.4 g H_3BO_3 and dilute 190 mL concentrated HNO_3 to 1 L with water.

9.2.11 Nitric acid (7N): Dilute 438 mL concentrated HNO_3 to 1 L with water.

9.2.12 Nitric acid (3N): Dilute 188 mL concentrated HNO_3 to 1 L with water

9.2.13 Hydrochloric acid (12N): Concentrated.

9.2.14 Sodium Carbonate (2M): Dissolve 212 of Na_2CO_3 in 800 mL water and dilute to 1 L with water.

9.2.15 Hydrochloric acid (1N): Dilute 83 mL concentrated HCl to 1 L with water.

9.2.16 Hydrochloric acid (5N)-oxalic acid (0.05M): Dissolve 6.3 g $H_2C_2O_4 \cdot 2H_2O$ in 400mL water. Add 417mL concentrated HCl. Dilute to 1L with water.

9.2.17 Hydrochloric acid (9N): Dilute 750 mL concentrated hydrochloric acid to 1 L with water.

9.2.18 Nitric acid (0.05N) - Hydrofluoric acid (0.05M) - titanium chloride (0.02M): Dilute 3.2mL of concentrated HNO_3, 1.8mL of concentrated HF and 30.8mL of 10% $TiCl_3$ to 1 L with water. Dilute to 1L with water.

9.2.19 Sodium nitrite (3M): Dissolve 208 g of $NaNO_2$ in 900 mL of water. Dilute to 1L with water.

6. Prepare fresh daily.

9.2.20 Ferric Nitrate Solution (5 mg/mL) in 0.1M nitric acid: Dilute 100 mL 50 mg/mL iron carrier and 6.25 mL concentrated HNO_3 to 1 L with water.

9.2.21 Sulfamic acid (1.5M): Dissolve 146 g of NH_2SO_3H in 800 mL of water. Dilute to 1 L with water.

9.2.22 TEVA resin cartridge, 2 mL, 50-100 µm, Eichrom Part # TE-R50-S

9.2.23 UTEVA resin cartridge, 2 mL, 50-150 µm, Eichrom Part # UT-R50-S

9.2.24 Barium carrier (16 mg/mL): Dissolve 28.46 g of $BaCl_2 \cdot 2H_2O$ in 800 mL of water, add 5 mL concentrated HNO_3, and dilute to 1 L with water.

9.2.25 EDTA (0.25M)-sodium hydroxide (0.5M): Dissolve 20 g of NaOH and then 93 g of EDTA in 750 mL of water and dilute to 1 L with water.

9.2.26 Ammonium sulfate (200 mg/mL): Dissolve 200 g (NH4)2SO4 in 800 mL of water and dilute to 1 L with water.

9.2.27 Acetic acid (17.4M): Concentrated, glacial.

9.2.28 Flexible colloidon containing 2% amyl acetate: Commercially prepared.

XVII. 10 CALIBRATION AND STANDARDIZATION

10.1 ALPHA SPECTROMETRY CALIBRATION

Total detector efficiency and energy calibrations are performed on each detector individually with an traceable electroplated multi-nuclide standard. Overall detector efficiency is calculated as a weighted average and the energy is calculated as a linear curve. Peak centroid energies are shifted according to tracer centroid observed in individual samples to account for alpha attenuation in the counting source. NIST-traceable tracers are added to the uranium/plutonium aliquant to account for overall separation yield.

Backgrounds are determined utilizing blank discs with filters attached and are collected at least monthly or immediately before samples are counted.

See AlphaVision 7 User Manual and Rad-SOP 9.13 for further information.

10.2 GAMMA SPECTROMETRY CALIBRATION

Precise volumes of a nominal Barium-133 standard are spiked onto three separate stainless steel planchets, dried under heat lamps, placed in petri dishes, and counted on the end cap of the gamma spectrometer to achieve 10,000 net counts in the 81 keV gamma-ray peak. This is converted into an activity concentration to determine 100% yield. The standard deviation of this activity concentration between the three planchets is used to determine the standard uncertainty for the 100% tracer yield.

