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The Trusted Integrator for Sustainable Solutions

REMOVAL SUPPORT TEAM 3
EPA CONTRACT EP-S2-14-01

July 6, 2016

Eric Daly, On-Scene Coordinator
U.S. Environmental Protection Agency
Response & Prevention Branch
2890 Woodbridge Avenue
Edison, NJ 08837

EPA CONTRACT NO: EP-S2-14-01
TDD NO: TO-0007-0012
DOCUMENT CONTROL NO: RST3-03-D-0230
SUBJECT: SITE-SPECIFIC UFP QUALITY ASSURANCE PROJECT PLAN
HOLY TRINITY CEMETERY SITE

Dear Mr. Daly,

Enclosed please find the Site-Specific UFP Quality Assurance Project Plan (QAPP) for the soil sampling event to be conducted at the Holy Trinity Cemetery Site located in Lewiston, Niagara County, New York, from July 7 through 15, 2016.

If you have any questions or comments, please do not hesitate to contact me at (732) 585-4413

Sincerely,

Weston Solutions, Inc.

Bernard Nwosu
RST 3 Site Project Manager

Enclosure
cc: TDD File No.: TO-0007-0012

Site-Specific UFP Quality Assurance Project Plan

Holy Trinity Cemetery Site

Lewiston, Niagara County, New York

DC No: RST3-03-D-0230
TDD No: TO-0007-0012
EPA CONTRACT No: EP-S2-14-01

Prepared for:

U.S. Environmental Protection Agency
Region II – Removal Action Branch
2890 Woodbridge Avenue
Edison, New Jersey 08837

Prepared by:

Removal Support Team 3
Weston Solutions, Inc.
Engineering, Science, and Technology Division
Edison, New Jersey 08837

July 2016

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Attachment A – Figure 1: Site Location Map
Figure 2: Areas of Concern Map
Attachment B – Sampling SOPs: EPA/SERAS SOP # 2001, 2006, 2012
Attachment C – Pace Analytical Services Laboratory SOPs: HASL 300, EPA 901.1, EPA 903.1, and EPA 904.0

LIST OF ACRONYMS

ADR Automated Data Review
ANSETS Analytical Services Tracking System
AOC Acknowledgment of Completion
ASTM American Society for Testing and Materials
CEO Chief Executive Officer
CERCLA Comprehensive Environmental Response, Compensation and Liability Act
CLP Contract Laboratory Program
CFM Contract Financial Manager
CO Contract Officer
COI Conflict of Interest
COO Chief Operations Officer
CRDL Contract Required Detection Limit
CRTL Core Response Team Leader
CRQL Contract Required Quantitation Limit
CQLOSS Corporate Quality Leadership and Operations Support Services
CWA Clean Water Act
DCN Document Control Number
DESA Division of Environmental Science and Assess ment
DI Deionized Water
DPO Deputy Project Officer
DQI Data Quality Indicator
DQO Data Quality Objective
EM Equipment Manager
EDD Electronic Data deliverable
ENVL Environmental Unit Leader
EPA Environmental Protection Agency
ERT Environmental Response Team
FASTAC Field and Analytical Services Teaming Advis ory Committee
GC/ECD Gas Chromatography/Electron Capture Detecto r
GC/MS Gas Chromatography/Mass Spectrometry
HASP Health and Safety Plan
HRS Hazard Ranking System
HSO Health and Safety Officer
ITM Information Technology Manager
LEL Lower Explosive Limit
MSA Mine Safety Appliances
MS/MSD Matrix Spike/Matrix Spike Duplicate
NELAC National Environmental Laboratory Accreditat ion Conference
NELAP National Environmental Laboratory Accreditat ion Program
NIOSH National Institute for Occupational Safety a nd Health
NIST National Institute of Standards and Technolo gy
OSC On-Scene Coordinator
OSHA Occupational Safety and Health Administratio n

LIST OF ACRONYMS (Concluded)

OSWER Office of Solid Waste and Emergency Response
PARCCS Precision, Accuracy, Representativeness, Co mpleteness, Comparability, Sensitivity
PAH Polynuclear Aromatic Hydrocarbons
PCB Polychlorinated Biphenyls
PIO Public Information Officer
PM Program Manager
PO Project Officer
PRP Potentially Responsible Party
PT Proficiency Testing
QA Quality Assurance
QAL Quality Assurance Leader
QAPP Quality Assurance Project Plan
QMP Quality Management Plan
QA/QC Quality Assurance/Quality Control
QC Quality Control
RC Readiness Coordinator
RCRA Resource Conservation and Recovery Act
RPD Relative Percent Difference
RSCC Regional Sample Control Coordinator
RST Removal Support Team
SARA Superfund Amendments and Reauthorization Act
SEDD Staged Electronic Data Deliverable
SOP Standard Operating Practice
SOW Statement of Work
SPM Site Project Manager
START Superfund Technical Assessment and Response Team
STR Sampling Trip Report
TAL Target Analyte List
TCL Total Compound List
TDD Technical Direction Document
TDL Technical Direction Letter
TO Task Order
TQM Total Quality Management
TSCA Toxic Substances Control Act
UFP Uniform Federal Policy
VOA Volatile Organic Analysis

CROSSWALK

The following table provides a "cross-walk" between the QAPP elements outlined in the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAP P Manual), the necessary information, and the location of the information within the text documen t and corresponding QAPP Worksheet. Any QAPP elements and required information that are not applicable to the project are circled.

QAPP Element(s) and Corresponding Section(s) of UFP-QAPP Manual		Required Information	Crosswalk to QAPP Section	Crosswalk to QAPP Worksheet No.
Project Management and Objectives				
2.1	Title and Approval Page	- Title and Approval Page	Approval Page	1
2.2	Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.4 QAPP Identifying Information	- Table of Contents - QAPP Identifying Information	TOC Approval Page	2
2.3	Distribution List and Project Personnel Sign-Off Sheet 2.3.1 Distribution List 2.3.2 Project Personnel Sign-Off Sheet	- Distribution List - Project Personnel Sign-Off Sheet	Approval Page	3 4
2.4	Project Organization 2.4.1 Project Organizational Chart 2.4.2 Communication Pathways 2.4.3 Personnel Responsibilities and Qualifications 2.4.4 Special Training Requirements and Certification	- Project Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications - Special Personnel Training Requirements	2	5 6 7 8
2.5	Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	- Project Planning Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History, and Background - Site Maps (historical and present)	1	9 10
2.6	Project Quality Objectives and Measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	- Site-Specific PQOs - Measurement Performance Criteria	3	11 12
2.7	Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations	1 2	13

QAPP Element(s) and Corresponding Section(s) of UFP-QAPP Manual	Required Information	Crosswalk to QAPP Section	Crosswalk to QAPP Worksheet No.
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation - Project Schedule/Timeline	4	14 15 16
Measurement/Data Acquisition			
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	- Sampling Design and Rationale - Sample Location Map - Sampling Locations and Methods/SOP Requirements - Analytical Methods/SOP Requirements - Field Quality Control Sample Summary - Sampling SOPs - Project Sampling SOP References - Field Equipment Calibration, Maintenance, Testing, and Inspection	5	17 18 19 20 21 22
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	- Analytical SOPs - Analytical SOP References - Analytical Instrument Calibration - Analytical Instrument and Equipment Maintenance, Testing, and Inspection	6	23 24 25
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample Handling and Tracking System 3.3.3 Sample Custody	- Sample Collection Documentation Handling, Tracking, and Custody SOPs - Sample Container Identification - Sample Handling Flow Diagram - Example Chain-of-Custody Form and Seal	7	26 27
3.4 Quality Control Samples 3.4.1 Sampling Quality Control Samples 3.4.2 Analytical Quality Control Samples	- QC Samples - Screening/Confirmatory Analysis Decision Tree	5	28

QAPP Element(s) and Corresponding Section(s) of UFP-QAPP Manual	Required Information	Crosswalk to QAPP Section	Crosswalk to QAPP Worksheet No.
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	- Project Documents and Records - Analytical Services - Data Management SOPs	6	29 30
Assessment/Oversight			
4.1 Assessments and Response Actions 4.1.1 Planned Assessments 4.1.2 Assessment Findings and Corrective Action Responses	- Assessments and Response Actions - Planned Project Assessments - Audit Checklists - Assessment Findings and Corrective Action Responses	8	31 32
4.2 QA Management Reports	- QA Management Reports		33
4.3 Final Project Report	- Final Report(s)		
Data Review			
5.1 Overview			
5.2 Data Review Steps 5.2.1 Step I: Verification 5.2.2 Step II: Validation 5.2.2.1 Step IIa Validation Activities 5.2.2.2 Step IIb Validation Activities 5.2.3 Step III: Usability Assessment 5.2.3.1 Data Limitations and Actions from Usability Assessment 5.2.3.2 Activities	- Verification (Step I) Process - Validation (Steps IIa and IIb) Process - Validation (Steps IIa and IIb) Summary - Usability Assessment	9	34 35 36 37

QAPP Worksheet #1: Title and Approval Page

Title: Site-Specific UFP Quality Assurance Project Plan
Site Name/Project Name: Holy Trinity Cemetery Site
Site Location: Lewiston, Niagara County, New York
Revision Number: 00
Revision Date: Not Applicable

Weston Solutions, Inc.
Lead Organization

Bernard Nwosu
Weston Solutions, Inc.
1090 King Georges Post Road, Suite 201
Edison, NJ 08837
Email: ben.nwosu@westonsolutions.com

Preparer's Name and Organizational Affiliation

7 July 2016
Preparation Date (Day/Month/Year)

Site Project Manager:

Signature

Peter Lisichenko/Weston Solutions, Inc.
Printed Name/Organization/Date

QA Officer/Technical Reviewer:

Signature

Smita Sumbaly/Weston Solution, Inc.
Printed Name/Organization/Date

EPA, Region II On-Scene Coordinator (OSC):

Eric Daly/EPA, Region II
Printed Name/Organization/Date

EPA, Region II Quality Assurance Officer (QAO):

Signature

Printed Name/Organization/Date

Document Control Number: RST3-03-D-0230

QAPP Worksheet #2
QAPP Identifying Information

Site Name/Project Name: Holy Trinity Cemetery Site
Site Location: Lewiston, Niagara County, New York
Operable Unit: 00
Title: Site-Specific UFP Quality Assurance Project Plan
Revision Number: 00
Revision Date: Not Applicable

1. **Identify guidance used to prepare QAPP:**
   Uniform Federal Policy for Quality Assurance Project Plans. Refer to Laboratory Methods.

2. **Identify regulatory program:** EPA, Region II

3. **Identify approval entity:** EPA, Region II

4. **Indicate whether the QAPP is a generic or a <u>site-specific</u> QAPP.**

5. **List dates of scoping sessions that were held:** 4/13/2016, 6/27/2016

6. **List dates and titles of QAPP documents written for previous site work, if applicable:**

   Site-Specific UFP Quality Assurance Project Plan- Holy Trinity Cemetery Site, Lewiston, Niagara County, New York, dated August 6, 2015.

   Site-Specific UFP Quality Assurance Project Plan- Holy Trinity Cemetery Site, Lewiston, Niagara County, New York, dated April 14, 2016.

7. **List organizational partners (stakeholders) and connection with lead organization:**

   None

8. **List data users:** EPA, Region II (see Worksheet #4 for individuals)

9. **If any required QAPP elements and required information are not applicable to the project, then provide an explanation for their exclusion below:** None

10. **Document Control Number:** RST3-03-D-0230

QAPP Worksheet #3: Distribution List

[List those entities to which copies of the approved sitespecific QAPP, subsequent QAPP revisions, addenda, and amendments are sent]

QAPP Recipient	Title	Organization	Telephone Number	Fax Number	E-mail Address	Document Control Number
Eric Daly	On-Scene Coordinator	EPA, Region II	(732) 321-4350	(732) 321-4350	Daly.Eric@epa.epamail.gov	RST 3-03-D-0230
Peter Lisichenko	Site Project Manager	Weston Solutions, Inc., RST 3	(603) 512-4350	(732) 225-7037	peter.lisichenko@westonsolutions.com	RST 3-03-D-0230
Smita Sumbaly	QA Officer	Weston Solutions, Inc., RST 3	(732) 585-4410	(732) 225-7037	S.Sumbaly@westonsolutions.com	RST 3-03-D-0230
Site TDD File	RST 3 Site TDD File	Weston Solutions, Inc., RST 3	Not Applicable	Not Applicable	Not Applicable	RST 3-03-D-0230

QAPP Worksheet #4: Project Personnel Sign-Off Sheet

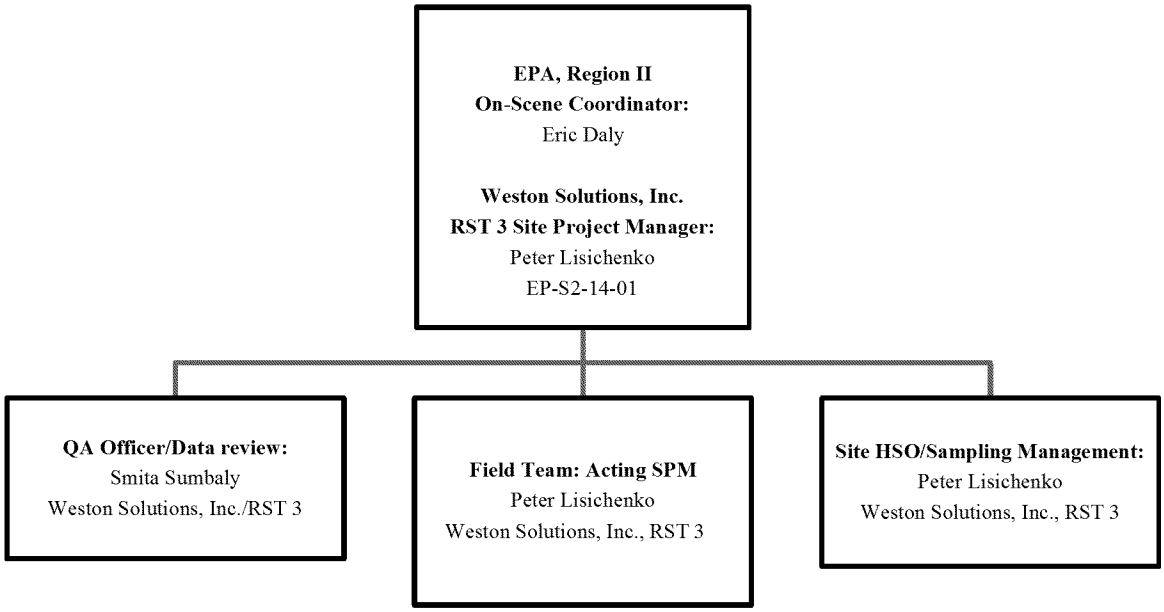
[Copies of this form signed by key project personnel from each organization to indicate that they have read the applicable sections of the site-specific QAPP and will perform the tasks as described; add additional sheets as required. Ask each organization to forward signed sheets to the central project file.]

Organization: Weston Solutions, Inc., RST 3

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Eric Daly	EPA OSC	(732) 321-4350	Eric M. Daly	07/16/2016
Peter Lisichenko	Site Project Manager, RST 3	(603) 512-4350		7/6/16
Smita Sumbaly	QAO, RST 3	(732) 585-4410	Smita Sumbaly	7/6/16
Timothy Benton	Operations Leader / HSO, RST 3	(732) 585-4425		7/6/16

QAPP Worksheet #5: Project Organizational Chart

Identify reporting relationship between all organizations involved in the project, including the lead organization and all contractor and subcontractor organizations. Identify the organizations providing field sampling, on-site and off-site analysis, and data review services, including the names and telephone numbers of all project managers, project team members, and/or project contacts for each organization.



Acronyms:

SPM: Site Project Manager
HSO: Health & Safety Officer

QAPP Worksheet #6: Communication Pathways

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure
Point of contact with EPA OSC	Acting Site Project Manager, Weston Solutions, Inc., RST 3	Peter Lisichenko, SPM	(603) 512-4350	All technical, QA and decision-making matters in regard to the project (verbal, written or electronic)
Adjustments to QAPP	Acting Site Project Manager, Weston Solutions, Inc., RST 3	Peter Lisichenko, SPM	(603) 512-4350	QAPP approval dialogue
Health and Safety On-Site Meeting	HSO, Weston Solutions, Inc., RST 3	Peter Lisichenko, SPM	(603) 512-4350	Explain Site hazards, personnel protective equipment, hospital location, etc.

OSC: On-Scene Coordinator
SPM: Site Project Manager
HSO: Health and Safety Officer

QAPP Worksheet #7: Personnel Responsibilities and Qualifications Table

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Eric Daly	EPA On-Scene Coordinator	EPA, Region II	All project coordination, direction and decision making.	NA
Peter Lisichenko	Field Personnel, RST 3	Weston Solutions, Inc.	Radiological survey and sample collection	10+ Years

*All RST 3 members, including subcontractor's resumes are in possession of RST 3 Program Manager, EPA Project Officer, and Contracting officers.

QAPP Worksheet #8: Special Personnel Training Requirements Table

Project Function	Specialized Training By Title or Description of Course	Training Provider	Training Date	Personnel / Groups Receiving Training	Personnel Titles / Organizational Affiliation	Location of Training Records / Certificates[1]
[Specify location of training records and certificates for samplers]						
QAPP Training	This training is presented to all RST 3 personnel to introduce the provisions, requirements, and responsibilities detailed in the UFP QAPP. The training presents the relationship between the site-specific QA Project Plans (QAPPs), SOPs, work plans, and the Generic QAPP. QAPP refresher training will be presented to all employees following a major QAPP revision.	Weston Solutions, Inc., QAO	As needed	All RST 3 field personnel upon initial employment and as refresher training	Weston Solutions, Inc.	Weston Solutions, Inc., EHS Database
Health and Safety Training	Health and safety training will be provided to ensure compliance with Occupational Safety and Health Administration (OSHA) as established in 29 CFR 1910.120.	Weston Solutions, Inc., HSO	Yearly at a minimum	All Employees upon initial employment and as refresher training every year	Weston Solutions, Inc.	Weston Solutions, Inc., EHS Database
Others	Scribe, ICS 100 and 200, and Air Monitoring Equipment Trainings provided to all employees	Weston Solutions, Inc., QAO/Group Leader's	Upon initial employment and as needed			
	Dangerous Goods Shipping	Weston Solutions, Inc., HSO	Every 2 years			

All team members are trained in the concepts and procedures in recognizing opportunities for continual improvement, and the approaches required to improve procedures while maintaining conformance with legal, technical, and contractual obligations.

[1] All RST 3 members, including subcontractor's certifications are in possession of RST 3 HSO.

QAPP Worksheet #9: Project Scoping Session Participants Sheet

Site Name/Project Name: Holy Trinity Cemetery Site
Site Location: Lewiston, Niagara County, New York
Operable Unit: 00
Date of Sessions: 4/13/2016, 6/27/2016
Scoping Session Purpose: To discuss questions, comments, and assumptions regarding technical issues involved with the sampling activities.

Name	Title	Affiliation	Phone #	E-mail Address	*Project Role
Eric Daly	EPA OSC	EPA, Region II	(732) 321-4350	Daly.Eric@epa.epamail.gov	OSC
Peter Lisichenko	Site Project Manager	Weston Solutions, Inc., RST 3	(603) 512-4350	peter.lisichenko@westonsolutions.com	Site Project Management/ QA Officer/ Technical Reviewer
Timothy Benton	HSO	Weston Solutions, Inc., RST 3	(732) 585-4425	tim.benton@westonsolutions.com	Health and Safety

Comments/Decisions: As part of the Removal Assessment of the Holy Trinity Cemetery Site (the Site), Weston Solutions, Inc., Removal Support Team 3 (RST 3) has been tasked by the U.S. Environmental Protection Agency (EPA) with performing ground radiological survey at three residential properties adjacent to the Site, following which RST 3 will collect soil samples from locations at the residences. The sampling locations will be determined based on results of the radiological survey and as directed by the EPA On-Scene Coordinator (OSC). The soil sampling event is being performed to verify if fill material utilized on the residential properties is impacted with site-related contaminants. Using non-dedicated hand shovels and pickaxes, test pits will be advanced to depths below ground surface (bgs), and up to 50 soil samples will be collected from all three properties. The soil samples will be collected for definitive data quality assurance/quality control (QA/QC) objectives. Field duplicates and matrix spike/matrix spike duplicates MS/MSD will be collected at the rate of one per 20 field samples. Rinsate blanks will be collected as needed to demonstrate the effectiveness of the decontamination procedure of non-dedicated sampling equipment *i.e.* hand shovels and pickaxes. The soil and rinsate (aqueous) samples will be submitted to an RST 3-procured laboratory for isotopic thorium, isotopic uranium, other alpha emitting actinides, radium-226 (ingrowth), radium-228, and gamma spectroscopy analyses.

Consensus Decisions: The Removal Assessment activities are scheduled to begin on July 7 through 15, 2016.

Action Items: A CLP Request Form was submitted on June 28, 2016, and the RST 3 Analytical Service Request Forms were submitted on June 30, 2016.

QAPP Worksheet #10: Problem Definition

PROBLEM DEFINITION

Radiological survey data from prior site investigat ions conducted by Weston Solutions Inc., Site Assessment Team (SAT) and Removal Assessments perfo rmed by RST 3 identified elevated levels of gamma radiation at locations throughout t he Site. Analytical results from soil sampling events conducted as part of the site investigation and Removal Assessment events indicated concentration of radium-226 (Ra-226) above the EPA Site-Specific Action Level in soil samples respectively collected by SAT and RST 3 from locations throughout the Site.

During the prior Removal Assessment conducted by RST 3, one property owner whose residence is at 5374 Robert Street (designated Area 5, Proper ty P005) located adjacent to the Site informed the EPA OSC that his property may have been potenti ally filled with site-related fill material and a portion of the Site's road network may have passe d through his property. As part of ongoing Removal Assessment activities, EPA is conducting a soil sampling event at Area 5, Property P005 and two other residences at 5380 Robert Street (designated Area 6, Property P006) and 5382 Robert Street (designated Area 7, Property P007) which are also located adjacent to the Site in order to verify if fill material utilized on the residential properties is impacted with site-relat ed contaminants

SITE HISTORY/CONDITIONS

The Site consists of an area of radionuclide contam ination located at a cemetery which is approximately 31.5 acres in Lewiston, New York. Th e Site is owned by Holy Trinity Cemetery, which has 2.91 acres of observed contamination loca ted in the northernmost portion of the property on a relatively flat and slightly elevated grassy field, as well as on existing roadbeds. There is one building on the Site which is utilized both as a residence and cemetery maintenance facility. The Site is bordered to the north and eas t by Interstate 190; to the south by another cemetery; and to the west by Robert Avenue and a residential area.

In 1978, the U.S. Department of Energy (DOE) conduc ted an aerial radiological survey of the Niagara Falls region and identified more than 15 pr operties having elevated levels of radiation above background levels. It is believed that, in th e early 1960s, slag from an unknown source was used as fill on the properties prior to paving. Based on the original survey and subsequent investigations, it is believed that the radioactive slag was deposited on the Site.

In February 1980, the New York State Department of Health (NYSDOH) Bureau of Radiological Health and the Niagara County Health Department con ducted a radiological survey of the Site to identify areas with elevated radioactivity resultin g from the use of radioactive slag as fill on the property. The survey was conducted based on informa tion that the slag used at the cemetery was from the same source used at two other locations in nearby Niagara Falls, which had been identified by the NYSDOH as containing elevated lev els of radioactivity. During the survey, cemetery personnel showed NYSDOH a slag pile locate d near the caretaker's garage in the western portion of the property. Cemetery personnel stated that this slag was used as fill for the cemetery roads throughout the property.

QAPP Worksheet #10: Problem Definition (Continued)

In addition, the slag was used as fill for the base of two proposed roadbeds that extended approximately 500 to 600 feet from the caretaker's garage, northwest toward Robert Avenue. At the time of the survey, the construction of these roads had been abandoned. The underlying slag base was covered with an unknown amount of soil and was left as an open field. Using an Eberline PRM 7 radiation meter, radiological survey of the slag pile indicated gamma radiation measuring 250 microroentgens per hour (μR/hr) and along cemetery roads, gamma readings ranged from 5 μR/hr (*i.e.*, background concentration) to 30 μR/hr. Gamma readings along the abandoned roadbeds ranged from 200 μR/hr to 400 μR/hr. Samples of the slag were collected as part of the investigation. Laboratory analyses of the samples indicated that the concentrations of isotopic uranium, isotopic thorium, radium-226 (Ra-226), and radium-228 (Ra-228), were significantly higher than background values.

In October 2006, the New York State Department of Environmental Conservation (NYSDEC) and the Niagara County Health Department conducted a reconnaissance of the Site. At the time, the slag pile previously observed near the caretaker's garage was no longer on the Site; the current caretaker had neither knowledge of the slag pile, nor what happened to it. The caretaker also indicated that children living nearby used this area for recreation. Since the 1980 NYSDOH site investigation, trees had grown through the abandoned slag roadbeds, pushing the slag to the surface. As part of the site visit, NYSDEC conducted a radiological survey with an Exploranium GR-135. Radiological measurements taken while walking along the roadbed indicated gamma readings ranging from 200 to 450 μR/hr at waist height (1 meter/3 feet above the ground) and at-contact reading (1 inch above the ground) ranging from 450 to 570 μR/hr. Contact reading taken next to exposed slag near a tree was documented at 700 μR/hr. The NYSDEC collected four slag samples which were analyzed for isotopic uranium and isotopic thorium via gamma-ray spectroscopy. Laboratory analytical results indicated the presence of uranium-238/234 at concentrations ranging from 114 picocuries per gram (pCi/g) to 1,664 pCi/g and thorium-232 from 114 pCi/g to 898 pCi/g.

In May 2007, NYSDEC visited the Site to verify contamination in an on-site debris pile using gamma-ray spectroscopy. During a 5-minute static survey, Ra-226 was the only nuclide identified. A similar survey conducted on one of the roadbeds confirmed the presence of thorium-232.