10.3 GAS-FLOW PROPORTIONAL COUNTER CALIBRATION

An efficiency for Radium-226 is determined by fortifying varying masses of barium sulfate on planchets with a constant activity of Radium-226 using a NIST-traceable standard. The masses of barium sulfate are selected to cover the acceptable ranges for chemical recovery of the barium yield tracer specified in EPA 903.0. The planchets are then held to reach equilibrium. The set of planchets is then counted in each detector, making sure to achieve 10,000 net counts, and individual efficiency curves are created by fitting a 2nd-order polynomial curve to the mass versus efficiency data.

The standard uncertainty for the efficiency terms is then calculated as the standard uncertainty of the y-estimate as calculate by excel; the uncertainty of the fit of the curve represents a much larger term than the counting uncertainty or the standard uncertainty, and is thus taken as the more conservative estimate of overall efficiency.

Background count rates are determined for each detector by averaging 50, 50-min daily check counts of a blank planchet. These counts are utilized to verify instrument stability on an ongoing basis. For uncertainty and detection calculations, a background counting duration of 2500 minutes is assumed.

See the M:\radchem\Eff folder for archived raw data and blank forms. For more information see section 9.0 in the RAD-QASP-001.

11 PROCEDURE, SAMPLE PREPARATION & ANALYSIS

11.1 FUSION

11.1.1 Weigh out a representative, finely ground 2-g dry aliquant of sample into a crucible

11.1.2 Add the proper amount of tracer or carrier appropriate for the method being used and the number of aliquants needed. This includes U-232, Pu-239, and Ba-133.

11.1.3 Place crucibles on a hot plate and heat to dryness on medium heat.

11.1.4 Remove crucibles from hot plate and allow to cool.

11.1.5 If sample the contains substantial organic material, as with loamy soil or vegetation, dry ash sample overnight by slowly ramping temperature to 600°C and hold overnight. Allow to cool before removing from the muffle furnace.

11.1.6 Add the following amounts of sodium hydroxide based on the aliquant size/analysis required:

11.1.6.1.1 2 g for Pu, U: 30 g NaOH 2 g for Ra: 20 g NaOH

11.1.7 Place the crucibles with lids in the 600 °C furnace using tongs.

11.1.8 Fuse samples in the crucibles for ~15 minutes. **NOTE: Longer times may be needed for larger particles.**

11.1.9 Remove hot crucibles from furnace very carefully using tongs, and transfer to hood.

11.1.10 Add ~25-50 mL of water to each crucible ~8 to 10 minutes (or longer) after removing crucibles from furnace, and heat on hotplate to loosen/dissolve solids.

11.1.11 If necessary for dissolution, add more water, and warm as needed on a hotplate.

11.1.12 Proceed to Section 11.2 for the actinide preconcentration procedure or 11.3 for Ra preconcentration steps.

11.2 PRECONCENTRATION OF ACTINIDES (PU, U) FROM HYDROXIDE MATRIX

11.2.1 Pipet 2.5 mL of iron carrier (50 mg/mL) into a labeled 250-mL centrifuge bottle for each sample.

11.2.2 Add La carrier to each 250 mL centrifuge bottle as follows: 5 mL 1 mg La/mL

11.2.3 Transfer each fused sample to a 250 mL centrifuge bottle, rinse crucibles well with water, and transfer rinses to each tube.

11.2.4 Dilute each sample to approximately 180 mL with water.

11.2.5 Cool the 250 mL centrifuge bottles to approximately room temperature as needed.

11.2.6 Pipet 3 mL 1.25M $Ca(NO_3)_2$ and 5 mL 3.2M $(NH_4)_2HPO_4$ into each bottle

11.2.7 Cap bottles and mix well.

11.2.8 Pipet 5 mL of 10 wt% $TiCl_3$ into each tube, and cap and mix immediately.

11.2.9 Cool 250 mL centrifuge tubes in an ice bath for ~ 10 minutes.

11.2.10 Centrifuge tubes for 6 minutes at 3500 rpm.

11.2.11 Pour off the supernatant, and discard to waste.

11.2.12 Add 1.5M HCl to each tube to redissolve each sample in a total volume of ~60 mL.

11.2.13 Cap and shake each tube to dissolve solids as well as possible. **NOTE: There will typically be undissolved solids, which is acceptable.**

11.2.14 Dilute each tube to ~170 mL with 0.01M HCl. Cap and mix.

11.2.15 Pipet 1 mL of 1.0 mg La/mL into each tube.

11.2.16 Pipet 3 mL of 10 wt% $TiCl_3$ into each tube. Cap and mix.

11.2.17 Add 22 mL of concentrated HF into each tube. Cap and mix well.

11.2.18 Place tubes to set in an ice bath for ~10 minutes to get the tubes very cold.

11.2.19 Centrifuge for ~10 minutes at 3000 rpm or more or as needed.

11.2.20Pour off supernatant, and discard to waste.

11.2.21 Pipet 5 mL of 3M HNO_3 - 0.25M boric acid into each tube.

11.2.22 Cap, mix, and transfer contents of the tube into a labeled 50 mL centrifuge tube.

11.2.23 Pipet 6 mL of 7M HNO_3 and 7 mL of 2M aluminum nitrate into each tube, cap and mix (shake or use a vortex stirrer), and transfer rinse to 50-mL centrifuge tube.

11.2.24 Pipet 3 ml of 3M HNO_3 directly into the 50 mL centrifuge tube.

11.2.25 Warm each 50 mL centrifuge tube in a hot water bath for a few minutes, swirling to dissolve.

11.2.26 Remove each 50 mL centrifuge tube from the water bath and allow to cool to room temperature.

11.2.27 Centrifuge the 50 ml tubes at 3500 rpm for 5 minutes to remove any traces of solids (may not be visible prior to centrifuging), and transfer solutions to labeled beakers or tubes for further processing. Discard any solids.

11.2.28 Proceed to Section 11.4.

11.3 PRECONCENTRATION OF ^{226}RA FROM HYDROXIDE MATRIX

11.3.1 Transfer each sample to a 250 mL centrifuge bottle, rinse crucibles well with water, and transfer rinses to each tube.

11.3.2 Dilute to approximately 150 mL with water.

11.3.3 Add 20 mL of concentrated HCl to each tube.

11.3.4 Cap and mix each tube well.

11.3.5 Pipet 0.5 mL of 1.25M $Ca(NO_3)_2$ into each tube.

11.3.6 Add 25 mL of 2M Na_2CO_3 to each tube.

11.3.7 Cap tubes and mix.

11.3.8 Cool 250 mL centrifuge bottles in an ice bath for ~ 5–10 minutes.

11.3.9 Centrifuge tubes for 6 minutes at 3500 rpm.

11.3.10 Pour off the supernatant, and discard to waste.

11.3.11 Pipet 10 mL 1.5M HCl into each tube to dissolve precipitate. Cap and mix.

11.3.12 Transfer sample solution to a 50 mL centrifuge tube.

11.3.13 Pipet 10 mL 1.5M HCl into each 250 mL bottle to rinse. Cap and rinse well.

7. 11.3.14 **Transfer rinse solution to 50 mL-tube and mix well. NOTE: Typically the HCl added to dissolve the carbonate precipitate is sufficient to acidify the sample. If the precipitate was unusually large and milky suspended solids remain, indicating additional acid is needed, the pH can be checked to verify it is pH 1 or less. To acidify the pH <1, 1 or 2 mL of concentrated hydrochloric acid may be added to acidify the solution further and get it to clear. Undissolved solids may be more likely to occur with brick samples. Tubes may be warmed in a water bath to help dissolve samples.**

11.3.15 If solids remain, add 5 mL 1.5M HCl to each tube, cap and mix well, centrifuge for 5 minutes and add the supernatant to the sample solution. Discard any residual solids.

11.3.16 Proceed to Section 11.5.

11.4 Pu, U Separation

11.4.1 Add 2-mL of 1.5M sulfamic acid, 0.5-mL of 5 mg/mL Fe solution, and 2-mL of 1M ascorbic acid to each sample. Swirl to mix and wait 5 minutes.

11.4.2 Add 1-mL of 3M $NaNO_2$. Mix well and wait for 5 minutes. **Note: $NaNO_2$ is added to oxidize Pu(III) to Pu(IV).**

11.4.3 Set up of TEVA and UTEVA cartridges in tandem on the vacuum box system

11.4.4 Place the inner tube rack into the vacuum box with the centrifuge tubes in the rack. Fit the lid to the vacuum system box.

11.4.5 Place the yellow outer tips into all 12 or 24 openings of the lid of the vacuum box. Fit an inner support tube into each yellow tip.