During a reconnaissance performed by the NYSDOH and NYSDEC in July 2013, a radiological survey of on-site roadways and along the back roadway leading off site was conducted using a pressurized ion chamber (PIC) and a sodium iodide (NaI) 2x2 detector. Measurements taken along the roadways with the PIC indicated gamma levels up to 51 μR/hr and up to 50,000 counts per minute (cpm) with the NaI detector.

On December 12 and 13, 2013, SAT personnel collected a total of 14 subsurface soil samples and three slag samples from the Site. Soil samples were also collected from two locations suspected to be outside of the source area in order to document background conditions. At each sample location, soil samples were collected directly beneath slag material; at locations where a radioactive fill layer was not visually observed, the soil sample was collected at the equivalent depth interval. Each slag sample consisted of one single piece of slag material. The soil samples

QAPP Worksheet #10: Problem Definition (Continued)

were analyzed by Test America Laboratories (Test Am erica) for target analyte list (TAL) metals via EPA SW846; isotopic thorium and isotopic uranium, via DOE alpha spectroscopy Health and Safety Laboratory (HASL)-300 Method A-01-R; Ra-226, Ra-228, and other gamma emitting radioisotopes, via DOE gamma spectroscopy HASL-300 Method GA-01-R. The slag samples were analyzed for the same parameters as the soil s amples excluding TAL metals. Analytical results indicated that concentrations of radionucli des in all the slag samples and seven soil samples, including the field duplicate, were significantly higher than at background conditions.

On August 12, 2015, RST 3 conducted a soil sampling event to verify the presence of residual radiation-containing material in soil. Based upon the radiological survey data from SAT's prior site investigation and survey data from the radiolo gical investigation conducted by RST 3 during the August 2015 Removal Assessment event, soil samp ling locations suspected to contain radionuclides and metals/metalloids were identified on-site by EPA. A total of nine soil samples including one field duplicate, were collected by RS T 3 from eight location on-site. The soil samples were analyzed by Test America for TAL metal s (including mercury) via EPA SW846; isotopic thorium and isotopic uranium via alpha spe ctroscopy HASL-300-A-01-R; Ra-226 (21 days ingrowth), Ra-228 and other gamma emitting rad ioisotopes via gamma spectroscopy HASL-300-GA-01-R. Analytical results indicated con centrations of Ra-226 above the EPA SSAL of 4.06 pCi/g in three of the nine soil sample s. The concentration of cobalt was above the EPA Removal Management Level (RML) of 70 mg/kg in one soil sample with a concentration of 110 mg/kg. Thallium concentration was above the EP A RML of 2.3 mg/kg in one soil sample with a concentration of 2.4 mg/kg.

PROJECT DESCRIPTION

RST 3 has been tasked by EPA with performing ground radiological survey at three residential properties designated as Area 5, Area 6, and Area 7, located adjacent to the Site, following which RST 3 will collect soil samples from locations at t he residences. The sampling locations will be determined on-site based on results of the radiolog ical survey and at the discretion of the EPA OSC. Using non-dedicated hand shovels and pickaxes, test pits will be advanced to depths bgs, and up to 50 soil samples will be collected from al l three properties. The soil samples will be submitted to an RST 3-procured laboratory for isoto pic thorium, isotopic uranium, other alpha emitting actinides, radium-226 (ingrowth), radium-2 28, and gamma spectroscopy analysis. The soil sampling event is being performed to verify if fill material utilized on the residential properties is impacted with site-related contaminants.

OBSERVATION FROM ANY SITE RECONNAISSANCE REPORT

In December 2013, SAT collected a total of 14 subsu rface soil samples and three slag samples from locations at the Site. The slag samples each consisted of one single piece of slag. The soil samples were analyzed for TAL metals, isotopic thor ium, isotopic uranium, radium-226, radium-228, and gamma spectroscopy. The slag samples were analyzed for the same parameters excluding TAL metals. Analytical results indicated that concentrations of radionuclides in all the slag samples and the seven soil samples were significantly higher than at background conditions.

QAPP Worksheet #10: Problem Definition (Concluded)

In August 2015, RST 3 collected a total of nine soil samples including one field duplicate from eight location on-site. The soil samples were analyzed for TAL metals (including mercury), isotopic thorium, isotopic uranium, Ra-226 (ingrowth), Ra-228, and gamma spectroscopy. Analytical results indicated that concentrations of Ra-226 were above the EPA SSAL of 4.06 pCi/g in three of the nine soil samples. The concentration of cobalt was above the EPA Removal Management Level (RML) of 70 mg/kg in one soil sample with a concentration of 110 mg/kg. Thallium concentration was above the EPA RML of 2.3 mg/kg in one soil sample with a concentration of 2.4 mg/kg.

PROJECT DECISION STATEMENTS

EPA will use the field measurements from the radiological survey at the three residential properties (Areas 5, 6, and 7) to determine spots with elevated gamma readings in order to identify soil sampling locations. The results from the soil sampling event will be utilized by EPA to verify the presence of residual contamination and potential releases of radiation-containing material in residential soil which may be associated with the Site and to determine the horizontal extent of the contamination at the three residences.

QAPP Worksheet # 11:
Project Quality Objectives/Systematic Planning Process Statement

Overall project objectives include: To verify the presence of residual contamination and potential releases of radiation-containing material in residential soil which may be associated with the Site and to determine the horizontal extent of the contamination at the three residences.

Who will use the data? Data will be used by EPA, Region II OSC.

What will the data be used for? The analytical data from this investigation will be used to assist the EPA in determining whether a Removal Action is warranted at the Site.

What types of data are needed?

Type of Data: Definitive data for soil samples

Analytical Techniques: Field survey equipment for soil/Off-site laboratory analyses for soil and rinsate (aqueous) samples

Parameters: Isotopic thorium, isotopic uranium, other alpha emitting actinides, radium-226 (ingrowth), radium-228, and gamma spectroscopy analysis for soil and aqueous matrices.

Type of survey/sampling equipment : Ludlum-2241, NaI scintillator, shovels, pickaxes, plastic scoops, aluminum pans, and sample jars for soil.

Access Agreement: To be provided by EPA, Region II OSC.

Sampling locations: Soil sampling locations will be determined based on data from radiological surveys and as determined the EPA OSC.

How much data are needed? Up to 50 soil samples, including field duplicates will be collected during the sampling event, and rinsate blanks will be collected as needed.

How "good" does the data need to be in order to support the environmental decision?

Sampling/analytical measurement performance criteria for Precision, Accuracy, Representativeness, Completeness, and Comparability (PARCC) parameters will be established. Refer to Worksheet #12, criteria for performance measurement for definitive data.

Where, when, and how should the data be collected/generated? Soil sampling will be performed in three residences situated adjacent to the Site at locations that will be determined by the EPA OSC based on results from the radiological surveys. The soil sampling event is anticipated to begin on July 7 through 15, 2016. All soil samples will be collected using methods outlined in the Standard Operating Procedures (SOPs).

Who will collect and generate the data? The soil samples will be collected by RST 3 field personnel and analyzed by RST 3-procured laboratory . Soil analytical data will be reviewed and validated by RST 3 subcontracted data validator.

QAPP Worksheet # 11:
Project Quality Objectives/Systematic Planning Process Statement (Concluded)

How will the data be reported? All data will be reported by the assigned laboratory (Preliminary, Electronic, and Hard Copy format). The Site Project Manager will provide a Sampling Trip Report, Status Reports, Maps/Figures, Analytical Report, and Data Validation Report to the EPA OSC.

How will the data be archived? Electronic data deliverables will be archived in a Scribe database. Non-CLP data will be archived in EPA's document control room.

QAPP Worksheet #12A: Measurement Performance Criteria Table

Matrix	Soil/Aqueous[1]
Analytical Group	Isotopic Thorium
Concentration Level	Low/Medium

Sampling Procedure	Analytical Method/SOP	Sampling Procedure	Analytical Method/SOP	Sampling Procedure	Analytical Method/SOP
SOP # 2012	Alpha Spectrometry, HASL-300-A-01-R	Precision	% RPD < 25; RER <1%	Sample Duplicate	A
		Accuracy	Limits: Recovery Isotopic thorium 75- 125%	LCS and MS/MSD	A
		Accuracy	< MDC	Method Blank	A

[1]Aqueous samples will consist of rinsate blank samples only. Aqueous field duplicate and MS/MSD samples will not be collected.

Worksheet #12B: Measurement Performance Criteria Table

Matrix	Soil/Aqueous[1]
Analytical Group	Isotopic Uranium
Concentration Level	Low/Medium

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP # 2012	Alpha Spectrometry, HASL-300-A-01-R	Precision	% RPD < 25; RER <1%	Sample Duplicate	A
		Accuracy	Limits: Recovery Isotopic Uranium 75-125%	LCS and MS/MSD	A
		Accuracy	< MDC	Method Blank	A

[1]Aqueous samples will consist of rinsate blank samples only. Aqueous field duplicate and MS/MSD samples will not be collected.

QAPP Worksheet #12C: Measurement Performance Criteria Table

Matrix	Soil[1]/Aqueous[2]
Analytical Group	Radioisotopes by Gamma Spectrometry
Concentration Level	Low/Medium

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SOP # 2012	Soil: Gamma Spectroscopy HASL 300, EPA 901.1 modified Ra-226 (aqueous) 903.1 Ra-228 (aqueous) 904.0	Precision	% RPD < 40; RER <1%	Duplicate	A
		Accuracy	Limits: Recovery 75-125% (soil) Ra-226 (aqueous) 73-135% Ra-228 (aqueous) 60-135%	LCS	A
		Accuracy	< MDC	Method Blank	A

[1] Reference number from QAPP Worksheet #21 & #23
[2]Aqueous samples will consist of rinsate blank samples only. Aqueous field duplicate and MS/MSD samples will not be collected.

QAPP Worksheet #13: Secondary Data Criteria and Limitations Table

Any data needed for project implementation or decision making that are obtained from non-direct measurement sources such as computer databases, background information, technologies and methods, environmental indicator data, publications, photographs, topographical maps, literature files and historical data bases will be compared to the DQOs for the project to determine the acceptability of the data. Thus, for example, analytical data from historical surveys will be evaluated to determine whether they satisfy the validation criteria for the project and to determine whether sufficient data was provided to allow an appropriate validation to be done. If not, then a decision to conduct additional sampling for the site may be necessary.

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Org., Data Types, Data Generation/ Collection Dates)	How Data May Be Used (if deemed usable during data assessment stage)	Limitations on Data Use
EPA Investigation Site Inspection Report. DCN#: 2223-2A-BKYP		Weston Solutions, Inc. (SAT Region II)	To determine possible areas of observed contamination.	Screening-level data
EPA Removal Assessments, August 2015	RST 3 Removal Assessment Trip Report, DCN#: RST3-02-D-0253	Weston Solutions, Inc. (RST 3 Region II)	To verify the presence of residual radiological contamination in soil, identify potential releases of radiation-containing materials in soil and fill material, determine additional radiation source areas, and delineate the extent of on-site radiological contamination	Definitive data

QAPP Worksheet #14: Summary of Project Tasks

Sampling Tasks:

RST 3 has been tasked by EPA with collecting up to 50 soil samples from three residential properties, designated as Areas 5, 6, and 7, located adjacent to the Site. The soil sampling locations will be selected by the EPA OSC based on results of the radiological survey conducted at the properties and historical information provided by the property owners. Using non-dedicated hand shovels and pickaxes, test pits will be advanced to depths at all three properties. Using dedicated disposable plastic scoops, soil samples will be collected along the test pit sidewalls every 6 inch interval up 24 inches bgs. In order to prevent cross contamination of sampling intervals, soil samples will be collected in reverse order starting from the deepest interval up to the surface. Prior to sample collection at each interval, the bottom of the plastic scoop will be used to scrape each area of the sidewall being sampled in order to expose fresh soil which will be collected and placed into re-sealable plastic bags, homogenized in the plastic bags, and then placed into glass sample jars. Fresh nitrile gloves were donned between each sampling interval and location.

Analysis Tasks:

Soil samples will be analyzed by an RST 3-procured laboratory for isotopic thorium, isotopic uranium, and other alpha emitting actinides via alpha spectroscopy HASL-300 Method U-02; Ra-226 (21-day ingrowth), Ra-228, and other gamma emitting radioisotopes via gamma spectroscopy EPA Method 901.1 modified. Aqueous rinsate samples will be collected daily to demonstrate proper decontamination of non-dedicated sampling equipment (*i.e.,* hand shovels and pickaxes) and will be analyzed for isotopic thorium and isotopic uranium via HASL-300 Method U-02; Ra-226 via EPA Method 903.1 and Ra-228 via EPA Method 904.0. All samples will be analyzed by an RST 3-procured laboratory.

Data Management Tasks:

Activities under this project will be reported in status and trip reports and other deliverables (e.g., analytical reports, final reports) described herein. Activities will also be summarized in appropriate format for inclusion in monthly and annual reports.

The following deliverables will be provided under this project:

Trip Report: A trip report will be prepared to provide a detailed accounting of what occurred during each sampling mobilization. The trip report will be prepared within two weeks of the last day of each sampling mobilization. Information will be provided on time of major events, dates, and personnel on-site (including affiliations).

Maps/Figures: Maps depicting site layout, contaminant source areas, and sample locations will be included in the trip report, as appropriate.

QAPP Worksheet #14: Summary of Project Tasks (Continued)

Analytical Report: An analytical report will be prepared for samples analyzed under this plan. Information regarding the analytical methods or procedures employed, sample results, QA/QC results, chain-of-custody documentation, laboratory correspondence, and raw data will be provided within this deliverable.

Data Review: A review of the data generated under this plan will be undertaken. The assessment of data acceptability or usability will be provided separately, or as part of the analytical report.

Documentation and Records:

All sample documents will be completed legibly, in ink. Any corrections or revisions will be made by lining through the incorrect entry and by initialing the error.

Field Logbook: The field logbook is essentially a descriptive notebook detailing site activities and observations so that an accurate account of field procedures can be reconstructed in the writer's absence. Field logbook will be bound and paginated. All entries will be dated and signed by the individuals making the entries, and should include (at a minimum) the following

1. Site name and project number
2. Name(s) of personnel on-site
3. Dates and times of all entries (military time preferred)
4. Descriptions of all site activities, site entry and exit times
5. Noteworthy events and discussions
6. Weather conditions
7. Site observations
8. Sample and sample location identification and description*
9. Subcontractor information and names of on-site personnel
10. Date and time of sample collections, along with chain of custody information
11. Record of photographs
12. Site sketches

* The description of the sample location will be noted in such a manner as to allow the reader to reproduce the location in the field at a later date.

Sample Labels: Sample labels will clearly identify the particular sample, and should include the following:

1. Site/project number.
2. Sample identification number.
3. Sample collection date and time.
4. Designation of sample (grab or composite).
5. Sample preservation.
6. Analytical parameters.
7. Name of sampler.

QAPP Worksheet #14: Summary of Project Tasks (Concluded)

Sample labels will be written in indelible ink and securely affixed to the sample container. Tie-on labels can be used if properly secured.

Custody Seals: Custody seals demonstrate that a sample container has not been tampered with or opened. The individual in possession of the sample(s) will sign and date the seal, affixing it in such a manner that the container cannot be opened without breaking the seal. The name of this individual, along with a description of the sample packaging, will be noted in the field logbook.

Assessment/Audit Tasks: No performance audit of field operations is anticipated at this time. If conducted, performance and system audit will be in accordance with the project plan.

Data Review Tasks: All data will be validated by RST 3 subcontracted data validator.

Laboratory analytical results will be assessed by the data reviewer for compliance with required precision, accuracy, completeness, representativeness, and sensitivity.

QAPP Worksheet #15: Reference Limits and Evaluation Table

Analyte	CAS Number	Project Quantitation Limit	Method CRQLs (pCi/g)	Achievable Laboratory (Pace Analytical Services) Limits Target Soil MDCs (pCi/g)	Achievable Laboratory (Pace Analytical Services) Limits Target Aqueous MDCs (pCi/L)
Uranium-233/234	13966-29-5	NS	NS	1.00	1.00
Uranium-235/236	15117-96-1	NS	NS	1.00	1.00
Uranium-238	7440-61-1	NS	NS	1.00	1.00
Thorium-228	14274-82-9	NS	NS	1.00	1.00
Thorium-230	14269-63-7	NS	NS	1.00	1.00
Thorium-232	7440-29-1	NS	NS	1.00	1.00

NS – Not Specified

Analyte	CAS Number	Project Quantitation Limit	Method CRQLs (pCi/L)	Achievable Laboratory (Pace Analytical Services) Limits Target Soil MDCs (pCi/g)	Achievable Laboratory (Pace Analytical Services) Limits Target Aqueous MDCs (pCi/L)
Radium-226 (in-growth)	13982-63-3	NS	NS	1.00	1.00
Radium-228	15262-20-1	NS	NS	1.00	1.00
Radium-226 (Aqueous)	13982-63-3	NS	NS	1.00	1.00
Radium-228 (Aqueous)	15262-20-1	NS	NS	1.00	1.00

NS – Not Specified

QAPP Worksheet #16: Project Schedule/Timeline Table

Activities	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Preparation of QAPP	RST 3 Contractor Site Project Manager	Prior to sampling date	7/5/2016	QAPP	7/6/2016
Review of QAPP	RST 3 Contractor QAO and/or Group Leader	Prior to sampling date	7/6/2016	Approved QAPP	7/6/2016
Preparation of Health and Safety Plan	RST 3 Contractor Site Project Manager	Prior to sampling date	7/6/2016	HASP	7/6/2016
Procurement of Field Equipment	RST 3 Contractor Site Project Manager and/or Equipment Officer	Prior to sampling date	7/6/2016	NA	7/7/2016
Laboratory Request	Not Applicable	Prior to sampling date	6/28/2016	CLP/Non-CLP Request Form	NA
Field Reconnaissance/Access	RST 3 Contractor Site Project Manager; or EPA Region II OSC	7/7/2016	7/7/2016	NA	NA
Collection of Field Samples	RST 3 Contractor Site Project Manager	7/7/2016	7/15/2016	NA	NA
Laboratory Electronic Data Received	RST 3 Contractor and EPA Region 2 DEWSA	7/7/2016	7/7 – 7/15/2016	Preliminary Data	7/29 & 8/5/2016
Laboratory Package Received	RST 3 Contractor and EPA Region 2 DEWSA	7/16/2016	8/5/2016	Validated Data	NA
Validation of Laboratory Results	RST 3 Contractor and EPA Region 2 DEWSA	8/19/2016	9/2/2016	Final Report	9/2/2016
Data Evaluation/ Preparation of Final Report	RST 3 Contractor Site Project Manager	9/2/2016	9/16/2016	Final Report	9/16/2016

NA – Not Applicable

QAPP Worksheet #17: Sampling Design and Rationale

Soil sampling will be performed in accordance with EPA's Environmental Response Team (ERT)/Scientific, Engineering, Response, and Analytical Services (SERAS) contractor's Standard Operating Procedure (SOP) Numbers (Nos.) 2001: *General Field Sampling Guidelines* and 2012: *Soil Sampling* at the three residential properties designated as Areas 5, 6, and 7, located adjacent to the Site. Soil sampling locations will be selected by the EPA OSC based on results of the radiological survey conducted at the properties and historical information provided by the property owners. Using non-dedicated hand shovels and pickaxes, test pits will be advanced to depths at all three properties. Using dedicated disposable plastic scoops soil samples will be collected along the test pit sidewalls at every 6 inch interval up 24 inches bgs. In order to prevent cross contamination of sampling intervals, soil samples will be collected in reverse order starting from the deepest interval up to the surface. Prior to sample collection at each interval, the bottom of the plastic scoop will be used to scrape each area of the sidewall being sampled in order to expose fresh soil which will be collected and placed into re-sealable plastic bags, homogenized in the plastic bags, and then placed into glass sample jars. Fresh nitrile gloves were donned between each sampling interval and location. Decontamination of non-dedicated sampling equipment (*i.e.* hand shovels and pickaxes) will be conducted in accordance with EPA ERT/SERAS contractor's SOP 2006: *Sampling Equipment Decontamination* and will be performed before and after the sampling event and between soil sampling locations, and will consist of a soap (Alconox®) solution scrub and tap water rinse. In order to confine potential surface runoff to areas of contamination, the decontamination fluid will be discarded on-site at the locations indicating the highest levels of contamination based on radiological survey results.

The soil samples will be collected for definitive data QA/QC objectives. Field duplicate and MS/MSD samples will be collected at the rate of one per 20 field samples. All sample information will be transcribed into EPA's SCRIBE database, an environmental data management system, from which sample labels and chain of custody (COC) records will be generated. All the samples will be stored on ice in a cooler and shipped to an RST 3-procured laboratory for analysis. All the soil samples will be analyzed for isotopic thorium, isotopic uranium, and other alpha emitting actinides via alpha spectroscopy HASL-300 Method U-02; Ra-226 (21-day ingrowth), Ra-228, and other gamma emitting radioisotopes via gamma spectroscopy EPA Method 901.1 modified. Aqueous rinsate samples will be collected daily to demonstrate proper decontamination of non-dedicated sampling equipment (*i.e.,* hand shovels and pickaxes) and will be analyzed for isotopic thorium and isotopic uranium via HASL-300 Method U-02; Ra-226 via EPA Method 903.1 and Ra-228 via EPA Method 904.0. All samples will be analyzed by an RST 3-procured laboratory.

The following laboratories will provide the analyses indicated:

Lab Name/Location	Sample Type	Parameters
Pace Analytical Services 1638 Roseytown Road, Suite 2,3,4 Greensburg PA 15601 Attention: Justin Hensley Phone: 724-850-5600 (Non-CLP Laboratory)	Soil	isotopic thorium, isotopic uranium, and other alpha emitting actinides via alpha spectroscopy EML HASL-300 Method U-02; radium-226, radium-226 (in-growth), radium-228, and other gamma emitting radioisotopes will be analyzed via gamma spectroscopy EPA Method 901.1 modified
	Aqueous	isotopic thorium and isotopic uranium via EML HASL-300 Method U-02; radium-226 via EPA Method 903.1 and radium-228 via EPA Method 904.0

Refer to Worksheet #20 for QA/QC samples, sampling methods, and SOPs.

QAPP Worksheet #18: Sampling Locations and Methods/SOP Requirements Table

Matrix	Sampling Location(s)	Units	Analytical Group(s)	Concentration Level	No. of Samples (identify field duplicates)	Sampling SOP Reference	Rationale for Sampling Location
Soil	10	pCi/g	Isotopic Thorium, Isotopic Uranium, and other alpha emitting actinides by HASL-300	Low/Medium	1/20 duplicate sample per matrix	SOP# 2001 2012	To determine contaminants
Soil	10	pCi/g	Radium-226, Radium-228 and other gamma emitting radioisotopes by EPA 901.1 modified	Low/Medium	1/20 duplicate sample per matrix	SOP# 2001 2012	To determine contaminants
Aqueous	3	µg/L	Isotopic Thorium, Isotopic Uranium by HASL-300	Low/Medium	1 per day	SOP# 2006	To demonstrate proper decontamination of non-dedicated sampling equipment
Aqueous	3	µg/L	Radium-226 by EPA 903.1	Low/Medium	1 per day	SOP# 2006	To demonstrate proper decontamination of non-dedicated sampling equipment
Aqueous	3	µg/L	Radium-228 by EPA 904.0	Low/Medium	1 per day	SOP# 2006	To demonstrate proper decontamination of non-dedicated sampling equipment

The website for EPA-ERT SOPs is: http://www.ert.org/mainContent.asp?section=Products&subsection=List

QAPP Worksheet #19: Analytical SOP Requirements Table

Matrix	No. of Samples	Analytical Group	Concentration Level	Analytical / Preparation Method SOP Reference[1]	Containers (number, size, and type)	Sample volume[3] (units)	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation / analysis)
Soil	50	Isotopic Uranium	Low/Medium	HASL-300	1x8oz Glass Jar	150 g	None	None
		Isotopic Thorium	Low/Medium	HASL-300	1x8oz Glass Jar	150 g	None	None
		Gamma spectroscopy	Low/Medium	EPA Method 901.1 modified	1x16oz Glass Jar	350 g	None	None
Aqueous[2]	3	Isotopic Uranium/ Isotopic Thorium	Low/Medium	HASL-300	1,000 mL	1,000 mL	HNO3, Cool to 4 ^{0}C	None
		Radium-226	Low/Medium	EPA 903.1	1L Plastic	1,000 mL	HNO3, Cool to 4 ^{0}C	None
		Radium-228	Low/Medium	EPA 904.0	1L Plastic	1,000 mL	HNO3, Cool to 4 ^{0}C	None

[1] Refer to the Analytical SOP References table (Worksheet #23).

[2] Only required if non-dedicated sampling equipment to be used.

[3] The minimum sample size is based on analysis allowing for sufficient sample for reanalysis. Additional volume is needed for the laboratory Matrix Spike/Matrix Spike Duplicate sample analysis.

[1] Only required if non-dedicated sampling equipment to be used.

QAPP Worksheet #20: Field Quality Control Sample Summary Table

Matrix	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference	No. of Sampling Locations	No. of Field Duplicate Pairs	No. of Extra Volume Laboratory QC (e.g., MS/MSD) Samples[1]	No. of Rinsate Blanks[1]	No. of Trip. Blanks	No. of PE Samples
Soil/Aqueous	Isotopic Uranium	Low/Medium	HASL-300	10	1 per 20 samples	1 per 20 samples	3	NR	NR
	Isotopic Thorium	Low/Medium	HASL-300	10	1 per 20 samples	1 per 20 samples	3	NR	NR
	Gamma spectroscopy	Low/Medium	EPA Method 901.1 modified	10	1 per 20 samples	1 per 20 samples	3	NR	NR
Aqueous	Isotopic Uranium	Low/Medium	HASL-300	NR	NR	NR	1	NR	NR
	Isotopic Thorium	Low/Medium	HASL-300	NR	NR	NR	1	NR	NR
	Radium-226	Low/Medium	EPA 903.1	NR	NR	NR	1	NR	NR
	Radium-228	Low/Medium	EPA 904.0	NR	NR	NR	1	NR	NR

NR – Not Required
[1] Only required if non-dedicated sampling equipment to be used

QAPP Worksheet #21: Project Sampling SOP References Table

Reference Number	Title, Revision Date and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
SOP#: 2001	General Field Sampling Guidelines (all media); Rev. 0.1, June 7, 2013	EPA/SERAS	Site Specific	N	--
SOP#: 2006	Sample Equipment Decontamination; Rev. 0.1, December 28, 2015	EPA/SERAS	Site Specific	N	--
SOP#: 2012	Soil Sampling; Rev. 0.1, July 11, 2001	EPA/SERAS	plastic scoops, aluminum trays, and appropriate sample jars	N	--

See attachment B for SOP # 2001, 2006, 2012
https://www.epaosc.org/site/doc_list.aspx?site_id=2107&category=Field%20Activities

QAPP Worksheet #22: Field Equipment Calibration, Maintenance, Testing, and Inspection Table

*Field Equipment
Trimble® GeoXT™ handheld, Ludlum-2241, Fluke Pressurized Ionization Chamber (PIC) Model 451P, Reuter-Stokes RSS-131ER High Pressure Ion Chamber (HPIC) gamma survey meters, and BNC SAM940 radioisotope identification system.