11.4.6 For each sample solution, fit a UTEVA cartridge on to the inner support tube. Attach TEVA cartridge to the top end of the UTEVA cartridge.

11.4.7 Attach syringe barrels (funnels/reservoirs) to the top end of the TEVA cartridge. **NOTE: The unused openings on the vacuum box should be sealed. Yellow caps can be used to plug unused white tips to achieve good seal during the separation. Alternatively, unused vacuum box holes can be sealed with scotch tape affixed to the vacuum box lid.**

11.4.8 Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.

11.4.9 Add 5mL of 3M HNO_3 to each reservoir to precondition the TEVA and UTEVA cartridges. Adjust the vacuum pressure to achieve a flow-rate of 1.0 ml/minute.

11.4.10 Th and Pu separation from U using TEVA and UTEVA Resin

11.4.10.1 Transfer each solution from step 7.1.6.17. into the appropriate reservoir. Allow solution to pass through both the cartridges at a flow rate of 1.0 mL/minute.

11.4.10.2 Add 5mL of 3M HNO3 to rinse to each sample beaker and transfer each solution into the appropriate reservoir. (the flow rate can be adjusted to 2mL/minute).

11.4.10.3 Add 15mL of 3M HNO3 into each reservoir. Allow liquid to pass through cartridges at 2mL/minute.

11.4.10.4 Disengage vacuum. Separate TEVA cartridge from UTEVA cartridge. Place a new set of reservoirs on the UTEVA cartridges. Empty liquid from centrifuge tubes below each column (dispose as waste). Set TEVA cartridges aside, while Uranium is separated from UTEVA. Replace centrifuge tubes below each cartridge.

11.4.10.5 Add 5mL of 3M HNO3 into each UTEVA cartridge. Engage vacuum and allow liquid to pass through cartridges at 2mL/min.

11.4.10.6 Add 5mL of 9M HCl into each UTEVA cartridge. Allow liquid to pass through cartridges at 2mL/min.

11.4.10.7 Add 20mL of 5M HCl- 0.05M oxalic acid into each UTEVA cartridge. Allow liquid to pass through cartridges at 2mL/min. Note: The rinses remove any residual neptunium, thorium and americium if present on UTEVA. Also removes any residual ferrous ion that might interfere with electrodeposition. ^{210}Po will have been removed by the TEVA cartridge.

11.4.10.8 Disengage the vacuum and place a clean, labeled tube below each cartridge. Replacing outer yellow vacuum box tips and inner tube supports at this time will help ensure clean uranium fractions in the following step.

11.4.10.9 Add 15mL of 1M HCl into each cartridge reservoir to strip the uranium from UTEVA. Engage vacuum and strip uranium at 1mL/min.

11.4.10.10 Set U samples aside for alpha source preparation.

11.4.11 Th, Pu Separation Using TEVA cartridge:

11.4.11.1 Place TEVA cartridges along clean reservoirs on the appropriate openings on the vacuum box lid.

11.4.11.2 Add 15mL of 3M HNO3 to each cartridge reservoir. Allow solution to pass through cartridges at 2mL/min.

11.4.11.3 Ensure that clean, labeled tubes are placed in the tube rack. Replacing outer yellow vacuum box tips and inner white vacuum box tips at this time will help ensure clean thorium fractions in the following step.

11.4.11.4 M HCl to each cartridge. Elute thorium at 1mL/min.

11.4.11.5 Disengage vacuum and remove centrifuge tubes containing Th. Set Th samples aside for alpha source preparation.

11.4.11.6 Ensure that clean, labeled tubes are placed in the tube rack under each cartridge. Replacing outer yellow vacuum box tips and inner support tubes at this time will help ensure clean plutonium fractions in the following step.

11.4.11.7 Add 25mL of 0.05M HNO3/0.05M HF/0.02M TiCl3 to each reservoir. Engage vacuum and elute plutonium at 1mL/min. Note: Electrodeposition CANNOT be carried out on the Pu fraction because of TiCl3 in the strip solution. If electrodeposition is desired then another suitable stripping agent may be used, such as 0.1M ammonium bioxalate.

11.4.11.8 Set Pu samples aside for alpha source preparation.

11.4.12 Proceed to section 11.6.

11.5 RA SEPARATION

11.5.1 Add 2 mL 16 mg/mL barium carrier to each tube and mix well.

11.5.2 Coprecipitate radium with barium sulfate by adding 1 mL 200 mg/mL ammonium sulfate, 2 mL 17.4M glacial acetic acid, and warming tubes in a hot water bath for 15 minutes.

11.5.3 Centrifuge tubes for 3 minutes at 3000 rpm.

11.5.4 Pour off supernatant, and discard to waste.

11.5.5 Dissolve precipitate by adding 20 mL 0.25M EDTA/0.5M NaOH and warming tubes in a hot water batch for 15 minutes.

11.5.6 Precipitate barium sulfate by adding 1 mL 200 mg/mL ammonium sulfate, 2 mL 17.4M glacial acetic acid, and warm tubes in a hot water bath for 15 minutes. Record this time as the beginning of Ra-226 ingrowth.

11.5.7 Centrifuge tubes for 3 minutes at 3000 rpm.

11.5.8 Pour off supernatant, and discard to waste.

11.5.9 Wash precipitate with 10 mL deionized water and centrifuge tubes for 3 minutes at 3000 rpm.

11.5.10 Pour off supernatant, and discard to waste.

11.5.11 Transfer precipitate to a tared stainless steel planchet and dry under heat lamps.

11.5.12 Count samples for Ba-133 tracer recovery via HPGe.

11.5.13 Hold samples for 2-3 weeks to allow for ingrowth of Ra-226 daughter products and the decay of Ra-224.

11.6 RARE EARTH MICROPRECIPITATION

11.6.1 Add 50 mg Ce^{3+} to the plutonium fraction eluted in step 11.4.11.8 and mix well.

11.6.2 Add 1 mL concentrated HF, cap tubes, and swirl to mix. Let solutions sit for 15-30 minutes before filtering.

11.6.3 Add 100 mg Ce^{3+} to the uranium fraction eluted in step 11.4.10.10 and mix well. Attempt to keep the total uranium present to less than 10 µg to maintain good spectral resolution and high tracer yields.

11.6.4 Add 0.25 mL 20 %wt titanium (III) chloride to the uranium fraction.

11.6.5 Add 1 mL concentrated HF, cap tubes, and swirl to mix. Let solutions sit for 15-30 minutes before filtering.

11.6.6 Place an Eichrom 0.1 micron 25 mm polypropylene filter on a Pall filter apparatus, with 50 mL polysulfone funnel. Insert the stem of the filter apparatus into a vacuum box yellow outer tip. Insert the yellow outer tip into a hole on a 12 or 24 hole Eichrom vacuum box. Repeat for each filter assembly available. Plug unused vacuum box holes with scotch tape or vacuum box tip assembly with appropriate plug.

11.6.7 Apply vacuum (~10in. Hg). Add 3-5 mL of 80% ethanol to wet each filter. Make sure that there are no leaks along the sides of the filter assembly. Allow all liquid to pass through filter.

11.6.8 Add 2-3 mL of water to each filter. Allow all liquid to pass through filter.

11.6.9 Add each sample to the appropriate filter funnel apparatus. Rinse centrifuge tube with 3-5mL of DI water and add to the appropriate filter funnel. Allow all liquid to pass through the filter.

11.6.10 Wash the sides of each filter funnel with 3-5 mL of water. Allow all liquid to pass through the filter. **NOTE: Take care not to forcibly spray the rinse directly onto the filter.**

8. **Gently rinse the sides of the filter funnel and allow the rinse solution to fall down to the filter by gravity.**

11.6.11 Wash the sides of each filter funnel with 2-3mL of anhydrous denatured ethanol. **NOTE: Take care not to forcibly spray the rinse directly onto the filter. Gently rinse the sides of the filter funnel and allow the rinse solution to fall down to the filter by gravity.**

11.6.12 Run vacuum until all liquid has passed through filter.

11.6.13 Remove the reservoir portion of the filter apparatus.

11.6.14 Remove filters from filter assembly using tweezers to lift and grab the outer edge of each filter. Mount filters in the center of stainless planchets, with the top of the filter facing out, adhering them with double-sided tape or glue stick. Place in plastic Petri dishes, and use a heating (IR) lamp to dry (normally 3-5 minutes).