* All on-site field equipment will be provided and operated by the EPA.

QAPP Worksheet #23: Analytical SOP References Table

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
PGH-R-008-10	Analysis of Samples for Alpha Emitting Actinides and Plutonium-241, Methods: ASTM Method D-3972-90 and HASL 300 Method U-02, 7/27/15	Definitive	Soil/Aqueous, Isotopic Uranium	Alpha Spectrometer	Pace Analytical Services	N
		Definitive	Soil/Aqueous, Isotopic Thorium	Alpha Spectrometer	Pace Analytical Services	N
		Definitive	Soil, Alpha emitting actinides	Alpha Spectrometer	Pace Analytical Services	N
PGH-R-023-9	Gamma Spectroscopy Instrument Operations, Method: EPA 901.1, 12/3/15	Definitive	Soil, Ra-226, Ra-228, and other gamma emitting radioisotopes	Gas Flow Proportional Counter	Pace Analytical Services	N
PGH-R-007-16	Analysis of Water Samples for Radium-226, Methods: EPA 903.1, SM7500-Ra C, 12/14/15	Definitive	Aqueous, Radium-226	Alpha Scintillation Systems	Pace Analytical Services	N
PGH-R-003-17	Analysis of Water Samples for Ra-228, Methods: EPA 904.0 and 9320/SM7500-RaD (Ra-228), 12/17/15	Definitive	Aqueous Radium-228	Gas Flow Proportional Counter	Pace Analytical Services	N

Refer to Attachment C for Pace Analytical Services Laboratory SOPs: HASL 300, EPA 901.1, EPA 903.1, and EPA 904.0

QAPP Worksheet #24: Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action	Person Responsible for CA	SOP Reference[1]
Alpha Spectrometer	Micro-precipitated sources prepared using Cm-244, Th-230, and Pu-239. Filtrate analyzed to ensure greater than 99% recovery of analytes. Sources counted to acquire 10,000 net counts per isotope. Average of efficiencies used as system efficiency. Peak positions used for energy calibration.	Initially upon detector setup. Re-calibrated if detector is changed. Cal verifications performed annually using original sources.	Following calibration, second sources are analyzed to ensure source activities are within 10% of known. Annual cal verifications must be within 10% of original source efficiencies.	Recalibrate system until requirements are satisfied. Re-calibrate if cal verification does not meet requirements.	Laboratory Supervisor.	Pace SOP PGH-R-008
Alpha Scintillation Systems	Calibrations are made on each Lucas Cell/Detector System combination utilized. Bubblers containing Ra-226 are flushed to remove Rn-222 gas then sealed to allow re-ingrowth of radon. Following ingrowth, radon is flushed from bubblers into Lucas Cells. Cells are stored to allow buildup of alpha-emitting radon daughters then sources are analyzed to acquire 10,000 net counts on a Radon Flask Reader scintillation system.	Initially upon detector setup. Re-calibrated if detector is changed. Cal verifications performed annually using original sources.	New calibration efficiency values must be between 2.20 and 2.50 cpm/dpm. Re-calibrations are compared against previous calibrations and must be within 10% of the previous calibration values. Annual cal verifications must be within 10% of original source efficiencies.	Recalibrate system until requirements are satisfied. Re-calibrate if cal verification does not meet requirements.	Laboratory Supervisor.	Pace SOP PGH-R-007.
Gas Flow Proportional Counter	For Ra-228 analysis, Sr-89 is used for instrument calibration. Calibration sources are prepared using Sr-89 with added elemental strontium precipitated as a carbonate. Each of four prepared sources are counted on each GFPC unit to obtain 10,000 net counts per source. The average efficiency of the four sources is used for the system efficiency.	Initially upon detector setup. Re-calibrated if detector is changed. Cal verifications performed annually using newly prepared sources.	The four calibration sources must have a calculated relative standard deviation of 5% or less. Annual cal verification is made using new Sr-89 sources. Two cal ver sources are used per detector. The average recovery of the two CV sources must be within 10% of known.	Recalibrate system until requirements are satisfied. Re-calibrate if cal verification does not meet requirements.	Department Supervisor	Pace SOP PGH-R-003

QAPP Worksheet #25: Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table (Concluded)

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Alpha Spectrometer	Clean planchette holders	Physical check	Physical check	Monthly	Acceptable background and calibration efficiencies	• Recalibrate • Instrument maintenance • Consult with Technical Director	Pace Analytical Services	Pace SOP PGH-R-008
Alpha Scintillation Systems	Clean instrument	Physical check	Physical check	Monthly	Acceptable background and calibration efficiencies	• Recalibrate • Instrument maintenance • Consult with Technical Director	Pace Analytical Services	Pace SOP PGH-R-007.
Gas Flow Proportional Counter	1. Clean instrument 2. Inspect windows 3. QA check	1. Physical check 2. Background and source count	1. Physical check 2. Check deviation	1. Daily 2. High counts and/or background 3. Daily	1. None applicable 2. No physical defects 3. Within 3 sigma of 20 day population	• Recalibrate • Instrument maintenance • Consult with Technical Director	Pace Analytical Services	Pace SOP PGH-R-003

[1] Specify the appropriate letter or number form the Analytical SOP References table (Worksheet #23)

QAPP Worksheet #26: Sample Handling System

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): RST 3 Site Project Manager, Weston Solutions, Inc., Region II
Sample Packaging (Personnel/Organization): RST 3 Site Project Manager and sampling team members, Weston Solutions, Inc., Region II
Coordination of Shipment (Personnel/Organization): RST 3 Site Project Manager, sampling team members, Weston Solutions, Inc., Region II
Type of Shipment/Carrier: FedEx
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Sample Custodian, RST 3-Procured Non-RAS Laboratory
Sample Custody and Storage (Personnel/Organization): Sample Custodian, RST 3-Procured Non-RAS Laboratory
Sample Preparation (Personnel/Organization): Sample Custodian, RST 3-Procured Non-RAS Laboratory
Sample Determinative Analysis (Personnel/Organization): Sample Custodian, RST 3-Procured Non-RAS Laboratory
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): Samples to be shipped same day of collection, and arrive at laboratory within 24 hours (1 day) of sample shipment
Sample Extract/Digestate Storage (No. of days from extraction/digestion): As per analytical methodology; see Worksheet #19
SAMPLE DISPOSAL
Personnel/Organization: Sample Custodian, RST 3-Procured Non-RAS Laboratory
Number of Days from Analysis: Until analysis and QA/QC checks are completed; as per analytical methodology; see Worksheet #19.

QAPP Worksheet #27: Sample Custody Requirements

Sample Identification Procedures Each sample collected by Region II RST 3 will be identified by a property number (N002), a sample location number (001), the matrix identifier of the sample collected (SS for soil sample), specifically for soil samples, the depth interval from where the sample was collected will be identified as a range (0612), and the sample number (01). The last number will represent the sample number collected from each location. Duplicate samples will be identified in the same manner but will be the next sequential sample number (in most cases 02).

e.g. P002-SS001-0612-01: whereas, P002 = Property Number 002, SS001 = Soil Sample Location 001, 0612 = Soil sample collected at 6 to 12 feet, 01 = Sample Number 01

Location of the sample collected will be recorded in the project database and site logbook. A duplicate sample will be identified in the same manner as other samples and will be distinguished and documented in the field logbook. Each sample will also be labeled with a non-CLP assigned number. Depending on the type of sample, additional information such as sampling round, date, etc. will be added.

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory): Each sample will be individually identified and labeled after collection, then sealed with custody seals and enclosed in a plastic cooler. The sample information will be recorded on chain-of custody (COC) forms, and the samples shipped to the appropriate laboratory via overnight delivery service or courier. Chain-of-custody records must be prepared in Scribe to accompany samples from the time of collection and throughout the shipping process. Each individual in possession of the samples must sign and date the sample COC Record. The chain-of-custody record will be considered completed upon receipt at the laboratory. A traffic report and chain-of-custody record will be maintained from the time the sample is taken to its final deposition. Every transfer of custody must be noted and signed for, and a copy of this record kept by each individual who has signed. When samples are not under direct control of the individual responsible for them, they must be stored in a locked container sealed with a custody seal. Specific information regarding custody of the samples projected to be collected on the weekend will be noted in the field logbook. The chain-of-custody record should include (at minimum) the following: 1) Sample identification number; 2) Sample information; 3) Sample location; 4) Sample date; 5) Sample Time; 6) Sample Type Matrix; 7) Sample Container Type; 8) Sample Analysis Requested; 9) Name(s) and signature(s) of sampler(s); and 10) Signature(s) of any individual(s) with custody of samples.

A separate chain-of-custody form must accompany each cooler for each daily shipment. The chain-of-custody form must address all samples in that cooler, but not address samples in any other cooler. This practice maintains the chain-of-custody for all samples in case of mis-shipment.

QAPP Worksheet #27: Sample Custody Requirements (Concluded)

Laboratory Sample Custody Procedures (receipt of sa mples, archiving, and disposal): A sample custodian at the laboratory will accept custody of the shipped samples, and check th em for discrepancies, proper preservation, integrit y, etc. If noted, issues will be forwarded to the laboratory manager for corrective action. The sample custodian will relinquish custo dy to the appropriate department for analysis. At this time, no samples will be arc hived at the laboratory. Disposal of the samples wi ll occur only after analyses and QA/QC checks are completed.

QAPP Worksheet #28A: QC Samples Table
Gamma Spectroscopy

Matrix	Soil/Aqueous[1]
Analytical Group	Isotopic Uranium
Concentration Level	Low/Medium
Sampling SOP	2012
Analytical Method/ SOP Reference	Pace SOP PGH-R-023
Sampler's Name	Peter Lisichenko
Field Sampling Organization	Weston Solutions, Inc. , RST 3
Analytical Organization	Pace Analytical Services
No. of Sample Locations	10

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per batch of up to 20 samples	Reported analytes must be less than the Reporting Limit (RL)	Assess MB analyte concentration against project sample analyte concentration. Report sample results if sample analyte level is greater than ten times the MB analyte concentration. Otherwise, re-analyze all samples and associated QC samples.	Laboratory analyst	B	Z-blank. The calculated analyte concentration divided by the one-sigma uncertainty value must be less than 3.0.
Laboratory Control Sample	One per batch of up to 20 samples	Each analyte assessed must be within 25% of known.	If the LCS is assessed at levels outside of the acceptance criteria, re-analyze the affected samples and all associated QC samples.	Laboratory analyst	NA	Target analytes must be within 25% of known.
Duplicate sample	One per batch of up to 20 samples	Analytes between sample and duplicate must have a calculated Z-dup value between -3 and +3.	Re-analyze new aliquots of the sample and duplicate to determine if sample homogeneity was the cause. If sample is exhausted, report results with narration.	Laboratory analyst	NA	The absolute value of the sample analyte result minus the duplicate analyte result divided by the square root of the sum of the squares of the sample and duplicate one-sigma analyte uncertainties must be less than 3.0

[1] Aqueous samples will consist of rinsate blank samples only. Aqueous field duplicate and MS/MSD samples will not be collected.

QAPP Worksheet #28B: QC Samples Table
Alpha Spectroscopy

Matrix	Soil/Aqueous[1]
Analytical Group	Alpha Spectroscopy
Concentration Level	Low/Medium
Sampling SOP	2012
Analytical Method/ SOP Reference	Pace SOP PGH-R-008-09
Sampler's Name	Peter Lisichenko
Field Sampling Organization	Weston Solutions, Inc. , RST 3
Analytical Organization	Pace Analytical Services
No. of Sample Locations	10

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per preparatory batch per 20 samples	< MDC	Assess MB analyte concentration against project sample analyte concentration. Report sample results if sample analyte level is greater than ten times the MB analyte concentration. Otherwise, re-analyze all samples and associated QC samples.	Laboratory analyst	B	< MDC
Laboratory control sample	1 per preparatory batch per 20 samples	< 25%	If the LCS is assessed at levels outside of the acceptance criteria, re-analyze the affected samples and all associated QC samples.	Laboratory analyst	NA	< 25%
Matrix spike	1 per preparatory batch per 20 samples	+/- 25%	Reanalyze sample	Laboratory analyst	NA	+/- 25%
Duplicate analysis	1 per preparatory batch per 20 samples	% RPD < 25%	If failed, the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.	Laboratory analyst	NA	% RPD < 25%

[1] Aqueous samples will consist of rinsate blank samples only. Aqueous field duplicate and MS/MSD samples will not be collected.

QQAPP Worksheet #29: Project Documents and Records Table

Sample Collection Documents and Records	Analysis Documents and Records	Data Assessment Documents and Records	Data Assessment Documents and Records	Other
Field Notes Digital Photographs Chain-of-Custody (COC) Records Air Bills Copies of Pertinent e-mails. Field Instrument Records	Record of Field Instrument. Measurements and Radiological Readings. Radiological Dosimetry Records. Corrective Action Reports. Radiological Instrument Calibration Readings.	Copies of all Analytical Data Deliverables; hard copies of raw data are archived; The raw data files from the laboratory include Analytical Instrument Calibration Records, COC Records, and Sample Preparation and Analysis Files, Sample Receipt Records	Copies of all Analytical Data Deliverables; hard copies of raw data are archived; The raw data files from the laboratory include Analytical Instrument Calibration Records, COC Records, and Sample Preparation and Analysis Files, Sample Receipt Records	Staff Health and Safety Records; CLP Request Form and RST 3 Analytical Request Form

QAPP Worksheet #30: Analytical Services Table

Matrix	Analytical Group	Concentration Level	Analytical SOP	Data Package Turnaround Time	Laboratory/Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/Organization (Name and Address, Contact Person and Telephone Number)
Soil/Aqueous	Radiochemistry	Low/Medium	See Worksheet #23	28 Days	Pace Analytical Services 1638 Roseytown Road, Suite 2,3,4 Greensburg PA 15601 Attention: Justin Hensley Phone: 724-850-5600 (Non-CLP Laboratory)	NA

NA – Not Applicable

QAPP Worksheet #31: Planned Project Assessments Table

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organizational Affiliation)	Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of Corrective Actions (Title and Organizational Affiliation)
Laboratory Technical Systems/ Performance Audits	Every year	External	Regulatory Agency	Regulatory Agency	RST 3-Procured Laboratory	RST 3-Procured Laboratory	EPA, State, NRC, or other Regulatory Agency
Performance Evaluation Samples	Every year	External	Regulatory Agency	Regulatory Agency	RST 3-Procured Laboratory	RST 3-Procured Laboratory	EPA, State, NRC, or other Regulatory Agency
Proficiency Testing	Semiannually	External	NELAC	PT provider	Lab Personnel	Lab Personnel	Lab QA Officer
NELAC	Every two years	External	NELAC	NELAC Representative	Lab QA Officer	Lab Personnel	NELAC Representative
Internal Audit	Annually	Internally	Pace Analytical Services	Lab QA Officer	Lab Personnel	Lab Personnel	Lab QA Officer

NRC: Nuclear Regulator Commission

QAPP Worksheet #32: Assessment Findings and Corrective Action Responses

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (Name, Title, Org.)	Timeframe for Response
Project Readiness Review	Checklist or logbook entry	RST 3 Site Project Manager, Weston Solutions, Inc.	Immediately to within 24 hours of review	Checklist or logbook entry	RST 3 Site Project Leader	Immediately to within 24 hours of review
Field Observations/ Deviations from Work Plan	Logbook	RST 3 Site Project Manager, Weston Solutions, Inc. and EPA OSC	Immediately to within 24 hours of deviation	Logbook	RST 3 Site Project Manager and EPA OSC	Immediately to within 24 hours of deviation
Laboratory Technical Systems/ Performance Audits	Written Report	RST 3-Procured Laboratory	30 days	Letter	RST 3-Procured Laboratory	14 days
On-Site Field Inspection	Written Report	QAO/HSO Weston Solutions, Inc.	7 calendar days after completion of the audit	Letter/Internal Memorandum	Weston's regional QAO and/or EPA OSC	To be identified in the cover letter of the report

QAPP Worksheet #33: QA Management Reports Table

Type of Report	Frequency (Daily, weekly, monthly, quarterly, annually, etc.)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (Title and Organizational Affiliation)	Report Recipient(s) (Title and Organizational Affiliation)
RST 3-Procured Laboratory Data (preliminary)	As performed	Two weeks from the sampling date	RST 3-Procured Laboratory	RST 3 Subcontracted Data Validator and RST 3 Site Project Manager
RST 3-Procured Laboratory Data (validated)	As performed	Up to 14 days after receipt of preliminary data	RST 3 Subcontracted Data Validator	RST 3 Site Project Manager and OSC, EPA Region II
On-Site Field Inspection	As performed	7 calendar days after completion of the inspection	RST 3 Site Safety Officer	RST 3 Site Project Manager
Field Change Request	As required per field change	Three days after identification of need for field change	RST 3 Site Project Manager	EPA, Region II OSC
Final Report	As performed	2 weeks after receipt of EPA approval of data package	RST 3 Site Project Manager	EPA, Region II OSC

QAPP Worksheet #34: Verification (Step I) Process Table

Verification Input	Description	Internal/ External	Responsible for Verification (Name, Organization)
Site/field logbooks	Field notes will be prepared daily by the RST 3 Site Project Manager and will be complete, appropriate, legible and pertinent. Upon completion of field work, logbooks will be placed in the project files.	I	RST 3 Site Project Manager
Chains of custody	COC forms will be reviewed against the samples packed in the specific cooler prior to shipment. The reviewer will initial the form. An original COC will be sent with the samples to the laboratory, while copies are retained for (1) the Sampling Trip Report and (2) the project files.	I	RST 3 Site Project Manager
Sampling Trip Reports	STRs will be prepared for each week of field sampling [for which samples are sent to an EPA CLP RAS laboratory]. Information in the STR will be reviewed against the COC forms, and potential discrepancies will be discussed with field personnel to verify locations, dates, etc.	I	RST 3 Site Project Manager
Laboratory analytical data package	Data packages will be reviewed/verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal.	E	RST 3-Procured Laboratories
Laboratory analytical data package	Data packages will be reviewed as to content and sample information upon receipt by EPA.	I	RST 3 Site Project Manager
Final Sample Report	The project data results will be compiled in a sample report for the project. Entries will be reviewed/verified against hardcopy information.	I	RST 3 Site Project Manager

QAPP Worksheet #35: Validation (Steps IIa and IIb) Process Table

Step IIa/IIb	Validation Input	Description	Responsible for Validation (Name, Organization)
IIa	SOPs	Ensure that the sampling methods/procedures outlined in QAPP were followed, and that any deviations were noted/approved.	RST 3 Site Project Manager
IIb	SOPs	Determine potential impacts from noted/approved deviations, in regard to PQOs.	RST 3 Site Project Manager
IIa	Chains of custody	Examine COC forms against QAPP and laboratory contract requirements (e.g., analytical methods, sample identification, etc.).	RST 3- procured laboratory - RST 3 data validator
IIa	Laboratory data package	Examine packages against QAPP and laboratory contract requirements, and against COC forms (e.g., holding times, sample handling, analytical methods, sample identification, data qualifiers, QC samples, etc.).	RST 3- procured laboratory - RST 3 data validator
IIb	Laboratory data package	Determine potential impacts from noted/approved deviations, in regard to PQOs. Examples include PQLs and QC sample limits (precision/accuracy).	RST 3- procured laboratory - RST 3 data validator
IIb	Field duplicates	Compare results of field duplicate (or replicate) analyses with RPD criteria	RST 3- procured laboratory - RST 3 data validator

QAPP Worksheet #36
Validation (Steps IIa and IIb) Summary Table

Step IIa/IIb	Matrix	Analytical Group	Validation Criteria	Data Validator (title and organizational affiliation)
IIa / IIb	Soil	Radiological Parameters	Refer to methods listed in worksheet # 19 & 20, and Laboratory SOPs in Attachment C	RST 3 Subcontracted Data Validation Personnel

QAPP Worksheet #37: Usability Assessment

Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used: Data, whether generated in the field or by the laboratory, are tabulated and reviewed for Precision, Accuracy, Representativeness, Completeness, and Comparability (PARCCS) by the SPM for field data or the data validator for laboratory data. The review of the PARCC Data Quality Indicators (DQI) will compare with the DQO detailed in the site-specific QAPP, the analytical methods used and impact of any qualitative and quantitative trends will be examined to determine if bias exists. A hard copy of field data is maintained in a designated field or site logbook. Laboratory data packages are validated, and final data reports are generated. All documents and logbooks are assigned unique and specific control numbers to allow tracking and management.

Questions about Non-CLP data, as observed during the data review process, are resolved by contacting the respective site personnel and laboratories as appropriate for resolution. All communications are documented in the data validation record with comments as to the resolution to the observed deficiencies.

Where applicable, the following documents will be followed to evaluate data for fitness in decision making: EPA QA/G-4, *Guidance on Systematic Planning using the Data Quality Objectives Process,* EPA/240/B-06/001, February 2006, and EPA QA/G-9R, *Guidance for Data Quality Assessment,* A reviewer's Guide EPA/240/B-06/002, February 2006.

Describe the evaluative procedures used to assess overall measurement error associated with the project:
As delineated in the ***Uniform Federal Policy for Implementing Environmental Quality Systems: Evaluating, Assessing and Documenting Environmental Data Collection and Use Programs Part 1: UFP-QAPP (EPA-505-B-04-900A, March 2005); Part 2A: UFP-QAPP Workbook (EPA-505-B-04-900C, March 2005); Part 2B: Quality Assurance/Quality Control Compendium: Non-Time Critical QA/QC Activities (EPA-505-B-04-900B, March 2005);*** "Graded Approach" will be implemented for data collection activities that are either exploratory or where specific decisions cannot be identified, since this guidance indicates that the formal DQO process is not necessary.

The data will be evaluated to determine whether they satisfy the PQO for the project. The validation process determines if the data satisfy the QA criteria. After the data pass the data validation process, comparison results with the PQO is done.

QAPP Worksheet #37: Usability Assessment (Concluded)

EPA will use the field measurements from the radiological survey to determine areas with elevated gamma readings in order to identify soil sampling locations. The results from the soil sampling event will be utilized by EPA to verify the presence of residual contamination and potential releases of radiation-containing material in soil associated with the Site and to ascertain the horizontal extent of on-site and potential offsite contamination.

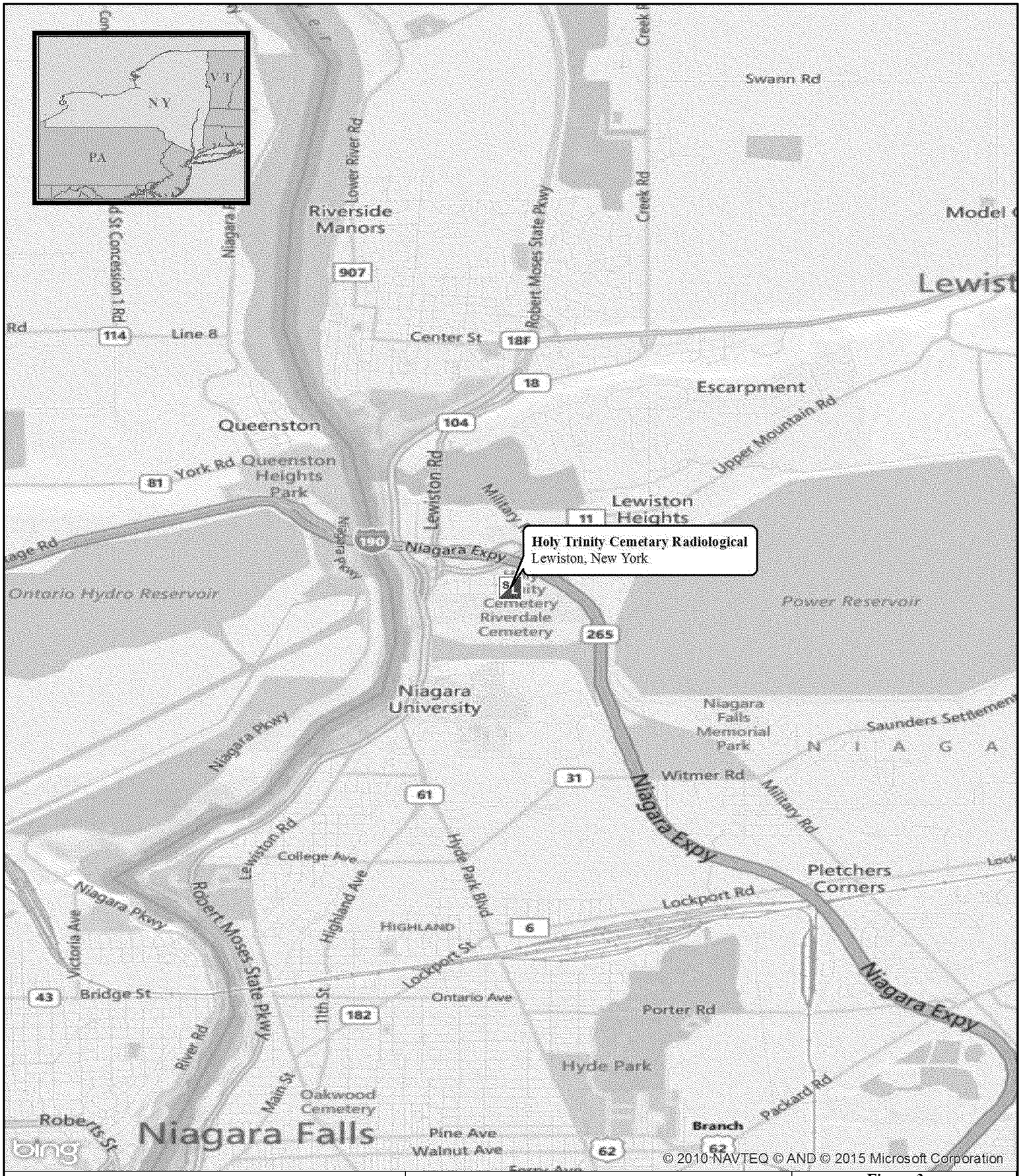
Identify the personnel responsible for performing the usability assessment: Site Project Manager, Data Validation Personnel, and EPA, Region II OSC

Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations), and anomalies:

A copy of the most current approved QAPP, including any graphs, maps and text reports developed will be provided to all personnel identified on the distribution list.

ATTACHMENT A

Figure 1: Site Location Map
Figure 2: Areas of Concern Map



Legend

Site Location

0 0.3 0.6 1.2 1.8 2.4 Miles

Weston Solutions, Inc.
East Division

In Association With
Scientific and Environmental Associates, Inc.,
Environmental Compliance Consultants, Inc.,
Avatar Environmental, LLC, On-Site Environmental,
Inc.and Sovereign Consulting, Inc

Figure 3:
Site Location Map

Holy Trinity Cemetery Radiological
Lewiston, New York

U.S. ENVIRONMENTAL PROTECTION AGENCY
REMOVAL SUPPORT TEAM 3
CONTRACT # EP-S2-14-01

DATE MODIFIED: 7/30/2015

GIS ANALYST:	T. Benton
EPA OSC:	E. Daly
RST SPM:	B. Nwosu
FILENAME:	140730_HT_SITELOCATIONMAP.MXD

C:\TEMP\00060064\MXD\140730_HT_SITELOCATIONMAP.MXD

115.00-1-18

Irving Dr

115.15-1-20
5374 Robert St

Area 5

115.15-1-19
556 Irving Dr

Area 1

115.15-1-18
552 Irving Dr

115.15-1-17
548 Irving Dr

Area 6

115.15-1-21
5380 Robert St

115.00-1-7
5401 Robert St

Area 7

Roberts Ave

115.15-1-22
5382 Robert St

115.15-1-47
547 Colt Ave

115.15-1-50
557 Colt Ave

115.15-1-23
561 Colt Ave

Colt Ave

Source: Esri, DigitalGlobe, GeoEye, i-cubed, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Legend

Designated Area

Parcel Boundary

0 37.5 75 150 225 300 Feet

Weston Solutions, Inc.

In association with
Scientific and Environmental Associates, Inc.,
Avatar Environmental, LLC, Environmental Compliance Consultants,
On-Site Environmental, Inc., and Sovereign Consulting, Inc.

Figure 2:
Areas of Concern Map

HOLY TRINITY CEMETERY
LEWISTON, NEW YORK

U.S. ENVIRONMENTAL PROTECTION AGENCY
REMOVAL SUPPORT TEAM 3
CONTRACT # EP-S2-14-01

DATE MODIFIED: 3/24/2017

GIS ANALYST:	T. BENTON
EPA OSC:	E. DALY
RST SPM:	B. NWOSU
FILENAME:	160929_HT_RobertsStreetArea.mxd

ATTACHMENT B

Sampling SOPs

EPA ERT/SERAS SOP # 2001, 2006, 2012,

GENERAL FIELD SAMPLING GUIDELINES

CONTENTS

1.0 OBJECTIVE

2.0 APPLICABILITY

3.0 DESCRIPTION

- 3.1 Planning Stage
- 3.2 Sampling Design
  - 3.2.1 Judgmental Sampling
  - 3.2.2 Systematic Sampling
  - 3.2.3 Simple and Stratified Random Sampling
- 3.3 Sampling Techniques
  - 3.3.1 Sample Collection Techniques
  - 3.3.2 Homogenization
  - 3.3.3 Filtration
- 3.4 Quality Assurance/Quality Control (QA/QC) Samples
- 3.5 Sample Containers, Preservation, Storage and Holding Times
- 3.6 Documentation

4.0 RESPONSIBILITIES

- 4.1 SERAS Task Leaders
- 4.2 SERAS Field Personnel
- 4.3 SERAS Program Manager
- 4.4 SERAS QA/QC Officer
- 4.5 SERAS Health and Safety Officer

Complete Rewrite: SOP #2001; Revision 1.0; 03/15/13; U.S. EPA Contract EP-W-09-031

SUPERCEDES: SOP #2001; Revision 0.0; 08/11/94; U.S. EPA Contract 68-C4-0022

1.0 OBJECTIVE

The objective of this standard operating procedure (SOP) is to describe the general field sampling techniques and guidelines that will assist the Scientific Engineering Response and Analytical Services (SERAS) personnel in planning, choosing sampling strategies and sampling locations, and frequency of Quality Control (QC) samples for proper assessment of site characteristics. The ultimate goal is to ensure data quality during field collection activities.

2.0 APPLICABILITY

This SOP applies to the collection of aqueous and non-aqueous samples for subsequent laboratory analysis to determine the presence, type, and extent of contamination at a site.

3.0 DESCRIPTION

Representative sampling ensures that a sample or a group of samples accurately reflect the concentration of the contaminant at a given time and location. Depending on the contaminant of concern and matrix, several variables may affect the representativeness of the samples and subsequent measurements. Environmental variability due to non-uniform distribution of the pollutant due to topographic, meteorological and hydrogeological factors, changes in species, and dispersion of contaminants and flow rates contribute to uncertainties in sampling design.

Determining the sampling approach depends on what is known about the site from prior sampling (if any) and the site history, variation of the contaminant concentrations throughout a site, potential migration pathways, and human and environmental receptors. The objectives of an investigation determine the appropriate sampling design.

The frequency of sampling and the specific sample locations that are required must be defined in the site-specific Quality Assurance Project Plan (QAPP).

3.1 Planning Stage

The objectives of an investigation are established and documented in the site-specific QAPP. The technical approach including the media/matrix to be sampled, sampling equipment to be used, sampling design and rationale, and SOPs or descriptions of the procedure to be implemented are included in the QAPP. Refer to the matrix-specific SOPs for sampling techniques which include the equipment required for sampling.

During the planning stage, the data quality objectives (DQOs) will be determined. In turn, the project's DQOs will determine the need for screening data or definitive data. Screening data supports an intermediate or preliminary decision but eventually is supported by definitive data before the project is complete (i.e., placement of monitor wells, estimation of extent of contamination). Definitive data is suitable for final decision making, has defined precision and accuracy requirements and is legally defensible (i.e., risk assessments, site closures).

3.2. Sampling Design

Representative sampling approaches include judgmental, random, systematic grid, systematic simple random, stratified random and transect sampling. Sampling designs may be applied to soil,

sediment and water; however, the random and systematic random approaches are not practical for sampling water systems, especially flowing water systems.

3.2.1 Judgmental Sampling

Judgmental sampling is the subjective selection of sampling locations based on the professional judgment of the field team. This method is useful to locate and to identify potential sources of contamination. It may not be representative of the full site and is used to document worst case scenarios. For example, groundwater sampling points are typically chosen based on professional judgment, whether permanently installed wells or temporary well points.

3.2.2 Systematic Sampling

Systematic grid sampling involves the collection of samples at fixed intervals when the contamination is assumed to be randomly distributed. A random point is chosen as the origin for the placement of the grid. A grid is constructed over a site and samples are collected from the nodes (where the grid lines intersect). Depending on the number of samples that are required to be collected, the distance between the sampling locations can be adjusted. The representativeness of the sampling may be improved by shortening the distance between sample locations.

Systematic random sampling is used for estimating contaminant concentrations within grid cells. Instead of sampling at each node, a random location is chosen within each grid cell. The systematic grid and random sampling approaches are useful for delineating the extent of contamination, documenting the attainment of clean-up goals, and evaluating and determining treatment and disposal options.

Transect sampling involves one or more transect lines established across the site. Samples are collected at systematic intervals along the transect lines. The number of samples to be collected and the length of the transect line determines the spacing between the sampling points. This type of sampling design is useful for delineating the extent of contamination at a particular site, for documenting the attainment of clean-up goals, and for evaluating and determining treatment and disposal options.

3.2.3 Simple and Stratified Random Sampling

Statistical random sampling includes simple, stratified and systematic sampling. Simple random sampling is appropriate for estimating means and total concentrations, if the site or population does not contain a major trend or pattern of contamination. A statistician will generate the sampling locations based on sound statistical methods. Stratified random sampling is a useful tool for estimating average contaminant concentrations and total amounts of contaminants within specified strata and across the entire site. It is useful when a heterogeneous population or area can be broken down into regions with less variability within the boundaries of a stratum then between the strata. Additionally, strata can be defined based on the decisions that will be made. This type of sampling design uses historical information, known ecological and human receptors, soil type, fate and transport mechanism and other ecological factors to divide the sampling area into smaller regions or strata. Sampling locations are selected from each stratum using random sampling.

The simple random sampling approach is applied when there are many sample locations and the concentrations are assumed to be homogeneous across a site with respect to the parameter(s) that are going to be analyzed or monitored for. The stratified random sampling approach is useful for sampling drums, evaluating and determining treatment and disposal options, and locating and identifying sources of contamination.

3.3 Sampling Techniques

Sampling is the selection of a representative portion of a larger population or body. The primary objective of all sampling activities is to characterize a site accurately in a way that the impact on human health and the environment can be evaluated appropriately.

3.3.1 Sample Collection Techniques

Sample collection techniques may be either grab or composite. A grab sample is a discrete aliquot representative of a specific location at a given time and collected all at once from one location. The representativeness of such samples is defined by the nature of the materials that are sampled. Samples collected for volatile organic compounds (VOCs) are always grab samples and are never homogenized. Composite samples are non-discrete samples composed of more than one specific aliquot collected at selected sampling locations. Composite samples must be homogenized by mixing prior to putting the sample into containers. Composite samples can, in certain instances, be used as an alternative to analyzing a number of individual grab samples and calculating an average value. Incremental sampling conducted over a grid is a special case of composite sampling and is detailed in SOP #2019, *Incremental Soil Sampling.* Choice of collecting discrete or composite samples is based on project's DQOs.

3.3.2 Homogenization

Mixing of soil and sediment samples is critical to obtain a representative sample. An adequate volume/weight of sample is collected and placed in a stainless steel or Teflon® container, and is thoroughly mixed using a spatula or spoon made of an inert material. Once the sample is thoroughly mixed the sample is placed into sample containers specific for an analysis. Avoid the use of equipment made of plastic or polyvinyl chloride (PVC) when sampling for organic compounds when the reporting limit (RL) is in the parts per billion (ppb) or parts per trillion (ppt) ranges. Refer to SERAS SOP #2012, *Soil Sampling*, for more details on homogenization.

3.3.3 Filtration

In-line filters are used specifically for collecting groundwater samples for dissolved metals analysis and for filtering large volumes of turbid groundwater. Groundwater samples collected for VOCs are typically not filtered due to potential VOC losses. Filtering groundwater is performed to remove silt particulates from samples to prevent interference with the laboratory analysis. The filters used in groundwater sampling are either cartridge type filters inserted into a reusable housing, or are self-contained and disposable. Filter chambers are usually made of polypropylene housing an inert filtering material that removes particles larger than 0.45 micrometers (μm). Refer to SERAS SOP

#2007, *Groundwater Well Sampling* and SERAS SOP #2013, *Surface Water Sampling*, for more details on filtration techniques.

3.4 Quality Assurance /Quality Control Samples

QA/QC samples provide an evaluation of both the laboratory's and the field sampling team's performance. Including QA/QC samples in a sampling design allows for identifying and measuring sources of error potentially introduced from the time of sample container preparation through analysis. The most common QA/QC samples collected in the field are collocated field duplicates, field replicates, equipment blanks, field blanks and trip blanks. Extra volume/mass is collected for a matrix spike/matrix spike duplicate (MS/MSD) at a frequency of 5% (one in 20 samples). Spiking is performed in the laboratory. For additional information or other QA/QC samples pertinent to sample analysis, refer to SERAS SOP #2005, *Quality Assurance/Quality Control Samples*.

Collocated field duplicates may be collected based on site objectives and used to measure variability associated with the sampling process including sample heterogeneity, sampling methodology, and analytical procedures. Field replicates are field samples obtained from one location, homogenized, and divided into separate containers. This is useful for determining whether the sample has been homogenized properly. Equipment blanks (also known as rinsate blanks) are typically collected at a rate of one per day. The equipment blank is used to evaluate the relative cleanliness of non-dedicated equipment.

3.5 Sample Containers, Preservation, Storage and Holding Times

The amount of sample to be collected, the proper sample container type (i.e., glass, plastic), chemical preservation, and storage requirements are dependent on the matrix sampled and the analyses to be conducted. This information is provided in SERAS SOP #2003, *Sample Storage, Preservation, and Handling*. Field personnel need to be cognizant of any short holding times that warrant immediate shipment/transfer to the laboratory.

3.6 Documentation

Field conditions and site activities must be documented. Scribe will be used to document sample locations and generate chain of custody records. Other field measurements not typically entered into Scribe will be documented in a site-specific logbook or in a personal logbook. All sample documentation will be maintained in accordance with SERAS SOP #2002, *Sample Documentation* and SERAS SOP #4005, *Chain of Custody Procedures.*

4.0 RESPONSIBILITIES

4.1 SERAS Task Leaders

Task Leaders (TLs) are responsible for the overall management of the project. Task Leader responsibilities include ensuring that field personnel are well informed of the sampling requirements for a specific project and that SOP and QA/QC procedures stated in the site-specific QAPP are adhered to, issuing a Field Change Form that documents any changes to sampling activities after the QAPP has been approved and maintaining sample documentation.

4.2 SERAS Field Personnel

Field personnel are responsible for reading the QAPP prior to site activities and performing sample collection activities as written. They are responsible for notifying the TL of deviations from sample collection protocols which occurred during the execution of sampling activities. Field staff will collect samples and prepare documentation in accordance with SERAS SOP #2002, *Sample Documentation*. In addition, field personnel are responsible for reading and conforming to the approved site-specific Health and Safety Plan (HASP).

4.3 SERAS Program Manager

The SERAS Program Manager is responsible for the overall technical and financial management of the project.

4.4 SERAS QA/QC Officer

The QA/QC Officer is responsible for reviewing this SOP and ensuring that the information in this SOP is updated on a timely basis. Compliance to this SOP may be monitored by either conducting a field audit or reviewing deliverables prepared by the SERAS TL.

4.5 Health and Safety (H&S) Officer

The H&S Officer is responsible for ensuring that a HASP has been written in conformance with SOP # 3012, *SERAS Health and Safety Guidelines for Field Activities* and approved prior to field activities. Additionally, the H& S Officer is responsible for ensuring that SERAS site personnel's H&S training is current as per SOP # 3006, *SERAS Field Certification Program* and that their medical monitoring is current as per *SERAS SOP #3004, SERAS Medical Monitoring Program.*

STANDARD OPERATING PROCEDURE APPROVAL AND CHANGE FORM

Scientific, Engineering, Response and Analytical Services 2890 Woodbridge Avenue Building 209 Annex Edison New Jersey 08837-3679	
STANDARD OPERATING PROCEDURE	
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STANDARD OPERATING PROCEDURES

SAMPLING EQUIPMENT DECONTAMINATION

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SUPERSEDES: SOP #2006, Rev. 0.0, 08/11/94; US EPA Contract EP-W-09-031

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SAMPLING EQUIPMENT DECONTAMINATION

1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to describe the methods for preventing or limiting cross-contamination of samples due to inappropriate or inadequate equipment decontamination and to provide general guidelines for developing decontamination procedures for sampling equipment to be used during environmental investigations as per 29 Code of Federal Regulations (CFR) 1910.120. This SOP does not address personnel decontamination.

A Quality Assurance Project Plan (QAPP) in Uniform Federal Policy (UFP) format describing the project objectives must be prepared prior to deploying for a sampling event. The sampler needs to ensure the methods used are adequate to satisfy the data quality objectives.

The procedures in this SOP may be varied or changed as required, dependent on site conditions, equipment limitations or other procedural limitations. In all instances, the procedures employed must be documented on a Field Change Form and attached to the QAPP. These changes must be documented in the final deliverable.

2.0 METHOD SUMMARY

Removing or neutralizing contaminants from equipment minimizes the possibility of sample cross contamination, reduces or eliminates transfer of contaminants to clean areas, and prevents the mixing of incompatible substances. Some equipment may have specific decontamination procedures that do not follow this SOP. Refer to the user manual for each piece of equipment before utilizing this SOP.

Gross contamination can be removed by physical decontamination procedures. These abrasive and non-abrasive methods include the use of brushes and high and low pressure water cleaning.

The first step is the physical removal of gross contamination on sampling equipment which may include steam or a high pressure water wash. The second step is a soap and water wash that removes the remainder of visible material and residual oils and grease. The third step involves a potable water rinse to remove any detergent, followed by a distilled/deionized water rinse.

For the removal of metals, an acid rinse with a 10% nitric acid solution is used prior to the final distilled/deionized water rinse. For the removal of organics, pesticide grade acetone, methanol or hexane, depending on the specific contaminant of concern, will be applied prior to the final distilled/deionized rinse. Acetone is typically chosen because it is excellent at removing organics, miscible in water, and not a target analyte on the Priority Pollutant List. If acetone is known to be a contaminant of concern or if Target Compound List analysis (which includes acetone) is to be performed, another solvent such as methanol will need to be substituted.

Hexane should be used when the contaminant of concern is polychlorinated biphenyls (PCBs) or in oily media. The solvent must be allowed to evaporate completely and then a final distilled/deionized water rinse is performed. This rinse removes any residual traces of the solvent.

A generalized decontamination procedure is:

1. Physical removal
2. Non-phosphate detergent wash with potable water
3. Potable water rinse
4. Solvent rinse (acetone, hexane, etc.)

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5. Air dry
6. 10% nitric acid solution rinse
7. Distilled/deionized water rinse
8. Air dry

In instances in which sampling equipment is being used to collect samples for biological pathogens, the acid is replaced with a 10% bleach solution. Modifications to the standard procedure are required to be documented in the site-specific QAPP, field log book and subsequent reports. All decontamination water is replaced daily at a minimum. If at any point throughout the day the water becomes too dirty, then it is no longer suitable for cleaning and is required to be replaced. All sampling equipment is required to be decontaminated before collecting samples on-site and after use of each piece of sampling equipment.

Waste materials generated from the decontamination processes are referred to as Investigation-Derived Waste (IDW). Management of this waste should be in coordination with SOP#2049, *Investigative-Derived Waste Management.*

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The amount of sample collected, along with the proper sample container type (i.e. glass, plastic), chemical preservation, and storage requirements are dependent upon the matrix sampled and analysis performed. For further information, refer to SERAS SOP #2003, *Sample Storage, Preservation and Handling*.

Sample collection and analysis of decontamination waste generated on-site may be required prior to disposal of decontamination liquids and solids. This should be determined prior to initiation of site activities or as soon as possible thereafter. For more information on handling of IDW, refer to SOP#2049, *Investigative-Derived Waste Management*.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Acetone is an excellent solvent since it is miscible with water; however, if volatile organic compounds (VOCs) are to be analyzed, the use of an alternate solvent (methanol, hexane) should be considered since acetone is a compound on the Target Compound List (TCL).

The use of deionized (distilled if only option) water is required for decontamination of sampling equipment. In addition, that water is required to be lab certified, analyte free (specifically for the contaminants of concern). The deionized water must be secured prior to field activities as it is not commonly found local to the site.

The use of solvents and acids on sensitive sampling equipment may cause damage. It is important avoid damaging the equipment. If acids or solvents are utilized, follow health and safety, and waste disposal guidelines.

When decontaminating equipment when temperatures are below freezing, water will freeze in pump spray hoses lines, tanks and in buckets/pails, etc. Additionally, equipment will require longer drying times.

Do not store sampling equipment or reagents used for decontamination near gasoline or any exhaust emissions. Improperly cleaned and prepared sampling equipment can lead to misinterpretation of analytical data due to cross contamination.

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Make sure that the decontamination station is set up as not to compromise a clean environment.

5.0 EQUIPMENT/APPARATUS

Decontamination equipment is selected based on the type of equipment to be cleaned and anticipated contaminants to be removed. For example, soft-bristle scrub brushes or long-handled bottle brushes are used to remove contaminants. Large galvanized wash tubs, stock tanks, buckets, or children's wading pools hold wash and rinse solutions. Large plastic garbage cans or other similar containers lined with plastic bags help segregate contaminated equipment. Drums are used to store liquid and solid site derived waste.

The following standard materials and equipment are recommended for decontamination activities:

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5.1 Decontamination Tools/Supplies

- Long and short handled brushes
- Bottle brushes, composed of nonmetallic material such as nylon
- Plastic sheeting
- Paper towels
- Plastic or galvanized tubs or buckets
- Pressurized sprayers filled with potable water
- Spray bottles
- Aluminum foil
- Pressure washer
- Garden hose
- Electrical cords
- Work lights (if working in the dark)
- Generator (if using a submersible pump or lights)
- Water tank
- Sump pump

5.2 Health and Safety Equipment

The use of personal protective equipment (PPE), (i. e. safety glasses or splash shield, Tyvek® suits, nitrile gloves, aprons or coveralls, steel toe boots, etc.), is required. Refer to the site-specific Health and Safety Plan (HASP) for site-specific requirements.

5.3 Waste Disposal

- Trash bags
- 55-gallon drums (open and closed top types)
- Metal/plastic buckets/containers for storage and disposal of decontamination solutions

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6.0 REAGENTS

Table 1 (Appendix A) lists solvents recommended for the elimination of particular chemicals. In general, solvents typically utilized during the decontamination process are:

- 10% Nitric Acid (HNO_3), typically used for inorganic compounds such as metals
- Acetone (pesticide grade)
- Hexane (pesticide grade)
- Methanol (pesticide grade)
- Deionized/Distilled Water that meets ASTM Type II specifications
- Non-Phosphate Detergent
- Potable Water

7.0 PROCEDURES

A decontamination area should be set up prior to sampling. Weather conditions (i.e. hot, cold, rain, snow, etc.) play an important role in the decontamination process. In hot, cold, rainy or snowy conditions, a tent or canopy may be erected around and over the decontamination area. In cold environments, the decontamination may need to occur inside a building or portable heaters may be needed to warm the area under the tent or canopy. In addition, in cold environments the potable and deionized water may freeze. Plan accordingly and consider your working conditions prior to field sampling activities.

A decontamination plan needs to be implemented and includes:

- The number, location, and layout of decontamination stations
- Decontamination equipment
- Selection of appropriate decontamination methods
- Methods of disposal of all investigative derived waste (i.e. PPE, solid and liquid waste, etc.)
- Work practices that minimize contact with potential contaminants.
- Protection procedures for monitoring and sampling equipment (i.e. covering with plastic, etc.)
- Considerations related to weather conditions
- The use of disposable sampling equipment, when possible

7.1 Decontamination Methods

All samples and equipment removed from site must bedecontaminated, removing all contamination that may have adhered to the equipment. Various decontamination methods remove contaminants by washing with water and another physical cleaning action. In addition, solvents and/or acids may be used to decontaminate the equipment.

Physical decontamination methods are grouped into two categories, abrasive and non-abrasive methods, and are listed below:

7.1.1 Abrasive Cleaning Methods

Abrasive cleaning methods work by rubbing and wearing away the top layer of the surface containing the contaminant. It involves the use of metal or nylon brushes. The amount and type of contaminants removed will vary with the brush type, length of time brushed,

degree of brush contact, degree of contamination, n ature of the contaminant and surface being cleaned.

7.1.2 Non-Abrasive Cleaning Methods

Non-abrasive cleaning methods work by forcing the c ontaminant off a surface with water pressure (i.e. sprayer or pressure washer).

Low-Pressure Water

This method consists of a pressure sprayer filled w ith water. The user pumps air into the sprayer tank to create pressure. The water is then discharged through a slender nozzle and hose, cleaning the equipment. Scrubbing with a brush is typically used in conjunction with this method.

High-Pressure Water

This method consists of the use of a pressure washer. The operator controls the directional nozzle which is attached to a high-pressure hose. Operating pressure usually ranges from 400 – 600 pounds per square inch (PSI). Scrubbing w ith large brushes can be used to aid in the decontamination process.

Rinsing

Contaminants and any remaining solvents and/or acid s are removed by thorough rinsing. The rinsing is done either by the use of a sprayer or a pressure washer depending on the equipment being cleaned.

Damp Cloth Removal

In some instances, due to sensitive, non-waterproof equipment or due to the unlikelihood of equipment being contaminated, it is not necessar y to conduct an extensive decontamination procedure. For example, air samplin g pumps attached to a fence, placed on a drum, or equipment protected by plastic or som e other material are not likely to become heavily contaminated.

A damp cloth is used to wipe off any contaminants which may have adhered to equipment through airborne contaminants or from surfaces upon which the equipment was set. The use of a different cleaning cloth for each piece ofequipment is required. Upon completion, dispose of all cloths with the site derived waste.

7.2 Field Sampling Equipment Decontamination Proced ures

7.2.1 Decontamination Setup

The decontamination area is set up by laying out a section of plastic sheeting large enough for the type and amount of equipment to be decontam inated and for the equipment drop and equipment air drying areas.

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Stage brushes, pressure sprayers, spray bottles (with appropriate solvents, acids and deionized water), 5-gallon buckets, plastic/galvanized wash tubs, pressure washer (if required) and detergent. Figure 1 (Appendix B) shows the decontamination area overall layout. Section 7.2.2 discusses the decontamination procedures depending on the contaminants of concern for a Site.

Stage the appropriate amount and type of sample bottles and a cooler, for the collection of rinsate samples. For specific rinsate sample information, refer to SERAS SOP #2005, *Quality Assurance/Quality Control Samples*.