11.6.15 Place the lid on each petri dish and store planchets until they are analyzed by alpha spectrometry or gas flow proportional counting.

11.6.16 Thin films are then created using a loop of wire, an evaporating dish, and a flexible collodion by filling the dish with water, placing loop in the dish, adding one drop of flexible collodion, waiting 20 seconds and removing the film. The thin film is then place directly over the filter and disk to prevent recoil contamination of the detector.

12 Quality Control / Quality Checks

Instrument checks are performed on a regular and routine basis in accordance with TNI standards. Analysis quality controls are performed with each batch of twenty samples. All samples are fortified with appropriate tracers; as a result of this fortification matrix spike samples are not analyzed for samples were the tracer is same element as the analyte being analyzed.

12.1 Instrument Quality Checks

12.1.1 Alpha Spectrometer

All detectors are calibrated for energy and efficiency on a weekly basis, or just before counting samples if more than one week has passed since an efficiency calibration was performed. Background spectra are collected on monthly basis if more than one month has passed since background spectra have been collected, unless activity of samples counted warrant an updated background spectra be collected due to concerns regarding detector chamber contamination.

12.1.2 Gas-flow Proportional Counter (GPC)

GPC detectors are calibrated on a yearly basis and checked for efficiency and background on a daily basis. If results for these instrument checks are consistently out of statistically-derived control limits, the detector is removed from service and corrective action, such as recalibration or cleaning is undertaken prior to the detector being placed back into service.

12.1.3 Gamma Spectrophotometer

Detectors are calibrated for efficiency, energy, and background for each geometry being analyzed on a yearly basis, or as needed due to shifts in energy or efficiency. Detector efficiency and energy is checked three times per week and detector background is check once per week. If results for these instrument checks are consistently out of statistically-derived control limits, the detector is removed from service and corrective action, such as recalibration or cleaning is undertaken prior to the detector being placed back into service.

12.2 Analysis Quality Control

12.2.1 Plutonium/Uranium Quality Control Samples

Each batch of 20 samples analyzed for plutonium and/or uranium includes a laboratory fortified blank (LFB/LCS), a sample duplicate, and a laboratory reagent blank (LRB).

12.2.2 Radium-226 Quality Control Samples

Each batch of 20 samples analyzed for radium-226 includes a laboratory fortified blank (LFB/LCS), a sample duplicate, laboratory reagent blank (LRB), and matrix spike (MS).

13 DATA ANALYSIS, CALCULATIONS & INTERPRETATION

13.1 CALCULATIONS

$$A_n = \frac{R_g - R_b}{CfEf_d Cr_{tr} Brm_S IfDf} \quad (13.1.1)$$

$$If_{226Ra} = \frac{1 + 3(1 - e^{-0.007551Lt})}{} \quad (13.1.2)$$

$$TPU = k|A_n| \sqrt{\frac{a_{R_n}^2}{} + \frac{a_{Ef_d}^2}{} + \frac{a_{Cr_{tr}}^2}{} + \frac{a_{m_s}^2}{}} \quad (13.1.3)$$

$$R_n^2 \quad Ef_d^2 \quad Cr_{tr}^2 \quad m_s^2$$

$$a_{R_n} = \frac{\frac{R_b t_s^2}{t_b} + R_g t_s}{t} \quad (13.1.4)$$

$$CL = \frac{k_a \sqrt{R_b t_s (1 + \frac{t_s}{t_b})}}{t_s CfEf_d Cr_{tr} Brm_S IfDf} \quad (13.1.5)$$

$$MDC = \frac{k_{/3}^2 + 2k_a \sqrt{R_b t_s (1 + \frac{t_s}{t_b})}}{t_s CfEf_d Cr_{tr} Brm_S IfDf} \quad (13.1.6)$$

$$MQC = \frac{\frac{k_Q^2}{2A_s I_Q} \left(1 + \sqrt{1 + \frac{4I_Q}{k_Q^2} R_b t_s (1 + \frac{t_s}{t_b})}\right)}{} \quad (13.1.7)$$

$$A_s = t_s CfEf_d Cr_{tr} Brm_S IfDf \sqrt{a_{Ef_d}^2 \quad a_{Cr_{tr}}^2 \quad a_{m_s}^2} \quad (13.1.8)$$

$$I_Q = 1 - k_Q < p_{A_s} = 1 - k_Q \sqrt{Ef_d^2 + Cr_{tr}^2 + m_s^2} \quad (13.1.9)$$