7.2.2 Decontamination Procedures

There are various stations of the cleaning process in which the equipment move through that are designed to remove all visible contamination. Stations 1 and 2 are designed to remove all visible contamination. Additional stations after 1 and 2 remove materials that require dissolution and a final rinse. Once the equipment has passed through all stations, it is laid out to air dry.

Decontamination Process for Metals

Station 1 - Place the sampling equipment into the soapy water solution and thoroughly scrub with brushes or pressure washer. When there is no visible residue remaining, transfer to Station 2.

STATION 2 - Rinse the equipment in the bucket/tub with potable water. Then remove from the bucket/tub and rinse with the pressure sprayer. When satisfied with the cleanliness of the sampling equipment, transfer to Station 3.

STATION 3 - Apply the acid solution and air dry on the plastic sheeting, behind Station 3. Once equipment has fully dried, transfer to Station 4.

Station 4 - Rinse the equipment with the pressure sprayer filled with deionized water. When satisfied the rinsing process is complete, transfer to the equipment drying area. After drying, the equipment should be wrapped in aluminum foil to prevent contamination of the equipment.

Decontamination Process for Organics

Station 1 - Place the sampling equipment into the soapy water solution and thoroughly scrub with brushes. When there is no visible residue remaining, transfer to Station 2

STATION 2 - Rinse the equipment in the bucket/tub with potable water. Then remove from the bucket/tub and rinse with the pressure sprayer. When satisfied with the cleanliness of the sampling equipment, transfer to Station 3.

STATION 3 - Apply the appropriate solvent or solvents and air dry on the plastic sheeting, behind Station 3. Once equipment has fully dried, transfer to Station 4.

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STATION 4 - Rinse the equipment with the pressure sprayer fil led with deionized water. When satisfied the rinsing process is complete, transfer to the equipment drying area.

Decontamination process for Metals and Organics

Station 1 - Place the sampling equipment into the soapy wate r solution and thoroughly scrub with brushes. When there is no visible resid ue remaining, transfer to Station 2.

STATION 2 - Rinse the equipment in the bucket/tub with potab le water. Then remove from the bucket/tub and rinse with the pressure sprayer. When satisfied with the cleanliness of the sampling equipment, transfer to Station 3.

Station 3 - Apply the acid solution and transfer to Station 4.

Station 4 - Rinse the equipment with the pressure sprayer fill ed with deionized water. When satisfied the rinsing process is complete, transfer to Station 5.

Station 5- Apply the solvent or solvents and air dry on the plastic sheeting behind Station 5. Once equipment has fully dried, transfer to Sta tion 6.

Station 6 - Rinse the equipment with the pressure sprayer fill ed with deionized water. When satisfied the rinsing process is complete, tra nsfer to the equipment drying area. After drying, the equipment should be wrapped in aluminum foil to prevent contamination of the equipment.

7.2.3 Post Decontamination Procedures

1. Fill out the appropriate labels for the all the various wastes and affix the labels to the drums and/or containers.

2. Clean up the entire work area. Collect solid waste(i.e. nitrile gloves, plastic sheeting, etc.) and store in an appropriate DOT certified drum.

3. Return any remaining unused solvents or acid soluti ons to their respective labeled containers and properly store.

4. Transfer potable water rinse waste into an appropri ate Department of Transportation (DOT) certified drum or container.

5. Transfer the solvent and acid solution rinse waterwaste into the appropriately labeled DOT certified drums or containers.

6. Using a pressure sprayer, rinse the basins/buckets.

7. Transfer liquid generated from this process into th e potable water rinse waste container.

8. Transfer the decontamination brushes into the solid waste container.

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9. Empty the pressure sprayer filled with potable water onto the ground.

10. Return all equipment into their carrying cases or shipping containers.

11. Make arrangements for the pickup of all liquid and solid waste.

For further information on waste disposal, refer to SERAS SOP 2049, *Investigation Derived Waste Management*.

7.3 Decontamination of Earth Moving Equipment/Drilling Equipment and Accessories

The decontamination of earth moving and/or drilling equipment and their accessories will require the use of a pressure washer. In addition, an on-site water supply will need to be available. If an on-site water supply is not available, a water tank along with a pump, hoses and a generator will be required. Finally, a designated area on-site needs to be designated as a decontamination area. Some sites already have a concrete pad set-up for this very purpose. If this is not the case, work with the Work Assignment Manager (WAM) to assign a location for these activities to take place on-site.

An area for decontamination can be built with 4x4 lumber or hay bales, heavy duty plastic sheeting and a sump pump. The area will need to extend at least 4 feet beyond the outer dimensions of the equipment being cleaned. Either slope the decontamination area down to one corner or dig a small hole about 2 feet by 2 feet square and about 2 feet deep to allow for the collection of the decontamination water. Cover the decontamination area with plastic sheeting, wrapping the sides around and under the 4 x 4 lumber or bales of hay. If equipment being decontaminated includes equipment with tracks that might tear through the plastic sheeting, appropriate surfaces need to be included for the equipment to drive on. Finally, place a sump pump into this area and periodically empty the water as necessary, into the appropriately labeled liquid waste drum.

7.3.1 Decontamination Set-up Procedures:

1. Move the equipment into the decontamination area.

2. Stage all the decontamination equipment and supplies (i.e. Pressure Washer, Hoses, PPE, etc.)

3. Connect all hoses and fill the pressure washer with fuel.

4. Dress out in the appropriate PPE (refer to the site-specific HASP).

At a minimum, Tyvek®, safety glasses/goggles, steel toe boots, and nitrile gloves must be worn. If handling any equipment (i.e. drill rods, etc.) work gloves must also be worn to prevent possible injury. For site specific requirements refer to the site-specific HASP.

7.3.2 Decontamination Cleaning Procedures:

1. Physically remove as much of the visible material as possible from the heavy equipment after use and prior to steam cleaning. If contaminated material is suspected as determined by visual observations, instrument readings, or other means, collect material in an appropriate waste container.

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2. Place the heavy equipment on the decontamination pad in the decontamination area. Verify the decontamination pad has no leaks and the sump pump is functioning properly before beginning the decontamination process.

3. Power on the pressure washer and begin cleaning from the top to the bottom. Thoroughly clean parts of the heavy machinery that come into contact with visible material (such as tires, bucket, augers, drill rods, tracks and the back and underneath of the drill rig). Scrub areas with excessive dirt/debris with large bristle brushes. A flat head shovel can be used to aide in the removal of the dirt/debris. Continue cleaning until all visible contamination has been removed. If required, apply solvents and/or acid solutions, rinse with deionized/distilled water and then let air dry.

The use of solvents and/or acid solutions will depend on site specific conditions. Check with the site-specific HASP for further guidance.

7.3.3 Post Decontamination Procedures

1. Fill out the appropriate labels for the all the various wastes and affix the labels to the drums and/or containers

2. Transfer potable water rinse waste into an appropriate Department of Transportation (DOT) certified drum or container. Transfer water from the decontamination pad to the liquid waste drums using a sump pump.

3. Collect and transfer solid waste (i.e. nitrile gloves, plastic sheeting, etc.) to a DOT-certified drum or container.

4. Transfer the solvent and acid solution rinse waterwaste into the appropriately labeled DOT-certified drums or containers.

5. Make arrangements for the pickup of all liquid and solid waste.

For further information on waste disposal, refer to SERAS SOP 2049, *Investigation Derived Waste Management*.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

Documentation of the decontamination process including date, time and personnel that conducted the decontamination activities must be recorded in a field logbook. Record manufacturer and lot numbers of the reagents used for the decontamination procedures.

A rinsate blank is a specific type of quality control sample associated with the field decontamination process. This sample will provide information on the effectiveness of the decontamination process employed in the field. Rinsate blanks are samples obtained by pouring analyte free deionized water over previously

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decontaminated sampling equipment, testing for residual contamination. The blank water is then collected in sample containers, processed, shipped and analyzed. The rinsate blank is used to assess possible cross-contamination caused by improper decontamination procedures. The most common frequency of collection is one rinsate blank per day per type of sampling device, to meet definitive data objectives. For further information for each analysis, refer to SERAS SOP #2005, *Quality Assurance/Quality Control Samples*.

For information on sample container types and preservation, refer to SERAS SOP #2003, *Sample Storage, Preservation and Handling*.

If sampling equipment requires the use of Teflon® or polyethylene tubing it is required to be disposed of into the on-site waste container and replaced with clean tubing before additional sampling occurs.

10.0 DATA VALIDATION

Data verification (completeness checks) must be conducted to ensure that all data inputs are present for ensuring the availability of sufficient information. These data are essential to providing an accurate and complete final deliverable. Results of quality control samples will be evaluated for possible cross-contamination of improperly or inadequately decontaminated sampling equipment. This data will be utilized to quantify the sample results in accordance with the project's data quality objectives. The SERAS Task Leader (TL) is responsible for completing the UFP-QAPP verification checklist for each project.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow Occupational Safety and Health (OSHA), U.S. EPA, corporate, and other applicable health and safety procedures.

The decontamination process can pose hazards under certain circumstances. Hazardous substances may be incompatible with decontamination materials. For example, the decontamination solution may react with contaminants to produce heat, explosion, or toxic products. Also, vapors from decontamination solutions may pose a direct health hazard to workers by inhalation, contact, fire, or explosion.

The decontamination solutions must be determined to be acceptable before their use. Decontamination materials may degrade protective clothing or equipment and some solvents can permeate protective clothing. If decontamination materials pose a health hazard, measures are to be taken to protect personnel. Alternatively, substitutions can be made to eliminate the hazard. The choice of respiratory protection based on contaminants of concern from the site may not be appropriate for solvents used in the decontamination process. Material generated from decontamination activities requires proper handling, storage, and disposal. PPE may be required for these activities.

Safety data sheets (SDS) are required for all decontamination solvents or solutions as required by the Hazard Communication Standard (i.e. acetone, alcohol, etc.).

12.0 REFERENCES

Field Sampling Procedures Manual, New Jersey Department of Environmental Protection, August 2005.

Compendium of Superfund Field Operations Methods, EPA 540/p-87/001.

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The Field Branches Quality System and Technical Pro cedures – Field Equipment Cleaning and Decontamination, USEPA Region IV Science and Ecosys tem Support Division, November 2007.

Guidelines for the Selection of Chemical Protective Clothing, Volume 1, Third Edition, American Conference of Governmental Industrial Hygienists, Inc., February 1987.

Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities, NIOSH/OSHA/USCG/EPA, October 1985.

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APPENDIX A
Tables
SOP #2006
December 2015

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TABLE 1. Soluble Contaminants and Recommended Solv ent Rinse

SOLVENT[1]	EXAMPLES OF SOLVENTS	SOLUBLE CONTAMINANTS
Water	Deionized water Potable water	Low-chain hydrocarbons Inorganic compounds Salts Some organic acids and other polar compounds
Dilute Acids	Nitric acid Acetic acid Boric acid	Basic (caustic) compounds (e.g., amines and hydrazine's) and inorganic compounds.
Dilute Bases	Sodium bicarbonate	Acidic compounds Phenol Thiols Some nitro and sulfonic compounds
Organic Solvents [2]	Acetone Alcohols Ketones Aromatics Alkanes (e.g., hexane) Common petroleum products (i.e. fuel, oil, kerosene)	Nonpolar compounds (e.g., some organic compounds)
Organic Solvent[2]	Hexane	PCBs

[1] - Safety data sheets are required for all decontam ination solvents or solutions as required by the Ha zard Communication Standard

[2] - WARNING: Some organic solvents can permeate an d/or degrade protective clothing

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APPENDIX B
Figures
SOP #2006
December 2015

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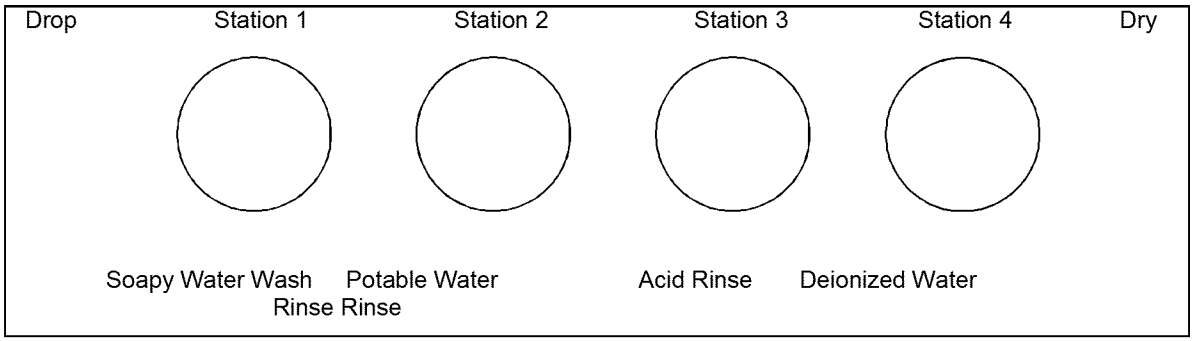
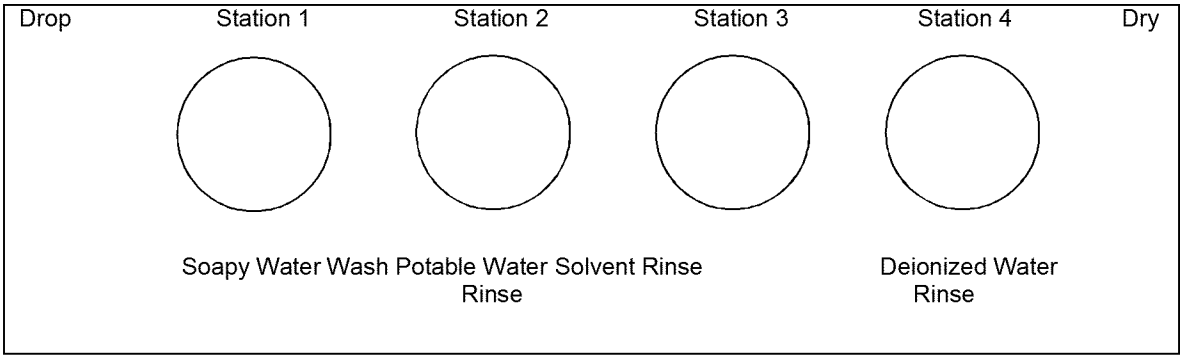
SAMPLING EQUIPMENT DECONTAMINATION

FIGURE 1. Sampling Equipment Decontamination Area

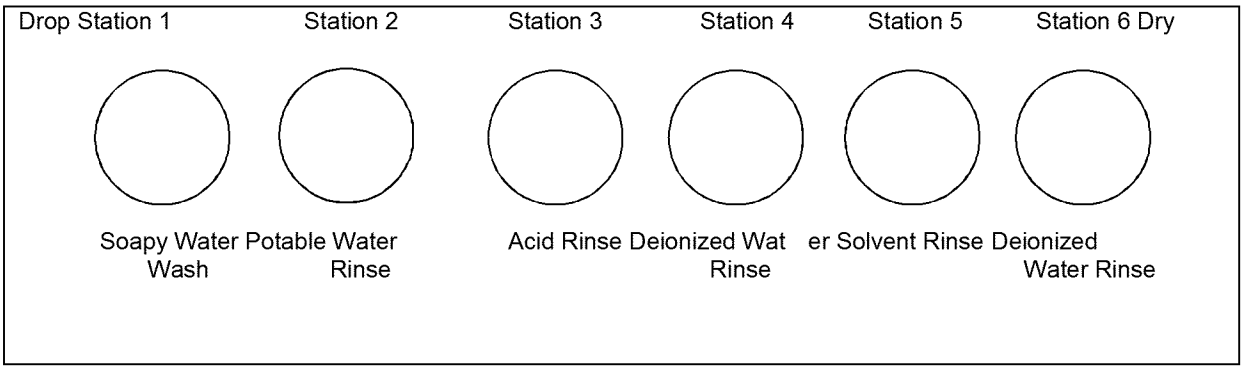
Configuration for the Removal of Metals



Configuration for the Removal of Organics



Configuration for the Removal of Metals and Organic s



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SOIL SAMPLING

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*These sections affected by Revision 1.0.

SUPERCEDES: SOP #2012; Revision 0.0; 2/18/00; U.S. EPA Contract 68-C99-223.

1.0 SCOPE AND APPLICATION

The purpose of this Standard Operating Procedure (SOP) is to describe procedures for the collection of representative surface soil samples. Sampling depths are assumed to be those that can be reached without the use of a drill rig, direct-push technology, or other mechanized equipment (except for a back-hoe). Sample depths typically extend up to 1-foot below ground surface. Analysis of soil samples may define the extent of contamination, determine whether concentrations of specific contaminants exceed established action levels, or if the concentrations of contaminants present a risk to public health, welfare, or the environment.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations, or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with a final report.

Mention of trade names or commercial products does not constitute United States Environmental Protection Agency (U.S. EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

Surface soil samples can be used to investigate contaminants that are persistent in the near surface environment. Contaminants that are detected in the near surface environment may extend to considerable depths, may migrate to the groundwater, surface water, the atmosphere, or may enter biological systems.

Soil samples may be collected using a variety of methods and equipment depending on the depth of the desired sample, the type of sample required (discrete or composite), and the soil type. Near-surface soils may be easily sampled using a spade, trowel, and/or scoop. Sampling at greater depths may be performed using a hand auger, continuous-flight auger, trier, split-spoon sampler, or, if required, a backhoe.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Samples must be cooled and maintained at 4°C and protected from sunlight immediately upon collection to minimize any potential reaction. The amount of sample to be collected, proper sample container type and handling requirements are discussed in the Scientific, Engineering, Response Analytical Services (SERAS) SOP #2003, *Sample Storage, Preservation and Handling.*

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

There are two primary problems associated with soil sampling: 1) cross contamination of samples, and 2) improper sample collection. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, decontamination of sampling equipment is necessary. The guidelines for preventing, minimizing and limiting cross contamination of samples are discussed in the Environmental Response Team (ERT)/SERAS SOP #2006, *Sampling Equipment Decontamination* . Improper sample collection procedures can disturb the sample matrix, resulting in volatilization of contaminants, compaction of the sample, or inadequate homogenization of the samples (when required), resulting in variable, non-representative results.

5.0 EQUIPMENT/APPARATUS

Soil sampling equipment includes the following:

- Site maps/plot plan
- Safety equipment, as specified in the site-specific Health and Safety Plan (HASP)
- Traditional survey equipment or global positioning system (GPS)
- Tape measure
- Survey stakes or flags
- Camera and image collection media
- Stainless steel, plastic*, or other appropriate homogenization bucket, bowl or pan
- Appropriate size sample containers
- Ziplock plastic bags
- Site logbook
- Labels
- Chain of Custody records and custody seals
- Field data sheets and sample labels
- Cooler(s)
- Ice
- Vermiculite
- Decontamination supplies/equipment
- Plastic sheeting
- Spade or shovel
- Spatula(s)
- Scoop(s)
- Plastic* or stainless steel spoons
- Trowel(s)
- Continuous flight (screw) auger
- Bucket auger
- Post hole auger
- Extension rods
- T-handle
- Sampling trier
- Thin wall tube sampler
- Split spoon sampler
- Soil core sampler
  - Tubes, points, drive head, drop hammer, puller jack and grip
- Photoionization detector (PID), Flame ionization detector (FID) and/or Respirable Aerosol Monitor (RAM)
- Backhoe (as required)
- En Core® samplers

* Not used when sampling for semivolatile compounds.

6.0 REAGENTS

Decontamination solutions are specified in ERT/SERAS SOP #2006, *Sampling Equipment Decontamination* , and the site specific work plan.

7.0 PROCEDURES

7.1 Preparation

1. Determine the extent of the sampling effort, the analytes to be determined, the sampling methods to be employed, and the types and amounts of equipment and supplies required to accomplish the assignment.

2. Obtain the necessary sampling and air monitoring equipment.

3. Prepare schedules and coordinate with staff, client, and regulatory agencies, as appropriate.

4. Perform a general site reconnaissance survey prior to site entry in accordance with the site specific HASP.

5. Use stakes or flags to identify and mark all sampling locations. Specific site factors, including extent and nature of contamination, should be considered when selecting sample locations. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. All staked locations should be utility-cleared prior to soil sampling; utility clearances must be confirmed before beginning intrusive work.

6. Pre-clean and decontaminate equipment in accordance with the site specific work plan, and ensure that it is in working order.

7.2 Sample Collection

7.2.1 Surface Soil Samples

The collection of samples from near-surface soil can be accomplished with tools such as spades, shovels, trowels, and scoops. The over-burden or over-lying surface material is removed to the required depth and a stainless steel or plastic scoop is used to collect the sample. Plastic utensils are not to be used when sampling for semivolatile compounds.

This method can be used in most soil types but is limited to sampling at or near the ground surface. Accurate, representative samples can be collected by this procedure depending on the care and precision demonstrated by the sample team member. A flat, pointed mason trowel to cut a block of the desired soil is helpful when undisturbed profiles are required. Tools plated with chrome or other materials must not be used.

The following procedure is used to collect surface soil samples:

1. If volatile organic compound (VOC) contamination is suspected, use a PID to monitor the sampler's breathing zone during soil sampling activities.

2. Using a pre-cleaned, stainless steel scoop, plastic spoon, or trowel, remove and discard sticks, rocks, vegetation and other debris from the sampling area.

3. Accumulate an adequate volume of soil, based on the type(s) of analyses to be performed, in

a stainless, plastic or other appropriate container.

4. If volatile organic analysis is to be performed, immediately transfer the sample directly into an appropriate, labeled sample container with a stainless steel spoon, or equivalent, and secure the cap tightly to ensure that the volatile fraction is not compromised. Thoroughly mix the remainder of the soil to obtain a sample that is representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly, or, if composite samples are to be collected, place a sample from another sampling interval or location into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.2 Sampling at Depth with Augers and Thin Wall Tube Samplers

This system consists of an auger, head, a series of extensions, and a "T" handle (Figure 1, Appendix A). The auger is used to bore a hole to a desired sampling depth, and is then withdrawn. The sample may be collected directly from the auger head. If additional sample volume is required, multiple grabs at the same depth are made. If a core sample is to be collected, the auger head is then replaced with a tube auger. The system is then lowered down the borehole, and driven into the soil to the completion depth. The system is withdrawn and the core is collected.

Several types of augers are available; these include bucket or tube type, and continuous flight (screw) or post-hole augers. Bucket or tube type augers are better for direct sample recovery because a large volume of sample can be collected from a discrete area in a short period of time. When continuous flight or post-hole augers are used, the sample can be collected directly from the flights or from the borehole cuttings. The continuous flight or post-hole augers are satisfactory when a composite of the complete soil column is desired, but have limited utility for sample collection as they cannot be used to sample a discrete depth.

The following procedure is used for collecting soil samples with an auger:

1. Attach the auger head to an extension rod and attach the "T" handle.

2. Clear the area to be sampled of surface debris (e.g., twigs, rocks, litter). It may be advisable to remove a thin layer of surface soil for an area approximately six inches in radius around the sampling location.

3. Begin augering, periodically removing and depositing accumulated soils onto a plastic sheet spread near the hole. This prevents the accidental brushing of loose material back down the borehole when removing the auger or adding extension rods. It also facilitates refilling the hole, and avoids possible contamination of the surrounding area.

4. After reaching the desired depth, slowly and carefully remove the auger from the hole. When sampling directly from the auger head, proceed to Step 10.

5. Remove auger tip from the extension rods and replace with a tube sampler. Install the

proper cutting tip.

6. Carefully lower the tube sampler down the borehole. Gradually force the tube sampler into the soil. Do not scrape the borehole sides. Avoid hammering the rods as the vibrations may cause the boring walls to collapse.

7. Remove the tube sampler and unscrew the extension rods.

8. Remove the cutting tip and the core from the device.

9. Discard the top of the core (approximately 1 inch), as this possibly represents material collected before penetration of the layer of concern. Place the core or a discrete portion of the core into the appropriate labeled sample container using a clean, decontaminated stainless steel spoon. If required, homogenize the sample as described in Step 10.

10. If VOC analysis is to be performed, transfer the sample directly from the auger head into an appropriate, labeled sample container with a stainless steel spoon, or equivalent and secure the cap tightly.

11. If another sample is to be collected in the same hole, but at a greater depth, reattach the auger head to the drill assembly, and follow steps 3 through 11, making sure to decontaminate the auger head and tube sampler between samples.

12. Abandon the hole according to applicable state regulations.

7.2.3 Sampling at Depth with a Trier

The system consists of a trier and a "T" handle. The auger is driven into the soil to be sampled and used to extract a core sample from the appropriate depth.

The following procedure is used to collect soil samples with a sampling trier:

1. Insert the trier (Figure 2, Appendix A) into the material to be sampled at a zero degree to forty-five degree (0° to 45°) angle from the soil surface plane. This orientation minimizes the spillage of sample.

2. Rotate the trier once or twice to cut a core of material.

3. Slowly withdraw the trier, making sure that the slot is facing upward.

4. If VOC analyses are required, transfer the sample directly from the trier into an appropriate, labeled sample container with a stainless steel spoon, or equivalent device and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container and mix thoroughly to obtain a sample that is representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; if composite samples are to be collected, place a sample from another sampling interval into the

homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.4 Sampling at Depth with a Split Spoon (Barrel) Sampler

Split spoon sampling is generally used to collect undisturbed soil cores of 18- or 24- inches in length. A series of consecutive cores may be extracted with a split spoon sampler to give a complete soil column profile, or an auger may be used to drill down to the desired depth for sampling. The split spoon is then driven to its sampling depth through the bottom of the augured hole and the core extracted.

When split spoon sampling is performed to gain geologic information, all work should be performed in accordance with American Society for Testing and Materials (ASTM) D1586-99, "*Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils*".

The following procedures are used for collecting soil samples with a split spoon:

1. Assemble the sampler by aligning both sides of the barrel and then screwing the drive shoe on the bottom and the head piece on top.

2. Place the sampler at a 90 degree (90 ^{o}) angle to the sample material.

3. Using a well ring, drive the sampler. Do not drive past the bottom of the head piece or compression of the sample will result.

4. Record in the site logbook or on field data sheets the length of the tube used to penetrate the material being sampled, and the number of blows required to obtain the sample.

5. Withdraw the sampler, and open it by unscrewing the bit and head, and then splitting the barrel. The amount of recovery and soil type shoul d be recorded on the boring log. If a split sample is desired, a cleaned, stainless steel knife should be used to divide the tube contents in half, longitudinally. This sampler is typically available in 2- and 3.5-inch diameter tubes. A larger barrel (diameter and/or length) may be necessary to obtain the required sample volume.

6. Without disturbing the core, transfer it to the appropriately labeled sample container(s) and seal tightly. Place the remainder of the sample into a stainless steel, plastic, or appropriate homogenization container, and mix thoroughly to obtain a sample that is representative of the entire sampling interval. Then, either place the sample into the appropriate, labeled containers and secure the caps tightly, or if composite samples are to be collected, place a sample from another sampling interval or location into the homogenization container and mix thoroughly. When compositing is complete, place the sample into the appropriate, labeled containers and secure the caps tightly.

7. Abandon the hole according to applicable state regulations.

7.2.5 Test Pit/Trench Excavation

A backhoe can be used to remove sections of soil when a detailed examination of stratigraphy and soil characteristics is required. The following procedures are used for collecting soil samples from test pits or trenches:

1. Prior to any excavation with a backhoe, it is imperative to ensure that all sampling locations are clear of overhead and buried utilities.

2. Review the site specific HASP and ensure that all safety precautions including appropriate monitoring equipment are installed as required.

3. Using the backhoe, excavate a trench approximately three feet wide and approximately one foot deep below the cleared sampling location. Place excavated soils on plastic sheets. Trenches greater than five feet deep must be sloped or protected by a shoring system, as required by Occupational Safety and Health Administration (OSHA) regulations.

4. A shovel is used to remove a one to two inch layer of soil from the vertical face of the pit where sampling is to be done.

5. Samples are taken using a trowel, scoop, or coring device at the desired intervals. Be sure to scrape the vertical face at the point of sampling to remove any soil that may have fallen from above, and to expose fresh soil for sampling. In many instances, samples can be collected directly from the backhoe bucket.

6. If VOC analyses are required, transfer the sample into an appropriate, labeled sample container with a stainless steel spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into the appropriate, labeled containers and secure the caps tightly.

7. Abandon the pit or excavation according to applicable state regulations.

7.2.6 Sampling for VOCs in Soil Using an En Core® Sampler

An En Core® sampler is a single-use device designed to collect and transport samples to the laboratory. The En Core® sampler is made of an inert composite polymer and reduces the open-air handling of soil samples in the field and in the laboratory; thereby, minimizing losses of VOCs.

1. Assemble the coring body, plunger rod and T-handle according to the instructions provided with the En Core® sampler.

2. Turn the T-handle with the T-up and the coring body down and push the sampler into the soil until the coring body is completely full. Remove the sampler from the soil. Wipe excess soil from the coring body exterior.

3. Cap the coring body while it is still on the T-handle. Push the cap over the flat area of the ridge. Be sure that the cap is seated properly to seal the sampler. Push and cap to lock arm in place.

4. Remove the capped sampler by depressing the locking lever on the T-handle while twisting and pulling the sampler from the T-handle.

5. Attach the label to the coring body cap, place in a plastic zippered bag, seal and put on ice.

Generally, three En Core® samplers are required for each sample location. These samplers are shipped to the laboratory where the cap is removed and the soil samples are preserved with methanol or sodium bisulfate.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

There are no specific quality assurance (QA) activities that apply to the implementation of these procedures. However, the following general QA procedures apply:

2. All data must be documented in site logbooks or on field data sheets. At a minimum, the following data is recorded:

   Sampler's name and affiliation with project
   Sample number
   Sample location
   Sample depth
   Approximate volume of sample collected
   Type of analyses to be performed
   Sample description
   Date and time of sample collection
   Weather conditions at time of sampling
   Method of sample collection
   Sketch of sample location

2. All instrumentation must be operated in accordance with applicable SOPs and/or the manufacturer's operating instructions, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and must be documented.

3. The types of quality control (QC) samples to be collected in the field shall be documented in the site-specific Work Plan.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA and corporate health and safety procedures, in addition to the procedures specified in the site specific HASP.

12.0 REFERENCES

Mason, B.J. 1983. *Preparation of Soil Sampling Protocol: Technique and Strategies*. EPA-600/4-83-020.

Barth, D.S. and B.J. Mason. 1989. *Soil Sampling Quality Assurance User's Guide*. EPA-600/8-89-046.

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American Society for Testing and Materials. *Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils*. Method D 1586-99.

En Novative Technologies, Inc. 2001. *En Core® Sampler Sampling Procedures*. Web site access. March 13, 2001.

APPENDIX A
Figures
SOP #2012
July 2001

FIGURE 1. Sampling Augers

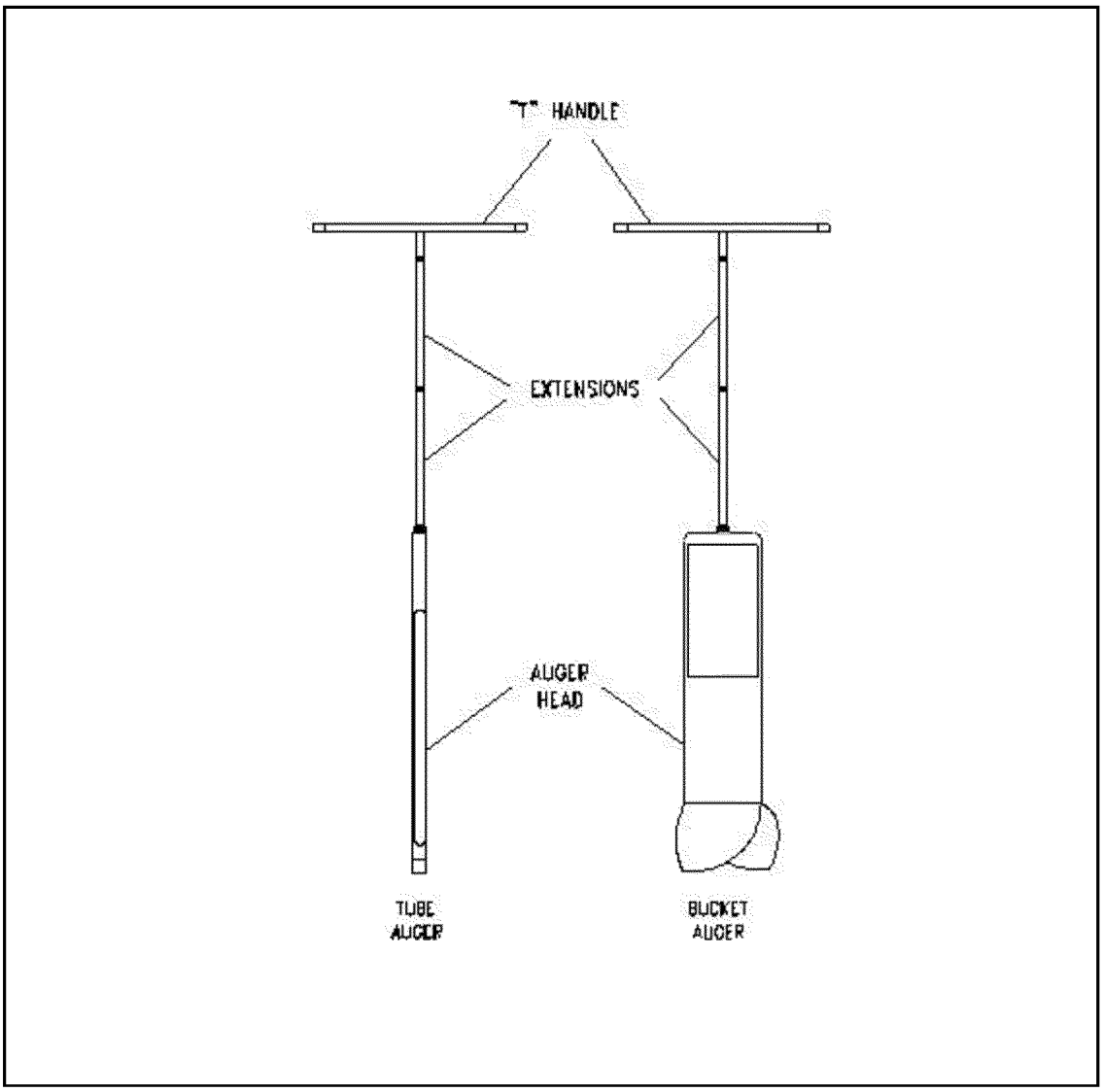
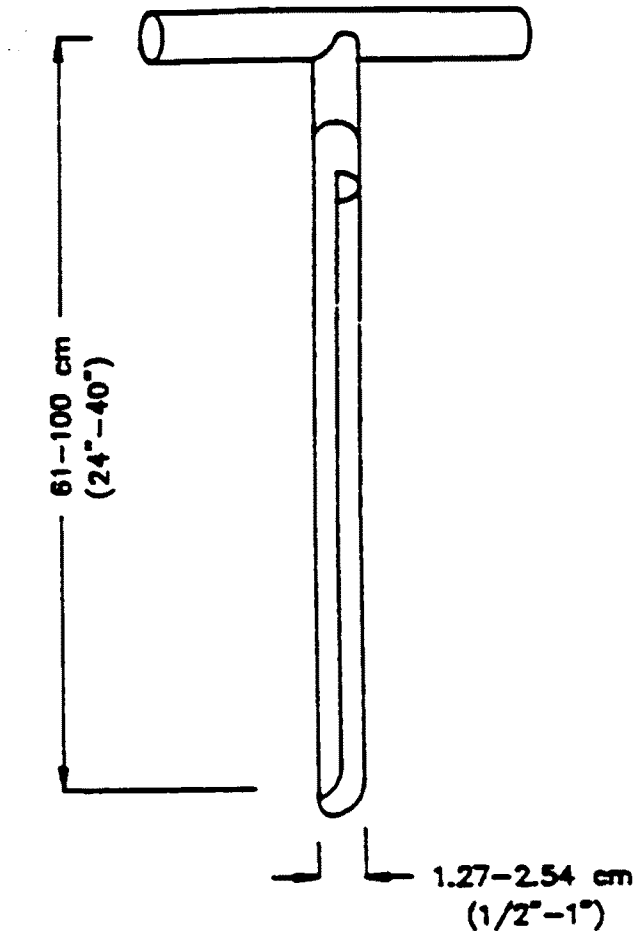


FIGURE 2. Sampling Trier


61–100 cm
(24"–40")
1.27–2.54 cm
(1/2"–1")

ATTACHMENT C

Pace Analytical Services Laboratory SOPs
HASL 300, EPA 901.1, EPA 903.1, and EPA 904.0

STANDARD OPERATING PROCEDURE

Analysis of Samples for Alpha Emitting Actinides and Plutonium-241

Methods: ASTM Method D-3972-90 and HASL 300 Method U-02

SOP NUMBER:	PGH-R-008-10
REVIEW:	R. Kinney
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-R-008-9
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager	07/27/15 Date
Senior Quality Manager	07/27/15 Date
Department Manager/Supervisor	07/24/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

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SOPs distributed as Controlled Documents are given a copy number on the signed Title Page.
Copies without a number are considered uncontrolled and must be verified as the most recent version prior to each use.

1. Purpose

1.1 This SOP describes the procedure to be used for the determination of micro-quantities of Americium, Curium, Thorium, Plutonium (including Pu-241), Neptunium and Uranium in various sample matrices. It also addresses routinely difficult matrices such as filters, solids in quantities over two grams, and aqueous samples where precipitation as described in the procedure may not be successful.

1.2 Samples not meeting the criteria outlined in this procedure should be brought to the attention of the Department Manager/Supervisor or designee for further direction.

1.3 This procedure is applicable for determining compliance for isotopic uranium in drinking water and is substantially compliant with ASTM Method D-3972-90 and HASL 300 Method U-02. Deviations from these methods are addressed in Section 19 of this procedure.

1.4 This procedure is designed for the determination of the following radio-nuclides:

Isotope	Half-life	Alpha Energy MeV (Abnd.)
Americium 241	*458 yrs*	*5.49 (86%) 5.44 (13%)*
Americium 243	*7370 yrs*	*5.28 (88%) 5.23 (11%)*
Curium 242	*162.79 days*	*6.069 (25%) 6.112 (74%)*
Curium 244	*18 yrs*	*5.80 (76%) 5.76 (23%)*
Plutonium 238	*87.8 yrs*	*5.50 (72%) 5.46 (28%)*
Plutonium 239	*24131 yrs*	*5.16 (73%) 5.14 (15%)*
Plutonium 240	*6569 yrs*	*5.17 (74%) 5.12 (26%)*
Plutonium 241	*14.35 yrs*	*Beta 20.81Kev (5.23 Ave)*
Plutonium 242	*375850 yrs*	*4.90 (78%) 4.86 (22%)*
Neptunium 237	*2140000 yrs*	*4.79 (47%) 4.77 (25%)*
Thorium 228	*1.9132 yrs*	*5.42 (73%) 5.34 (27%)*
Thorium 230	*77000 yrs*	*4.69 (76%) 4.62 (23%)*
Thorium 232	*14050000000 yrs*	*4.01 (77%) 3.95 (23%)*
Thorium 229	*7340 yrs*	*4.85 (56%) 4.90 (10%)*
Thorium 227	*18.718 days*	*6.03 (24%), 5.98 (23%), 5.76 (20%)*
Uranium 232	*72 yrs*	*5.32 (69%) 5.26 (31%)*
Uranium 238	*4468000000 yrs*	*4.19 (77%) 4.15 (23%)*
Uranium 235	*703800000 yrs*	*4.39 (55%) 4.36 (11%)*
Uranium 236	*23415000 yrs*	*4.49 (74%) 4.45 (26%)*
Uranium 234	*244500 yrs*	*4.78 (72%) 4.72 (27%)*
Uranium 233	*159200 yrs*	*4.82 (84%) 4.78 (13%)*

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2. Scope and Application

2.1 This procedure covers the measurement of various isotopic alpha emitters in various matrices including drinking water. Since all plutonium isotopes behave the same, this procedure also addresses the isolation of beta emitting Pu-241. With the exception of drinking water sources, most other matrices, especially soils and biota, contain elements, which may complex some actinides, making it necessary to aggressively treat such samples.

2.2 This method is a laboratory promulgated method based on multiple accredited methods and the behavior of individual alpha emitters.

2.3 Pace Analytical Services, Inc. (PASI) applies isotope decay correction only in those instances where the total impact in the analytical result is 2% or greater. Assuming a maximum hold time of 180 days, a 2% isotope decay would occur only for radioisotopes with a half-life of 17.14 years or less. Refer to the table in Section 1 for a list of the isotopes and their associated half lives to determine which require decay correction.

2.4 Alpha count sources generated as the product of this SOP are analyzed as documented in the current revision of Pace SOP PGH-R-020, “Alpha Spectroscopy Instrument Operations.”

2.5 Plutonium-241 count sources generated as the product of this SOP are analyzed as documented in the current revision of Pace SOP PGH-R-022, “Liquid Scintillation Counter Operations.”

2.6 Beta-emitting tracer sources produced from application of this SOP are analyzed for yield determination as documented in the current revision of Pace SOP PGH-R-002, “Gas Flow Proportional Counter Operation.”

3. Summary of Method

3.1 The nuclides listed in Section 1 are first separated from the interfering substances by iron hydroxide or calcium phosphate precipitation, and appropriately dissolved in either a hydrochloric acid or nitric acid solution. Uranium and Plutonium separation can be accomplished using an anion exchange column. Subsequent separation and purification of Americium and Curium are accomplished using Tru-Resin™ columns. For Thorium and Neptunium, separation can be accomplished using either anion exchange or TEVA-Resin™ columns. Additional options are available for isolating uranium using UTEVA-Resin™ and improving Americium/Curium spectral resolution by using TEVA-Resin™ columns.

3.2 A rapid extraction method is also available for the sequential determination of Americium, Neptunium, Thorium, Plutonium, and Uranium.

3.2.1 This particular method requires the use of special tracers to eliminate interferences from nuclides with similar alpha emission energies.

3.3 Following separation, the individual isotopes are micro-precipitated onto a filter and the corresponding alpha activity is determined using an alpha spectrometer.

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3.4 Counting efficiency is determined by micro-precipitating a solution composed of three different energy range alpha standards (such as Cm-244, Pu-239, and Th-230) and counting the sources in each detector of an alpha spectrometry system or using a commercially prepared source with at least 3 different energy range nuclides.

4. Interferences

4.1 Any nuclide with an alpha emission similar in energy to the isotopes in question that cannot be separated from the target nuclide will interfere with this analysis.

4.1.1 It is not always necessary to re-prep samples where both sufficient tracer counts and an interfering nuclide are present.

4.1.2 A clean-up may be performed on the micro-precipitated source to remove the interfering nuclides.

4.1.3 Analysts should consult with the Department Manager/Supervisor or the specified designee on how to proceed.

4.2 Samples that contain isotopes employed as working tracers will lead to an overestimate of yield and low bias in measured results. If the sample activity is known, or can be determined, and the tracer activity corrected to reflect the true concentration of the tracer nuclide present in the sample, accurate results can be obtained.

4.3 Daughters of Th-229 will interfere with Cm-244 analysis. Thorium and americium should be run separately in order to exclude such interferences.

4.3.1 If sample volume limits running these analyses separately, Method 6 (Purification of Americium Using Teva-Resin™) must be performed, subsequent to Method 5 (Purification of Americium Using Tru-Resin™), to remove any thorium decay daughters from the americium/curium fraction.

4.4 Unless isolated separately, Neptunium-237 will interfere with the Pu-242 yield calculation, therefore Pu-236 should be used as a tracer when it is desirable to extract and count plutonium with neptunium on the same counting source.

4.5 Plutonium-236 decays to U-232, which in turn decays to Th-228, therefore it is important to know when the last U-232 separation was performed on the Pu-236 working tracer.

4.5.1 Analysts should be mindful of the potential for a bias in the uranium tracer recovery depending on the length of time since the separation of U-232 from the working tracer.

4.5.2 Plutonium and thorium can be run sequentially if Th-228 is not desired or thorium decay daughters were previously separated from the Pu-236 working tracer.

4.6 Excess fluoride during sample digestions may produce insoluble actinide complexes leading to low yields. Addition of saturated boric acid solution must be performed at the completion of sample digestion to avoid this.

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4.7 Silica in solution may cause problems with uranium and thorium separations and analyte retention on columns.

4.8 Excess carbonate in solution will prevent the iron hydroxide precipitation of the uranium isotopes. To prevent this, it is extremely important to thoroughly boil water samples during the initial precipitation steps of uranium analysis.

4.9 The analysis volume for samples known to contain elevated concentrations of uranium should be controlled so as to limit the quantity of uranium carried through to the final source preparation. Excessive mass contained in the final micro-precipitated count source may negatively affect peak resolution (FWHM) for which there are control limits required by this SOP.

5. Safety

5.1 Procedures must be carried out in a manner that protects the health and safety of all personnel. Since this analysis is for a radioactive constituent, the sample must be treated as radioactive.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.3 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye-protection, gloves, and a lab coat must be worn.

5.4 Exposure to radioactivity and chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous and/or non-radioactive, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 In order to minimize the potential for cross contamination of high and low levels of radioactive samples, good housekeeping and good laboratory practices are essential and must be strictly adhered to.

5.6 Organic samples of unknown content must be handled with extreme caution and under the direct instruction of the Department Manager or Manager-specified designee. Direct treatment of organic matrices with strong oxidizing chemicals such as nitric acid and/or hydrogen peroxide is strictly prohibited.

5.7 Hydrofluoric acid is particularly hazardous because a serious skin exposure may cause no immediate sensation of pain. The acid penetrates the skin and spreads internally, causing tissue damage deep under the skin. The resulting burn is painful, difficult to treat, and easily infected. Gloves must be checked for pinhole leaks before use. They must be rinsed before they are removed and must be discarded after use. HF burn gel shall be put on suspected HF burns after flushing (except the eyes)

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until medical help can be obtained. Medical attention shall be sought even if suspicions arise after working hours. Contact your group leader immediately for further information if a HF burn is suspected.

5.8 In addition, HF vapors are also hazardous. Exposure can cause permanent damage. Breathing HF vapors even for a short time and at a low temperature can be injurious to the respiratory system and even fatal. All such direct contact must be avoided.

5.9 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory.

6. Definitions

6.1 Batch: For all analysis, an analytical batch contains 20 or fewer samples of a similar matrix, prepared at the same time, by the same analyst, using the same reagents.

6.2 SRM: Standard Reference Material.

6.3 Throughout this procedure, approximate weights and measures will be designated by the use of whole numbers when referring to masses exceeding 1g or volumes in excess of 1mL . Measurements of masses and volumes so designated can be made with top loading balances, graduated cylinders, etc. For approximate measures below 1g or 1mL, the word "approximately" must be used prior to the described mass or volume.

6.4 Throughout this procedure, exact or critical masses and volumes will be designated by the use of one or more decimal places. Measurements of weights and volumes so designated should be made with accurate analytical instruments such as analytical balances, calibrated pipettes, etc.

6.5 When aliquotting samples on a balance, the observed mass on the balance must be recorded in preparation logbooks to the lowest weight indicated on the balance. Sample aliquot masses must not be targeted. Once sample is removed from the sample container and transferred to a beaker, it must not be removed from the beaker.

6.6 The method utilized for obtaining the sample aliquot, whether on a balance, in a graduated cylinder, or by pipette, must be clearly annotated in the preparation logbook.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

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7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Aqueous Samples

8.1.1 Containers used for sample collection must never be re-used. Either plastic or glass containers may be used for sample collection.

8.1.1.1 Aqueous samples must be preserved at the time of collection by adding enough concentrated (16N) HNO_3 to the sample to make the sample pH <2. Typically, 2mL of 16N HNO_3 per liter of sample is sufficient to obtain the desired pH. Samples must be preserved within five days of collection. If samples are collected without preservation, they must be received by the laboratory and preserved within five days of collection. Following preservation with acid, samples must be held in the

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original container for a minimum of 16 hours before analysis or transfer of sample. For samples preserved at the time of receipt, the pH must be re-checked by laboratory personnel prior to removing sample for analysis. The pH re-check date and time, the initials of the analyst verifying the pH, as well as any adjustments or notes regarding the preservation must be recorded in the pH Verification Logbook.

8.1.1.2 mLFor dissolved analysis, samples must be filtered through a 0.45□m membrane filter and then preserved to a pH <2.

8.1.1.3 For total analysis, the sample is not filtered, but is preserved to a pH<2.

8.1.2 Refrigeration is not required for aqueous or solid samples, but is recommended for all biological samples, especially urine.

8.1.3 Urine: It is recommended that the sample be preserved before a sample aliquot is taken to ensure that the requested analytes do not adhere to the sample container.

8.1.3.1 This is especially true if the sample has visible solids present.

8.1.3.2 Analysts should consult with the Department Manager/Supervisor or specified designee for direction on such samples.

8.1.4 The maximum hold time for samples analyzed by this procedure is 180 days between sample collection and sample analysis.

9. Equipment and Supplies

9.1 Multi-channel Analyzer:

9.2 Alpha Spectrometer: Refer to SOP PGH-R-020, current revision “Alpha Spectroscopy Instrument Operation” for instructions on alpha spectroscopy system operation.

9.3 Electric hot plate or griddle.

9.4 Ion exchange columns, 2mL, disposable from Eichrom or equivalent.

9.5 TRU, TEVA, and UTEVA cartridges from Eichrom.

9.6 Vacuum box apparatus and applicable parts, disposable yellow and white tips, 10-50mL syringe barrels, etc from Eichrom or equivalent.

9.7 Polypropylene filters, 25mm, 0.1µm pore size from Environmental Express, or equivalent.

9.8 PTFE FEP Beakers, 100mL size and other assorted sizes, or equivalent.

9.9 Multi-port vacuum filtering apparatus for 25mm filters (referred to as the filter rig).

9.10 Miscellaneous glassware: beakers, watch glass covers, and stir rods.

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9.11 Membrane Filters, 5.5cm diameter, 0.45µm pore size.

9.12 Analytical Balance: Sensitivity to 0.1mg, capacity 0 - 160g.

9.13 Vacuum filtration apparatus for 5.5cm diameter membrane filters.

9.14 General-purpose centrifuge and disposable centrifuge tubes, 50mL made of high-density polyethylene or equivalent.

9.15 Vortex mixer.

9.16 Liquid scintillation vials, glass.

9.17 Muffle oven capable of 105ºC to 550ºC, with or without ramping capabilities.

9.18 Software supplied with the instrument to control instrument operation. Refer to SOP PGH-R-020, current revision "Alpha Spectroscopy Instrument Operation" for applicable software details.

9.19 Computer capable of running the Alpha spectrometer Counter System software, monitor, mouse, keyboard, and printer. Refer to SOP PGH-R-020, current revision "Alpha Spectroscopy Instrument Operation" for computer hardware specifications.

10. Reagents and Standards

10.1 Reagents must be prepared from reagent grade chemicals, unless specified otherwise. Distilled or deionized (DI) water. ASTM Type II as produced using the specifications documented in SOP PGH-C-027, current revision. Consult the Safety Data Sheets for the properties of these reagents, and how to work with them.

10.2 Anion exchange resin, Bio-Rad AG 1x8 (100 - 200 mesh, Cl^- form) or equivalent. Slurry the resin in a squirt bottle with ASTM Type II DI water.

10.3 Ammonium Bioxalate, 0.1N: Dissolve 6.31g oxalic acid and 7.11g ammonium oxalate in 750mL of ASTM Type II DI water and dilute to 1L with ASTM Type II DI water.

10.4 Ammonium Hydroxide, 15N, concentrated, sp. gr. 0.90, 56.6%.

10.5 Ammonium Hydrogen Phosphate, 3.2M: Dissolve 104 g of $(NH_4)_2HPO_4$ in 200mL of ASTM Type II DI water and dilute to 250mL with ASTM Type II DI water.