Where,

A_n =Activity at time n, pCi·g^{-1}

R_g = Gross count rate, min^{-1}

R_b = Background count rate, min^{-1}

Cf = Conversion factor, 2.22 dpm·pCi^{-1}

Ef_d = Detector efficiency

Cr_{tr} = Fractional tracer recovery

Br = Branching ratio for energy emission

m_s = Mass of sample analyzed, g

If = Ingrowth factor

Df = Decay factor

TPU = Total propagated uncertainty, 95% confidence interval, $pCi \cdot g^{-1}$

k = Coverage factor, 95% confidence level, 2

R_n = Net count rate, min^{-1}

CL = Critical Concentration /Lower limit of Detection, $pCi \cdot g^{-1}$

k_α = Type I error, 95% confidence level, 1.645

t_s = Sample count duration

t_b = Background count duration

MDC = Minimum Detectable Concentration, $pCi \cdot g^{-1}$

k_β = Type II error, 95% confidence level, 1.645

k_Q = Coverage factor, relative measurement error = $1/k_Q$ = 1%, 10

A_s = Sensitivity factor

φ_{As} = Relative variance of the sensitivity factor

XVIII. 14 Method Performance Specifications & Corrective Actions

14.1 Quality Control Limits

14.1.1 Quality Control Limits are established as follows:
Laboratory Fortified Blank, Matrix Spike: ±20%
Sample Duplicate: Relative Percent Difference ±20%, or Replicate Error Ratio <2 (if the RPD is out of control)

14.1.2 Before each analyst is allowed to perform the method, after training practice runs are done, the analyst will perform a run on their own for IDOC documentation and yearly DOC. PE and IDOC and DOC documentation are stored on the M drive Radchem section folder and QA training section. Raw data is kept with run files. See RAD-QASP-001 for more information.

14.2 CORRECTIVE ACTIONS

When a QC data point for accuracy or precision is of out of control, you can first recount the run if possible. If contamination is noticed because the blank yields a value greater than the detection limit or its associated uncertainty, reagents should be check for contamination and/or deterioration. Record all problems associated with the run on the in the comments section. If instrument troubleshooting has been performed record this information in the instrument log book. An assessment form should be generated if the problem affects client reported values or has a negative effect on the operation of the lab.

15 REPORTING RESULTS

Results are reported via OpenELIS, with applicable comments and qualifiers. Results are reported to a precision of one-thousandth (0.001) or three significant figures, unless other reporting is requested by the client.

XIX. 16 POLLUTION PREVENTION/WASTE MANAGEMENT (SPECIMEN AND REAGENT DISPOSAL)

16.1 SAMPLE/REAGENT DISPOSAL

Samples and reagents will be disposed of properly in accordance with all university, state, and federal regulations. Samples are routinely disposed of after six months (unless otherwise negotiated with the client). Prior to disposal all samples are scanned and a digital record of disposal is created.

16.2 DOCUMENT DISPOSAL

Documents related to sample analysis and quality control are kept for 10 years in either hard-copy or digital format. Sensitive documents are destroy prior to disposal.

XX. 17 PERSONNEL QUALIFICATIONS AND TRAINING REQUIREMENTS

17.1 MINIMUM QUALIFICATIONS

See RAD QASP for information. All analysts performing this method should have a bachelor's degree in chemistry or a related field, or at least 2 years of experience in related laboratory work.

17.2 DOCUMENTATION OF TRAINING

Individuals will not be allowed to perform this method without observation, proper training, IDOC, and/or annual DOC documentation. They will review with the supervisor and sign the general radiochemistry checklist listed in the RAD QASP.