10.6 Ammonium Thiocyanate, 6M: Dissolve 476g ammonium thiocyanate in 300mL of ASTM Type II DI water and dilute to 1.0L with ASTM Type II DI water.

10.6.1 CAUTION! The reaction is extremely exothermic and the bottle may become very slippery.

10.7 Ammonium Thiocyanate, 3M/ 0.1N Formic acid: Dilute 250mL 6M ammonium thiocyanate and 50mL 1.0N formic acid to 500mL with ASTM Type II DI water. Prepare fresh daily.

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10.8 Ammonium Thiocyanate, 1M/ 0.1N Formic acid: Dilute 100mL 6M ammonium thiocyanate and 60mL 1.0N formic acid to 600mL with ASTM Type II DI water. Prepare fresh daily.

10.9 Ascorbic Acid, 1.0M: Dissolve 17.6g ascorbic acid into 50mL ASTM Type II DI water and dilute to 100mL with ASTM Type II DI water. Prepare weekly.

10.10 Ascorbic Acid, 1.5M: Dissolve 26.4g ascorbic acid into 50mL ASTM Type II DI water and dilute to 100mL with ASTM Type II DI water. Prepare weekly.

10.11 Boric Acid, 5% Saturated Solution: Add 50g granulated boric acid to 500mL ASTM Type II DI water and dilute to 1L with ASTM Type II DI water. The boric acid should not completely dissolve.

10.12 Calcium Carrier (60mg/mL): 176.76g $Ca(NO_3)_2$ $4H_2O$ diluted to 500mL with ASTM Type II DI water.

10.13 Distilled or deionized DI water. Resistance value between 0.5 and 2.0 Mmhos (2.0 to 0.5µohms/cm specific conductivity) at 25˚C.

10.14 Deionized Water adjusted to a pH of 10.0 by the addition of 6-8 drops of ammonium hydroxide to each 500mL of DI.

10.14.1 The pH should be checked prior to each addition of ammonium hydroxide, since it is not always necessary to add the full 6-8 drops each time pH 10 DI is made up.

10.15 Ethanol, 80%. 800mL of reagent grade alcohol mixed with 200mL of ASTM Type II DI water.

10.16 Ferrous Sulfamate, 0.6N: In a 2L beaker, add 285g sulfamic acid to 750mL ASTM Type II DI water. Heat the solution on a hotplate until the sulfamic acid is completely dissolved. While stirring, carefully add 2-3galiquots of iron powder to the solution until a total of 35g has been added. Let the reactions in the beaker subside, and filter the solution through a 5.5cm glass fiber filter. Dilute the solution to 1L with ASTM Type II DI water. Prepare weekly.

10.17 Formic acid, concentrated, 88%.

10.18 Formic acid, 1.0N: Dilute 42.5mL concentrated formic acid to 1.0L with ASTM Type II DI water.

10.19 Hydrochloric acid, 12N, concentrated, sp. gr. 1.19, 37%.

10.20 Hydrochloric acid, 9N / 0.10% Hydrogen Peroxide: For every 100mL of 9N HCl, add 0.1mL of 30% H_2O_2. Shake well and allow to sit for 5 minutes prior to use. Prepare daily.

10.21 Hydrochloric acid, 9N: Dilute 750mL concentrated 12N HCl to 1L with ASTM Type II DI water.

10.22 Hydrochloric acid, 6N: Dilute 500mL concentrated 12N HCl to 1L with ASTM Type II DI water.

10.23 Hydrochloric acid, 4N: Dilute 332mL concentrated 12N HCl to 1L with ASTM Type II DI water.

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10.24 Hydrochloric acid, 0.1N: Dilute 8.3mL concentrated 12N HCl to 1L with ASTM Type II DI water.

10.25 Hydrochloric acid, 6N / 0.52N Hydrofluoric acid Solution: Dilute 500mL of concentrated 12N HCl and 18mL of concentrated HF to 1L with ASTM Type II DI water.

10.26 Hydrochloric acid, 9N / 0.05M Ammonium Iodide Solution: For every 100mL of 9N HCl, add 0.724g of NH_4I solid. Shake well and let stand for 5 minutes prior to use. Prepare daily.

10.27 Hydrochloric acid, 0.1N / 0.05N Hydrofluoric acid / 0.015M rongalite solution: Dilute 8.3mL conc. 12N HCl, and 1.7mL conc. HF acid, and 2.31g sodium formaldehyde sulfoxylate dihydrate to 1L with ASTM Type II DI water.

10.28 Hydrazine Dihydrochloride, 25% So lution: 25g hydrazine dihydrochloride dissolved in 75mL of ASTM Type II DI water.

10.29 Hydrogen Peroxide (30%) H_2O_2.

10.30 Hydrofluoric acid, 29N, concentrated, sp. gr. 1.18, 49%. Must be stored in a plastic container.

10.31 0.1% Hydrofluoric acid: Dilute 1.0mL concentrated HF to 1L with DI.

10.32 Iron Carrier: 10.0mg Fe/ml: Dissolve 72.4 g $[Fe(NO_3)_3]$ 9 H_2O in 500mL of ASTM Type II DI water and dilute to 1L with ASTM Type II DI water.

10.33 Neodymium carrier (0.5mg/mL): Dilute 5.0mL of 10mg/mL of neodymium carrier to 100mL of ASTM Type II DI water.

10.34 Nitric acid, 16N, concentrated, sp. gr. 1.42, 70%.

10.35 Nitric acid, 2N: Dilute 125mL of conc. 16N HNO_3 to 1L with DI water.

10.36 Nitric acid, 3N: Dilute 188mL of conc. 16N HNO_3 to 1L with DI water.

10.37 Nitric acid, 8N: Dilute 500mL of conc. 16N HNO_3 to 1L with DI water.

10.38 Nitric acid, 2N / 0.5M $Al(NO_3)_3$: Dissolve 188g aluminum nitrate nonahydrate in 500mL of ASTM Type II DI water. Add 125mL conc. 16N HNO_3 to the solution and then dilute to 1L with ASTM Type II DI water.

10.39 Nitric acid, 3N/ 1.0M $Al(NO_3)_3$: Dissolve 376g aluminum nitrate nonahydrate in 500mL of ASTM Type II DI water. Add 188mL of conc. 16N HNO_3 and dilute to 1L with ASTM Type II DI water.

10.40 Nitric acid, 0.02N/ 0.02N Hydrofluoric acid: Dilute 1.28mL conc. 16N HNO_3 and 0.72mL of conc. HF to 1L with ASTM Type II DI water.

10.41 Nitric acid, 2.5N/ 0.1N ferrous sulfamate: Dilute 159mL conc. 16N HNO_3 to 500mL and add 167mL 0.6N ferrous sulfamate. Dilute the solution to 1L with ASTM Type II DI water. Prepare daily.

10.42 Nitric acid, 2.5N: Dilute 159mL conc. HNO_3 to 1L with ASTM Type II DI water.

10.43 Nitromethane, ACS reagent.

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10.44 Potassium Thiocyanate Solution, 0.1N: purchased ready made from Fisher Scientific, or equivalent.

10.45 Sodium Nitrite, 4M: Dissolve 27.6g of sodium nitrite in 50mL ASTM Type II DI water and dilute to 100mL with ASTM Type II DI water. Prepare fresh daily.

10.46 Sulfamic acid, 1.5M: Dissolve 145.64g sulfamic acid in 750mL with ASTM Type II DI water. Place the solution on a hot plate set at low heat and stir occasionally. Once the sulfamic acid is completely dissolved, filter the solution through a glass fiber filter and dilute it to 1L with ASTM Type II DI water. Prepare fresh weekly.

10.47 Tru-Resin™: Eichrom Inc., Mix 100g (s-grade) of Tru-Resin with 428mL ASTM Type II DI water and 2mL of conc. 16N HNO_3.

10.48 TEVA-Resin™: Eichrom Inc., Mix 100g (s-grade) of TEVA-Resin with 428mL of ASTM Type II DI water and 2mL conc. 16N HNO_3.

10.49 Titanium (III) Chloride: 10% wt. Solution.

10.50 Standards

10.50.1 Tracer: A solution containing Am-243, Np-239 (prepared from Am-243), Pu-242, Pu-236, Th-229, Th-234 (prepared from U-238), or U-232 prepared from a NIST-traceable and certified solution, or equivalent. Tracer spike aliquots shall have DPM values consistent with the activity of the samples. Check the certificate for the expiration date.

10.50.2 Laboratory Control Sample (LCS)

10.50.2.1 Liquid: A solution of Am-241, Cm-244, Pu-239, Pu-241, Np-237, Th-230, or U-238 prepared from a NIST-traceable and certified source, or equivalent. Check the calibration certificate for the expiration date.

10.50.2.2 Solid: A soil containing Am-241, Cm-244, Pu-239, Pu-241, Np-237, Th-230, or U-238 prepared from a NIST-traceable and certified source, or equivalent. Check the certificate for the expiration date.

Note: Equivalent is defined as being traceable to any international source that provides a certificate of calibration. As the project requires, a solution may be used where the isotopic activity has been confirmed by multiple laboratory analyses.

11. Calibration

11.1 Plated sources can be purchased from a NIST supplier, but they must have the same size effective area and they must be positionable so the effective area is the same distance from the detector as those sources prepared for sample counting.

11.2 If plated sources cannot be purchased, sources can be prepared using NIST traceable standards as follows.

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11.3 Sources for alpha spectroscopy system calibration must be prepared in a fashion that will ensure >99% recovery of each calibration source analyte.

11.4 Concentrated standards or SRMs that limit the volume of the standard to less than 0.5mL per radioisotope must be used in order to ensure that the acid concentration is kept as dilute as practical. Quantitative precipitation of many actinides from acid solutions with concentrations greater than 0.5N is impossible and will lead to erroneous results.

11.5 Transfer an appropriate volume or mass of analytical standard to a labeled, disposable centrifuge tube. Record the standard numbers utilized and mass or volume information in the appropriate standard dilution logbook. Dilute the combination of standards to 20mL with 0.1N HCl.

11.6 Add the following to the solution in the centrifuge tube:

11.6.1 0.1mL of neodymnium carrier solution (0.5mg/mL)

11.6.2 Four drops of the iron carrier solution.

11.6.3 Seven drops of the 1M ascorbic acid solution

11.6.3.1 This reduces the iron to the +2 state.

11.6.3.2 Proper reduction of iron will result in a clear, colorless solution.

11.7 Cap each tube and swirl the solution to mix the contents. Place tubes in a warm water bath to ensure proper equilibration between the carrier and the radioisotopes.

11.8 After five minutes, add 3mL concentrated HF acid to each source and swirl the source to mix the contents. Let the sources sit in the warm water bath for 15 minutes, then remove them, and allow them to cool for 15 minutes.

11.9 Prepare a filter apparatus by placing a filter funnel into an HDPE vacuum flask. Turn on the vacuum and rinse the apparatus with severalmLs of ASTM Type II DI water.

11.10 Carefully wash and rinse a filter funnel that is dedicated to, and set aside for, the preparation of calibration sources.

11.11 Place a polypropylene filter onto the filtering apparatus and ensure it is centered.

11.12 Place the clean filter funnel on the rig and secure it, being careful not to rip the filter in the process.

11.13 Rinse the inside surface of each funnel with the 80% ethanol solution then rinse the inside surface of each funnel with approximately 10mL of ASTM Type II DI water.

11.14 Transfer the calibration solution to the filter funnel and allow it to pass through the filter. After all of the calibration solution has passed through the filter, rinse the centrifuge tube with approximately 5mL of the 80% ethanol solution and transfer it to the filter funnel as a rinse.

11.15 Rinse the inside of the funnel with an additional 2-3mL of the 80% ethanol solution.

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11.16 Label the metal backside of a one inch counting disk with the appropriate standard number as determined from the standard preparation logbook, and remove the paper backing from the pre-taped side of the disk.

11.17 Remove the filter funnel and carefully remove the calibration filter from the filtration rig and affix it to the disk.

11.18 Allow the disk to air dry for a minimum of 15 minutes.

11.19 When the calibration source has dried, place it in a labeled petri dish and submit it to the count room for counting.

11.20 Perform calibration of alpha spectrometry detectors as specified in the current version of Pace SOP PGH-R-020, "Alpha Spectroscopy Instrument Operations". Count sources long enough to obtain a minimum of 10000 net counts in each of the three nuclides regions of interest.

11.21 Transfer the contents of the vacuum flask to a 600mL PTFE beaker.

11.21.1 Rinse the flask three times with 50mL of ASTM Type II DI water and add the rinses to the beaker.

11.22 Evaporate the solution to dryness on a hotplate on a low to medium heat setting.

11.23 Carefully add 10mL of concentrated nitric acid and 1mL of 30% hydrogen peroxide solution to the beaker and evaporate the solution to dryness.

11.24 Carefully add 10mL of concentrated nitric acid and 1mL of 5% boric acid solution to the beaker and evaporate the solution to dryness.

11.25 Dissolve the residue into 20mL of 8N nitric acid solution by heating the solution.

11.26 Allow the solution to cool, then transfer it to a 100mL volumetric flask.

11.26.1 Rinse the beaker three times with 10mL of ASTM Type II DI water and add the rinses to the volumetric flask.

11.26.2 Dilute the solution to the mark with ASTM Type II DI water.

11.26.3 Transfer the diluted calibration effluent to a labeled HDPE bottle.

11.27 Analyze 10mL of each calibration effluent sample for gross alpha content using the most recent revision of SOP PGH-R-001.

11.27.1 Calculate the total alpha content for the entire source effluent.

11.27.2 Calculate the total alpha activity of each calibration source.

11.27.3 Compare the total effluent activity to the theoretical activity to ensure that the effluent contains less than 1% of the total activity. Calibration sources must contain >99% of each analyte in order to be accepted for calibration purposes.

11.27.4 Consult with the Department Manager/Supervisor or specified designee if the sources are not acceptable.

11.28 The Plutonium-241 calibration is performed separately on a liquid scintillation counter. Add 1000 to 2000 dpm of Pu-241 by mass to ten,

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labeled, glass scintillation vials. Add 1.0mL of concentrated HCl to each vial and heat the sources to dryness on a hotplate.

11.29 Add 1.0mL of 0.1N HCl to each vial to dissolve the residue. Then add 15mL of Ultima Gold AB liquid scintillation cocktail to each vial. Cap each vial and shake it vigorously to mix the contents.

11.30 Establish variations in quench by carefully opening the vials and adding nitro methane to each vial in increasing increments. Nitro methane is not added to one of the vials and not to the background vial. For example, add 10 µL to one vial, 20 µL to another, 40 µL, 70 µL, 100 µL and so on, documenting the amount of nitro methane added to each vial for future reference.

11.31 Count calibration sources according to the Pace SOP, PGH-R-022, "Liquid Scintillation Counter Operations". Count the samples long enough to obtain 10,000 net counts in the Pu-241 window. Count times will vary from source to source based on the quench factor. Adjust the amount of nitro methane in each vial and recount the set as necessary to achieve the most representative range of values for the quench curve.

11.32 Calculate the Pu-241 efficiency based on the quench values using Microsoft Excel or equivalent curve plotting software.

12. Procedure

Unless specified otherwise, the documented analysis process must be followed, as written, including the order of analytical process and the addition of chemicals.

12.1 Waters and Liquids, Including Drinking Water

12.1.1 Shake each sample and weigh 300g of aqueous sample into an appropriately sized beaker. Record the observed measured mass of sample to the lowest decimal on the balance. Do not remove sample from the beaker once it has been added. The actual quantity of sample used may be less than 300g if matrix interferences are expected or there is limited sample quantity available to the laboratory. If less than 300g of sample is used, dilute the sample with ASTM Type II DI water to the 300mL mark on the beaker. Fortify the pH of diluted samples by adding 2mL of HNO_3.

12.1.1.1 For the rapid extraction method proceed to step 12.6.4 and prepare the samples as specified for a urine matrix.

12.1.2 Prepare appropriate batch Quality Control samples including a Method Blank, Laboratory Control Sample (LCS), and LCS Duplicate (LCSD) by weighing an appropriate quantity of ASTM type II ASTM Type II DI water to an appropriate size beaker. To each QC sample add 5mL of concentrated 16N HNO_3.

12.1.3 Add the applicable spikes to the appropriate QC samples in the amounts specified in Section 14 of this SOP. Add a pre-selected amount of the applicable working tracers to each of the samples and QC samples.

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12.1.4 Add 1mL of iron carrier to each sample.

12.1.5 If there is a significant amount of residue present in the sample,

12.1.5.1 Filter the sample through a 0.45µm Metricel™ filter.

12.1.5.1.1 Transfer filtered sample to a labeled glass beaker

12.1.5.1.2 Transfer the Metricel™ filter and the residue to a labeled PTFE beaker.

12.1.5.2 To digest the filter and solids, add 10mL conc. 16N HNO_3, 10mL conc. 12N HCl, and 10mL conc. HF to the PTFE beaker. Cover the PTFE beaker with a cover and reflux on a hotplate for one hour.

12.1.5.3 Remove the cover and continue to heat the sample to dryness.

12.1.5.3.1 Repeat Step 12.1.5.2 as necessary based on the amount of residue remaining.

12.1.5.4 Dissolve the residue in 10mL conc. 12N HCl and 1mL saturated boric acid. Place the sample back on the hot plate and heat it to dryness again.

12.1.5.5 Dissolve the digested filter in 10mL of conc. 16N HNO_3. Place the sample back on the hotplate and heat to dryness.

12.1.5.6 Dissolve the digested filter in 10mL conc. 16N HNO_3. Use 8N HNO_3 to transfer the digested filter into the corresponding glass beaker (12.1.5.1.1) that contains the filtered aqueous sample fraction.

12.1.6 Place a watch glass on the glass beaker to cover the sample and heat it to boiling on a hotplate for a minimum of one hour.

12.1.7 Carefully add severalmLs of conc. 15N NH_4OH to the sample while stirring until the pH of the sample is adjusted to 10 and a visible precipitate forms within the sample.

12.1.8 Heat the sample to boiling for another thirty minutes or longer, until an iron hydroxide precipitate breaks up into small particles.

12.1.9 Remove the sample from the hot plate and allow it to cool and the precipitate to settle.

12.1.10 Decant the excess supernate from the sample and discard it in the appropriate waste stream. Transfer the precipitate to a labeled disposable centrifuge tube with pH 10 ASTM Type II DI water.

12.1.11 Centrifuge the sample, and discard the supernate in the appropriate waste stream.

12.1.12 Rinse the iron precipitate with at least double its volume in pH 10 ASTM Type II DI water.

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12.1.12.1 Vortex and centrifuge the sample. Discard the rinse in the appropriate waste stream. This rinse will eliminate excess ammonium hydroxide.

12.1.13 Proceed to the appropriate separation method beginning in Section 12.7. For Uranium in drinking water analysis, perform the uranium-specific method detailed in section 12.7.

12.2 Filter Samples

12.2.1 If the filter is cellulose:

12.2.1.1 Place a representative portion depending on the client requirements or radioactivity levels of the sample (usually one half or one quarter) of the filter into a clean ceramic crucible and pipette a selected amount of the working tracers onto it.

12.2.1.2 Cover the sample with aluminum foil and heat sample in a muffle furnace to ash filter.

12.2.1.2.1 Use the temperature ramping guidelines in the current revision of the sample preparation SOP.

12.2.1.2.2 NOTE: Mark the PACE sample ID on each crucible with a high temperature wax pencil.

12.2.2 If the filter is glass fiber or otherwise non-organic:

12.2.2.1 Place a suitable portion of the filter into a PTFE beaker and pipette a selected amount of the working tracers onto the sample.

12.2.3 Proceed to step 12.4.3 for the sample digestion.

12.3 Biota Samples

12.3.1 Samples must be prepared in accordance with the current Pace SOP, PGH-R-024, “Radchem Sample Preparation” prior to analysis.

12.3.2 Weigh a suitable amount of ashed sample into a PTFE beaker and pipette a selected amount of the working tracers onto the sample. Add 1mL iron carrier to the sample beaker.

12.3.3 Proceed to step 12.4.3.

12.4 Soil and Vegetation Samples

12.4.1 Weigh a suitable amount of the dried sample into a ceramic crucible and pipette a selected amount of the working tracers onto the sample. Prepare a crucible designated as the LCS and LCSD if applicable and spike with the appropriate spike solutions. Add 1mL iron carrier to the samples and QC samples.

12.4.2 Cover the crucible with a ceramic lid and place the crucible into a cold muffle furnace. Set the final temperature at 550ºC. Once this temperature has been reached, maintain for at least 4 hours or longer depending on the amount of material in the crucible.

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12.4.2.1 At the end of 4 hours, turn off the oven, allow the samples to cool to room temperature, and remove the samples from the furnace.

12.4.3 Remove the crucibles and re-label the crucibles. Add 10mL of conc. HNO_3 and 10mL of conc. HCl to the sample and heat it to dislodge the solids.

12.4.4 If the soil/solid sample does not require uranium or thorium then proceed to 12.5. Otherwise transfer the sample to a clean, labeled PTFE beaker.

12.4.4.1 Use a PTFE scraper to remove any residue that is stuck to the bottom of the crucible and rinse it into the PTFE beaker with 9N HCl.

12.4.5 Add 10mL of conc. HF to each sample in the PTFE beaker and then cover with a PTFE watch glass.

12.4.6 Reflux on an electric griddle or hotplate set at 250ºC for a minimum of thirty minutes. After 30 minutes, remove the watch glass cover and allow the sample to evaporate to dryness.

12.4.7 Add 10mLconc. HCl, 10mL conc. HNO_3, and 10mL conc. HF to the sample. Return the sample to the griddle, and allow it to evaporate dryness. This process may be repeated as often as necessary to ensure complete dissolution of the sample. In some matrices, high temperature oxides have been formed which severely limit analyte recovery. These highly insoluble oxides must be treated with repeated and prolonged contact with mineral acid. Acids must cover the samples for multiple days at low heat in order to properly dissolve the sample.

12.4.8 Add 10mL conc. HNO_3 and 10mL conc. HCl to the sample. Return the sample to the griddle and allow it to evaporate to dryness.

12.4.9 Add 10mL 12N HCl or 16N HNO_3 depending on the acid used for the load solution in order to minimize complexants. (For example, if the load solution for the column work will be 15mL 8N HNO_3, add 10mL 16N HNO_3 to the sample for the final cookdown to remove as much chloride as possible.) Add 1mL saturated boric acid to the sample and return it to the griddle and allow it to evaporate to dryness.

12.4.10 Dissolve the sample in the appropriate load solution depending on the column method to be utilized, for example 8N HNO_3 for uranium and thorium isolation using nitric conditioned anion columns, or 9N HCl/H_2O_2 for americium and plutonium isolation using chloride conditioned anion columns.

12.4.11 Heat to aid in dissolution of the sample solids. Scrape the bottom of the beaker to dislodge any solids. Centrifuge the sample as necessary prior to loading the sample onto columns.

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12.4.12 If the sample is suspected of containing interferences such as carbonate or lanthanides:

12.4.12.1 Dissolve the sample into 5mL 9N HCl and 30mL ASTM Type II DI water.

12.4.12.2 Heat the sample to aid in dissolution.

12.4.12.3 Stir the sample as necessary to aid the dissolution of solids on the bottom of the beaker.

12.4.12.3.1 For the rapid extraction method, dilute the sample to 300mL with ASTM Type II DI water and proceed to Step 12.6.4 and continue to prepare the sample as if a urine.

12.4.12.4 Transfer the sample to a 50mL disposable centrifuge tube and dilute it to 40mL with pH 10 adjusted ASTM Type II DI water.

12.4.12.5 Carefully add 5-7mL conc. 15N NH_4OH to the sample. Cap the tube and shake it to mix the solution.

12.4.12.6 Centrifuge the sample and discard the supernate.

12.4.12.7 Rinse the iron precipitate with at least double its volume in pH 10 ASTM Type II DI water.

12.4.12.8 Vortex and centrifuge the sample. Discard the rinse in the appropriate waste stream. This rinse will eliminate excess ammonium hydroxide.

12.4.13 Proceed to the appropriate separation method beginning in section 12.7.

12.5 Soil leach for samples not requiring Uranium or Thorium

12.5.1 Transfer the muffled and traced sample from the crucible to a labeled 100mL glass beaker. A larger beaker may be used if necessary.

12.5.2 Add 15mL HNO_3 and 5mL of HCl to each sample and cover with a watch glass. More acid may be necessary for larger aliquots but the ration of 3:1 should remain the same.

12.5.3 Reflux on a hotplate or griddle for a minimum of thirty minutes at medium to low heat. Samples must be kept from over heating, boiling or bumping.

12.5.4 Remove the samples from the hotplate and allow them to cool. Slurry the samples in the beaker and transfer the leachate and solids to a clean, labeled centrifuge tube with the aid of ASTM Type II DI water.

12.5.5 Centrifuge the samples for 15 minutes at maximum speed.

12.5.6 Decant the leachate to a 250mL labeled glass beaker. Place this beaker on a hotplate at medium and evaporate to dryness.

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12.5.7 To the solids in the centrifuge tube repeat the steps from 12.5.2 to 12.5.6 using the same labeled glass beaker until the solids appear light gray or tan.

12.5.8 After evaporating to dryness, solids must be converted to the appropriate acid type by treatment with a quantity of the appropriate concentrated acid. If the chemistry load solution is to be a nitrate column, add 10mL of concentrated nitric acid and evaporate to dryness. Likewise, if the chemical load solution is chloride-based, add 10mL of concentrated HCl and evaporate to dryness. This step is not necessary for the isotopic plutonium/neptunium analysis.

12.5.9 Proceed to the appropriate separation method beginning in Section 12.7.

12.6 Urine Samples

12.6.1 Using a clean graduated cylinder, measure a specified amount of urine into a clean and labeled glass beaker. Prepare QC samples (MB, LCS, LCSD) using an equivalent amount of ASTM Type II DI water and 5mL of concentrated HNO_3.

12.6.2 Pipette the appropriate amount of spike solution into the applicable QC samples. Pipette a selected amount of the required working tracers into each sample.

12.6.3 Check the pH of the sample.

12.6.3.1 If the sample has not been preserved, carefully add concentrated nitric acid to the sample while stirring it the with a stir rod until pH <2 is achieved.