XXI. 18 REFERENCES AND RELATED DOCUMENTS

SHL Chemical Hygiene Plan

SHL Quality Management Plan

SHL Rad QASP

SHL Radiochemistry Section SOPs

EPA 903.0: Alpha Emitting Radium Isotopes in Drinking Water

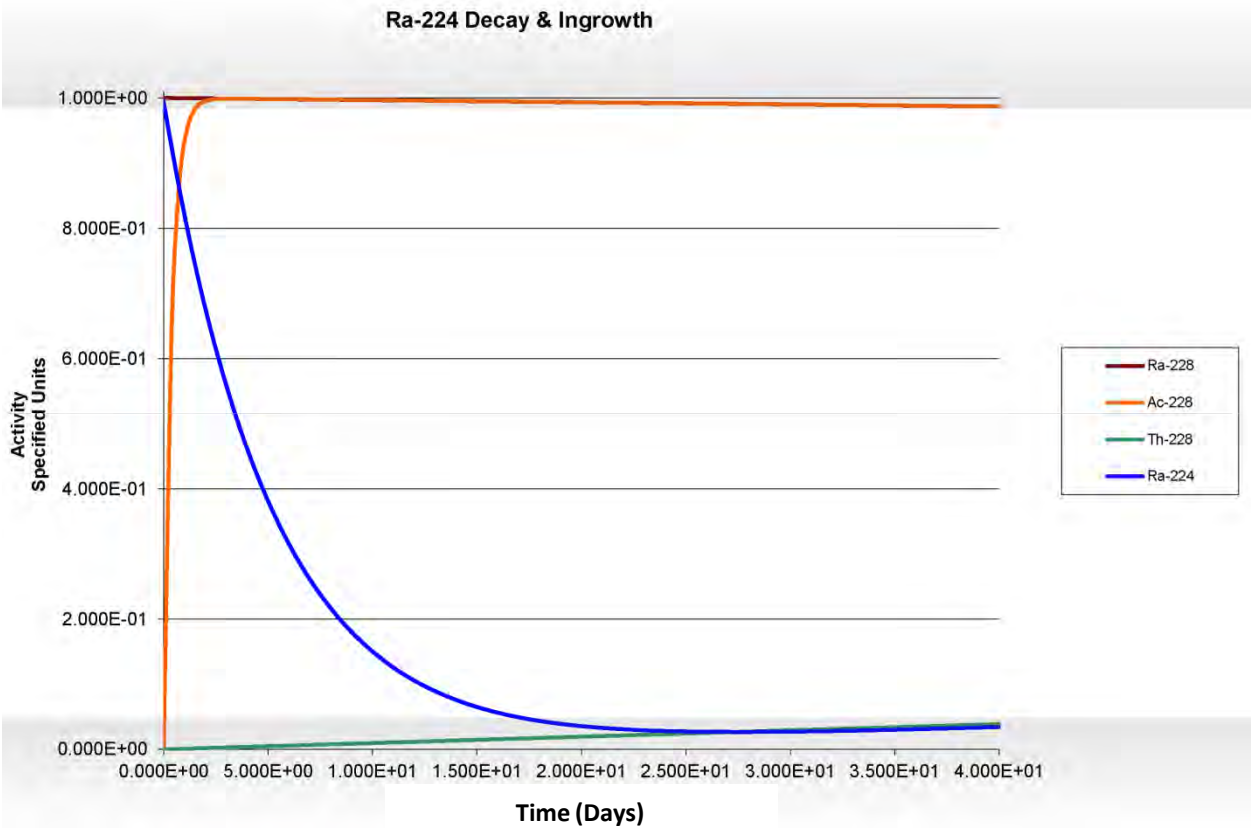
EPA 402-R-14-004 Revision 0: Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses for Environmental Remediation Following Radiological Incidents

Eichrom ACW13VBS, Revision 1.4: Thorium, Plutonium, and Uranium in Water with a Vacuum Box System

Eichrom SPA-01, Revision 1.2: Rare Earth Fluoride Microprecipitation

Inn, K. et al. Use of thin collodion films to prevent recoil-ion contamination of alpha spectrometry detectors. Journal of Radioanalytical and Nuclear Chemistry, 2008. **276**(2): p. 385-390.

19 APPENDICES


Ra-224 Decay & Ingrowth
1.000E+00
8.000E-01
6.000E-01
4.000E-01
2.000E-01
0.000E+00
Activity
Specified Units
0.000E+00
5.000E+00
1.000E+01
1.500E+01
2.000E+01
2.500E+01
3.000E+01
3.500E+01
4.000E+01
Time (Days)
Ra-228
Ac-228
Th-228
Ra-224