12.6.3.2 Add conc. HNO_3 up to an amount equivalent to ten percent of the sample aliquot volume. (i.e., 40mL of acid per 400mL of sample aliquot.) Check the pH to ensure it is less than 2.0. Add more nitric acid as necessary.

12.6.4 Add 1.0mL of the calcium carrier to the sample and cover it with a watch glass. Heat the sample to near boiling for a minimum of two hours on a hotplate.

12.6.5 Add 0.2mL of 3.2N ammonium hydrogen phosphate to each sample and stir.

12.6.6 Remove each sample individually from the hotplate and while stirring, carefully add conc. 15N NH_4OH to it until the pH has been adjusted to a pH of 9.0 and a white calcium phosphate precipitate forms.

12.6.7 Replace the sample(s) on the hotplate and heat them to boiling for an additional hour, then remove them from the hotplate and allow them to cool overnight.

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12.6.8 Suction the supernate from each sample into a vacuum flask and transfer the precipitate to a centrifuge tube, and centrifuge.

12.6.9 Discard the supernate and rinse the precipitate with 25mL ASTM Type II DI water and centrifuge. Discard the supernate (rinse).

12.6.10 Dissolve the precipitate in 10mL conc. HNO_3 and transfer it to a glass beaker.

12.6.10.1 Rinse the centrifuge tube with two additional 5mL conc. HNO_3 rinses, and transfer these to the glass beaker.

12.6.11 Heat the samples on a hotplate and slowly add 2mL of H_2O_2 to each sample. Continue to heat the samples and allow them to evaporate to dryness.

12.6.12 Add 5mL of conc. HNO_3 and 1mL H_2O_2 to each sample and continue to heat them allowing them to evaporate to dryness.

12.6.12.1 Repeat Step 12.6.12 as necessary until the residue is white to light yellow in color.

12.6.13 Proceed to the appropriate separation method beginning in Section 12.7.

12.7 Method 1: Separation of Actinides on Anion Resin Using Hydrochloric Acid Solution

12.7.1 This method uses an anion exchange resin and the parameters dissolved in a hydrochloric acid solution to separate and purify any of the following groups of actinides.

- Americium, Plutonium (Neptunium), and Uranium
- Thorium, Plutonium (Neptunium), and Uranium
- Plutonium, Neptunium, and Uranium

12.7.1.1 This is the default method for waters, biota, and soils (less than 2 grams) where little or no interferences are expected to be present.

12.7.1.2 It is not easy to separate americium/curium from thorium using this method, so if sequential analysis requires both analyses be performed on a single aliquot, start with Method 2 to isolate the thorium fraction first from all of the other nuclides.

12.7.1.3 This method may be modified to accommodate larger solids samples (equivalent to10g) by the increase of the load and rinse solution volumes, and the use of a larger column with either a 7cm or 10mL resin bed. These increased volumes are in brackets and double brackets, respectively, at the end of each applicable step. Analysts must consult with the Department Manager/Supervisor or specified designee prior to beginning analysis on such samples.

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12.7.2 Dissolve the sample precipitate in 15mL of 9N HCl / 0.10% H_2O_2. The hydrogen peroxide need only be used if plutonium will be isolated. [50mL] or [[100mL]]

12.7.3 Prepare a 2mL resin column using Bio-Rad AG 1x8.

12.7.3.1 Slurry the resin with ASTM Type II DI water to give a resin bed of about 3cm. The final resin volume must be consistent for all columns.

12.7.3.2 Once the ASTM Type II DI water has drained, condition the column with 10mL of 9N HCl. [7cm column conditioned with 40mL] or [[10mL column conditioned with 75mL]]

12.7.4 If heated, allow the sample to cool, then transfer it to the prepared resin column.

12.7.5 Collect the effluent from the column in a clean labeled centrifuge tube if either americium/curium or thorium analysis is desired.

12.7.5.1 Rinse the sample beaker or centrifuge tube with an additional 10mL 9N HCl / 0.10% H2O2 and collect. [25mL] or[[50mL]]

12.7.5.2 Rinse the column with 20mL of 9N HCl and collect. [40mL] or [[80mL]]

12.7.5.3 Transfer the contents of the centrifuge tube to a clean labeled glass beaker.

12.7.5.4 If the contents are to be analyzed for americium/curium, proceed to Method 3: Americium/Curium Purification on TRU-Resin™ for americium/curium analysis.

12.7.5.5 If the contents are to be analyzed for thorium, proceed to Method 5: Thorium Purification on TEVA-Resin™ for thorium analysis.

12.7.6 Elute the plutonium from the column into a clean, labeled glass beaker with 20mL 9N HCl / 0.05N NH_4I. [40mL] or [[80mL]]

12.7.6.1 If analysis for plutonium is not required, do not perform this step.

12.7.6.2 Add 10mL conc. HNO3 and 3-4 drops of the iron carrier to the plutonium fraction.

12.7.6.3 Allow enough time for the nitric acid and the hydrochloric acid to react.

12.7.6.4 With a disposable pipette, and in a drop wise fashion, slowly add approximately 1mL of 30% H_2O_2 to the solution.

12.7.6.5 Place the beaker on a hotplate and allow the plutonium fraction to evaporate to dryness.

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12.7.6.6 Add 5mL concentrated HCl to each beaker and evaporate the contents to dryness on a hotplate.

12.7.6.7 Dissolve the residue in the beaker with 10mL 9N HCl.

12.7.6.8 Transfer the plutonium fraction to a labeled centrifuge tube with ASTM Type II DI water and dilute to 20mL with ASTM Type II DI water.

12.7.6.9 Proceed to Step 12.15.2, Micro-Precipitation of Plutonium.

12.7.7 Rinse the column with 15mL of 6N HCl / 0.52N HF, which will elute any neptunium from the sample.[30mL] or [[75mL]]

12.7.7.1 Proceed to Step 12.15.5 for the Micro-Precipitation of Neptunium.

12.7.7.2 If analysis for neptunium is not required, discard the effluent.

12.7.8 Rinse the column with 10mL of 9N HCl and discard the effluent. [20mL] or [[35mL]]

12.7.9 Elute the uranium fraction from the column into a clean, labeled centrifuge tube with 20mL of 0.1N HCl. [40mL] or [[100mL]]

12.7.9.1 Proceed to Step 12.15.3 for the Micro-Precipitation of Uranium.

12.8 **Method 2: Separation of Actinides on Anion Resin using Nitric Acid Solution**

12.8.1 This method uses an anion exchange resin and the parameters dissolved in a nitric acid solution to separate and purify the following group of actinides.

- Americium, Plutonium and Uranium from Thorium

12.8.1.1 This method is best used for solids (any amount), waters, or filters (organic based, cellulose), and when it is desirable to reuse the resin column.

12.8.1.2 This method can be modified to accommodate plutonium, uranium and thorium on solids (less than two grams) by using sodium nitrite. It can also be used larger solid samples through the use of a 7cm column and resin bed, and the use of the adjusted volumes that are indicated at the end of each applicable step by brackets.

12.8.2 Dissolve the sample into 15mL of 8N HNO_3/ 2% Sodium Nitrite solution. [50mL] Exclude the sodium nitrate if plutonium is to be isolated later using Method 1.

12.8.2.1 Heat the solution if necessary to aid in the dissolution of the precipitate.

12.8.3 Prepare a 2mL resin column with Bio-Rad AG 1x8.

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12.8.3.1 Slurry the resin with ASTM Type II DI water to give a resin bed of about 3cm. [7cm columns]

12.8.3.2 When the ASTM Type II DI water has drained, condition the column with 20mL 8N HNO_3. [50mL]

12.8.4 Cool the sample and transfer it to the prepared resin column.

12.8.4.1 Collect the effluent from the column in a clean glass beaker if uranium analysis is required. (If sodium nitrite is omitted from the load solution, this fraction will also contain Americium and Plutonium.)

12.8.4.2 Rinse the column with an additional 15mL 8N HNO_3/ (2% Sodium Nitrite) and collect. The rinse will contain any residual americium, plutonium, and uranium from the sample. [40mL which is collected]

12.8.4.3 Repeat step 12.8.4.2. Collect this rinse.

12.8.4.4 Place the americium, plutonium, uranium fraction on a hotplate and allow it to evaporate to dryness.

12.8.4.5 Continue with the separation at Step 12.7.2. Add 15mL conc. HCl evaporate to dryness.

12.8.5 Elute the thorium from the column with 25mL of 9N HCl into a labeled centrifuge tube. [50mL]

12.8.5.1 Based on historical client data, if polonium is expected to be present in excessive quantities, transfer the thorium fraction to a clean labeled glass beaker and proceed to step 12.11.11 in Method 5, Thorium Purification on TEVA-Resin™.

12.8.5.2 Transfer the solution containing the thorium from the centrifuge tube to a clean, labeled plastic cup and add 0.8mL of 10mg/mL iron carrier.

12.8.5.3 Dilute the samples to approximately 220mL with ASTM Type II DI water.

12.8.5.4 Precipitate thorium with iron as a hydroxide by adding 22-25mL of concentrated ammonium hydroxide to each sample dilution. Stir the solution vigorously with a stir rod for several seconds until a distinct iron hydroxide precipitate forms.

12.8.5.5 Allow the samples to settle for about 15 minutes, and stir vigorously once more to further break up the iron hydroxide precipitate.

12.8.5.6 Remove the stir rod and allow the samples to completely settle for a minimum of one hour.

12.8.5.7 Decant the excess supernate and transfer the iron hydroxide precipitate to the original labeled centrifuge tubes from Step 12.8.5.

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12.8.5.8 Centrifuge the samples and discard the supernate. Dissolve the precipitate in 3mL 9N HCl. Dilute the samples to 25mL with ASTM Type II DI water.

12.8.5.9 Proceed to Step 12.15.4 for the Micro-Precipitation of Thorium.

12.8.6 If sodium nitrite was used, elute plutonium from the column with 25mL 1.2N HCl/ 2% hydrogen peroxide into a clean, labeled glass beaker. [N/A]

12.8.6.1 Add 3-4 drops of the iron carrier to the plutonium fraction and place it on a hotplate and allow it to evaporate to dryness.

12.8.7 Perform steps 12.7.6.2 to 12.7.6.9 in Method 1 on the plutonium fraction.

12.8.7.1 If the column is to be reused for the uranium purification, rinse the column with 25mL of ASTM Type II DI water. [N/A]

12.8.8 Perform all of steps listed in Method 1 to purify the americium, plutonium (if not isolated using sodium nitrite), and uranium as required. Save and reuse the current anion columns.

12.9 **Method 3: Purification of Americium/Curium Using Tru-Resin™**

12.9.1 This method may be used as the initial separation step for liquids, waters, or urines only if americium/curium is requested. It must be used subsequent to Method 1 in all other instances to purify americium/curium and separate them from thorium.

12.9.2 Add 3-4 drops of the iron carrier to the americium fraction collected in Step 12.7.5. Place the sample on a hotplate and evaporate the sample to dryness.

12.9.3 Add 5mL of concentrated nitric acid to each sample and evaporate to dryness to remove residual chlorides.

12.9.4 Dissolve the sample residue into 10mL of 2N HNO_3 /0.5M $Al(NO_3)_3$. Additional 2N HNO_3/0.5M $Al(NO_3)_3$ may be used to dissolve the sample fraction, but the total load volume must not exceed 15mL.

12.9.4.1 Heat the sample as necessary to aid in the dissolution.

12.9.5 Add one drop of 0.5M potassium thiocyanate to the sample and swirl it, then add 6-8 drops of 1.0M ascorbic acid to the sample and swirl it.

12.9.5.1 The color of the sample should go from clear to red and then back to clear again, unless there is no significant iron present in the sample.

12.9.6 The sample should be centrifuged prior to loading it on the column if there are any solids present.

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12.9.7 Prepare a resin column with 5 drops of pre-resin filter followed by 3.5mL (2 grams) of Tru-Resin™.

12.9.7.1 Allow any excess water to drain.

12.9.7.2 Condition the columns by passing 5mL of 2N HNO_3 through them and discarding the effluent.

12.9.8 Load the sample onto the column.

12.9.8.1 A change in resin color should be observed, usually pink, but it may be multi-colored.

12.9.8.2 Discard the effluent.

12.9.9 Rinse the column with three 5mL aliquots of 2N HNO_3 allowing each to pass through the column. Discard the effluents.

12.9.10 Place a clean, labeled centrifuge tube under the columns and elute the americium/curium from the resin with 2mL of 9N HCl.

12.9.11 Complete the elution of the americium/curium from the column by adding 10mL 4N HCl. Combine the effluent from the column in the centrifuge tube.

12.9.12 Proceed to Step 12.15.1 for the Micro-Precipitation of Americium.

12.10 **Method 4: Purification of Americium/Curium Using TEVA-Resin**

12.10.1 After Method 1 has been preformed, the following options are available to further purify the americium/curium. This may be necessary:

12.10.1.1 If a solid sample greater than 2-3g is analyzed, or

12.10.1.2 If Lanthanides are expected to be present.

12.10.2 If interferences are expected, but on a lower magnitude, proceed directly to step 12.10.6 upon completion of Method 3 Step 12.9.11.

12.10.3 Option 1 (For samples that contain lanthanides)

12.10.3.1 From Step 12.7.5, add 1.0mL calcium carrier and dilute the sample to 1N HCl in a sufficiently sized beaker. Cover the beaker with a watch glass cover and heat to boiling.

12.10.3.2 Add approximately 5g of solid oxalic acid to the solution and stir the sample with a stir rod.

12.10.3.3 When the oxalic acid has dissolved, carefully adjust the pH of the solution to 2.5 with 15N NH_4OH.

12.10.3.3.1 A white precipitate should form.

12.10.3.4 Place the sample back on the hotplate and allow it to boil for several minutes. Remove the sample from the heat, and allow it to cool.

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12.10.3.5 Decant the supernate from the sample and transfer the precipitate to a centrifuge tube with 0.1% oxalic acid as a rinse. Centrifuge the sample and discard the supernate.

12.10.3.6 Dissolve the sample precipitate in conc. HNO_3 and transfer it to a clean, labeled glass beaker.

12.10.3.7 Add 1mL of hydrogen peroxide to the sample, in a drop wise manner, to destroy the oxalate.

12.10.3.8 Place the sample on a hotplate and allow it to evaporate to dryness.

12.10.3.9 Repeat Steps 12.10.3.6 through 12.10.3.8 two additional times.

12.10.3.9.1 Do not allow the samples to bake on the hotplate.

12.10.3.10 Perform Steps 12.9.3 thru 12.9.11.

12.10.3.11 Proceed to Step 12.10.5.

12.10.4 Option 2 (For samples with large amounts of divalent minerals such as calcium and magnesium)

12.10.4.1 To the americium/curium fraction from Step 12.7.5, add 1.0mL of iron carrier (10mg/mL), and dilute the sample to a molarity equivalent to 1N HCl in an appropriately sized beaker.

12.10.4.2 Cover the sample with a watch glass and heat it to near boiling.

12.10.4.3 Perform the iron hydroxide precipitation as described in Steps 12.1.6 thru 12.1.11.

12.10.4.4 Dissolve the precipitate in 5-10mL of conc. 12N HCl and transfer the solution to a sufficiently sized PTFE beaker with ASTM Type II DI water.

12.10.4.5 Adjust the molarity of the sample using conc. HCl and/or ASTM Type II DI water to approximately 3N HCl. This can be accomplished by tracking the amount of concentrated acid added, and adjusting the final volume with ASTM Type II DI water until the resulting solution would be equivalent to 3N HCl.

12.10.4.6 Add 0.2mL of cerium carrier (10mg/mL) to the sample and heat it on a hotplate for 15 minutes.

12.10.4.7 (Carefully!) Add 10-20mL of conc. HF to the sample and then stir it with a PTFE stir rod.

12.10.4.8 Heat the samples for an additional 15-20 minutes to precipitate the cerium fluoride.

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12.10.4.9 Remove the sample from the hotplate and allow it to cool. Transfer the sample to a centrifuge tube with ASTM Type II DI water and centrifuge it and discard the supernate to the appropriate waste stream.

12.10.4.10 Dissolve the precipitate in 10mL 8N HNO_3 then add 1mL of the iron carrier and 5mL of the 5% saturated boric acid solution. Cap the centrifuge tube and shake it vigorously to mix the contents.

12.10.4.11 Dilute the sample to 40mL with ASTM Type II DI water.

12.10.4.12 (Carefully) Add 5-7mL conc. ammonium hydroxide to the centrifuge tube, then cap and shake the sample to precipitate the iron hydroxide.

12.10.4.13 Centrifuge the sample and discard the supernate.

12.10.4.14 Perform steps 12.9.3 thru 12.9.11.

12.10.5 Transfer the americium/curium eluate (from Step 12.9.11, Option 1 or Option 2 above) to a small glass beaker. Place the sample on a hotplate and allow it to evaporate to dryness

12.10.5.1 Do not allow the samples to bake.

12.10.6 Dissolve the residue in the beaker in 10mL conc. HCl and place it back on the hotplate allowing it to evaporate to dryness.

12.10.6.1 Do not allow the sample residue to bake.

12.10.7 Add 1mL conc. formic acid to each sample and allow them to evaporate to dryness.

12.10.8 Dissolve the sample in 15mL 3M ammonium thiocyanate/ 0.1N formic acid.

12.10.8.1 Heat the sample as necessary to aid in the dissolution.

12.10.8.2 The sample should take on a light pink color.

12.10.9 Prepare a 2cm column with 3.5mL prepared (2 grams) TEVA resin™.

12.10.9.1 Allow any excess water to drain through.

12.10.9.2 Condition the column with 5mL of the 3M ammonium thiocyanate/ 0.1N formic acid.

12.10.10 Ensure that the sample has cooled and load it onto the conditioned column.

12.10.10.1 Rinse the sample beaker with 2mL 1M ammonium thiocyanate/ 0.1N formic acid.

12.10.10.2 Pour the rinse onto the column when the sample has completely passed through.

12.10.11 Rinse the column first with 3mL and then with 5mL of the 1M ammonium thiocyanate/ 0.1N formic acid.

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12.10.11.1 Discard all rinses to waste. (Note: Ammonium thiocyanate should be neutralized with dilute nitric acid prior to disposal to avoid violent reactions.)

12.10.12 Elute the americium/curium from the column with 15mL of 2N HCl into a clean, labeled centrifuge tube.

12.10.13 Proceed with Step 12.15.1 for Micro-Precipitation of Americium.

12.11 **Method 5: Thorium Purification Using TEVA-Resin™**

12.11.1 This method may be used as the initial separation step for liquids, waters, and solids when thorium is requested.

12.11.1.1 It must be used after Method 1 in all other instances to purify thorium and separate it from americium and curium.

12.11.1.2 As an option it may be used to further purify thorium after Method 2 if past experience shows polonium may present a problem.

12.11.1.3 This method may also be used for sequential separation of uranium from thorium when uranium and thorium are both requested. If utilizing this method for this purpose, begin at Step 12.11.13.

12.11.2 Place the thorium fraction from Step 12.7.5.5 or 12.8.5.1 on a hotplate. If the sample was urine, Steps 12.11.3 through 12.11.9 must be performed. For all other sample matrices, begin with step 12.11.11.

12.11.3 Add 0.2mL of cerium carrier (10mg/mL) to the sample in a PTFE beaker and heat it on a hot plate allowing it to evaporate to dryness.

12.11.4 Dissolve the sample residue in 40mL 1N HCl.

12.11.4.1 Heat the solution as necessary to aid in the dissolution of the residue.

12.11.5 Transfer the entire sample to a centrifuge tube and add 5mL conc. HF. Cap and shake the sample vigorously.

12.11.6 Centrifuge the sample and discard the supernate in the appropriate waste stream.

12.11.7 Dissolve the residue in 10mL 8N HNO_3 and add 1mL iron carrier and 5mL of 5% saturated boric acid. Cap the centrifuge tube and shake it vigorously to mix the contents.

12.11.8 Dilute the sample to 40mL with ASTM Type II DI water and carefully add 5-7mL conc. 15N NH_4OH to precipitate the iron as a hydroxide.

12.11.9 Cap and shake to mix the sample, and centrifuge the sample. Discard the supernate.

12.11.10 Proceed to Step 12.11.13.

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12.11.11 Add 4-5 drops of iron carrier to the sample and place it on a hot plate allowing it to evaporate to dryness.

12.11.12 Add 10mL of conc. HNO_3 to the sample and heat it to dryness to convert it to the nitrate form.

12.11.13 Dissolve the sample residue in 10mL of 3N HNO_3/ 1.0M $Al(NO_3)_3$. Heat the sample if necessary to aid in dissolution of the residue. Up to an additional 10mL of 3N HNO_3/ 1.0M $Al(NO_3)_3$ may be added as necessary to completely dissolve the sample.

12.11.14 Prepare a 2cm column with 3.5mL prepared (2g) TEVA™ resin

12.11.14.1 Allow the excess water to drain away.

12.11.14.2 Condition the column with 5mL of 3N HNO_3.

12.11.14.3 If sequential uranium analysis is being conducted, place new labeled centrifuge tubes beneath each column after the conditioning solution has passed completely through the column.

12.11.15 Load the sample onto the column and collect the eluate for uranium analysis if desired. Rinse the sample beaker with 10mL 3N HNO_3.

12.11.16 When the sample has passed through the column, remove the centrifuge tubes and transfer the eluate liquid to a labeled and conditioned UTEVA™ column for uranium analysis. Replace the centrifuge tubes beneath the TEVA™ columns and pour the rinse from the sample beaker onto the column.

12.11.17 If uranium is not required, discard the load rinse and beaker rinses to waste, otherwise, once the rinse has completely passed through the column, add it to the appropriate UTEVA™ column and discard the centrifuge tubes. Proceed to step 12.12.6 to continue the uranium column work.

12.11.18 Rinse the TEVA™ column with an additional 20mL 3N HNO_3 after the first rinse has completely passed through.

12.11.19 Place a clean, labeled centrifuge tube or small glass beaker under each column and elute the thorium from the column with 20mL of 9N HCl.

12.11.19.1 Collect any residual thorium from the column by rinsing with an additional 5mL 6N HCl.

12.11.20 Transfer the solution containing the thorium from the centrifuge tube to a clean, labeled plastic cup and add 0.8mL of 10mg/mL iron carrier.

12.11.21 Dilute the samples to approximately 220mL with ASTM Type II DI water.

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12.11.22 Precipitate thorium with iron as a hydroxide by adding 22-25mL of concentrated ammonium hydroxide to each sample dilution. Stir the solution vigorously with a stir rod for several seconds until a distinct iron hydroxide precipitate forms.

12.11.23 Allow the samples to settle for about 15 minutes, and stir vigorously once more to further break up the iron hydroxide precipitate.

12.11.24 Remove the stir rod and allow the samples to completely settle for a minimum of 30 minutes.

12.11.25 Decant the excess supernate and transfer the iron hydroxide precipitate to the original labeled centrifuge tubes from Step 12.11.19.

12.11.26 Centrifuge the samples and discard the supernate. Dissolve the precipitate in 3mL 9N HCl. Dilute the samples to 25mL with ASTM Type II DI water.

12.11.27 Proceed to Step 12.15.4 for Micro-Precipitation of Thorium.

12.12 **Method 6: Uranium Purification Using UTEVA-Resin™**

12.12.1 Prepare a labeled 2cm column with 3.5mL prepared (0.7g) UTEVA resin. Allow the excess water to drain away.

12.12.2 If not dissolved already, dissolve the samples in 10-20mL of 3N HNO_3/ 1.0M $Al(NO_3)_3$

12.12.3 Condition the column with 5mL 3N HNO_3.

12.12.4 Centrifuge the load solution if necessary and load the sample onto the column. Discard the effluent.

12.12.5 Rinse the sample container or centrifuge tube with the 10mL 3N HNO_3 and add this rinse to the column. Discard the effluent.

12.12.6 Convert the column to chloride form by rinsing with 5mL 9N HCl.

12.12.7 Remove polonium and residual thorium by rinsing with 15mL 5N HCl/0.05 M oxalic acid.

12.12.8 Rinse the oxalic acid from the column with 10mL 6N HCl.

12.12.9 Pipette 2mL 6N HCl into each clean, labeled centrifuge tube and place the tubes under each column.

12.12.10 Elute uranium from the column with 20mL 0.01N HCl.

12.12.11 Proceed to Step 12.15.3 for the Micro-Precipitation of Uranium.

12.13 **Method 7: Neptunium Purification Using TEVA-Resin™**

12.13.1 This method may be used as the initial separation step for neptunium in aqueous and solid samples if it is the only parameter requested.

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12.13.1.1 Thorium may also be isolated at the same time if both thorium and neptunium are to be analyzed together on the same sample.

12.13.2 Dissolve the sample in 10mL of 3N HNO_3/1.0M $Al(NO_3)_3$ and add 3.0mL 0.6N ferrous sulfamate and 1.0mL of 1.0M ascorbic acid to it.

12.13.3 Swirl or shake the sample to mix it and allow it to sit for three minutes.

12.13.3.1 Centrifuge the sample if there are any visible solids.

12.13.4 Prepare a 2cm Eichrom column with 3.5mL prepared (2g) of TEVA Resin™.

12.13.4.1 Allow the excess water to drain.

12.13.4.2 Condition the column with 5mL 3N HNO_3.

12.13.5 Load the sample onto the column.

12.13.5.1 Rinse the sample container with 5mL 2.5N HNO_3/ 0.1N ferrous sulfamate.

12.13.5.2 Add the rinse to the column after the sample has passed through.

12.13.6 Rinse the column with 30mL 2.5N HNO_3/ 0.1N ferrous sulfamate.

12.13.6.1 Discard to waste and repeat the rinse step.

12.13.7 Rinse the column with an additional 5mL 2.5N HNO_3/ 0.1N ferrous sulfamate, and discard the rinse to waste.

12.13.8 Rinse the column with 20mL 9N HCl.

12.13.8.1 This will contain any thorium in the sample and may be collected into a clean, labeled centrifuge tube.

12.13.8.2 Rinse the column with 5mL 6N HCl to remove residual thorium.

12.13.8.3 Perform Steps 12.11.20 through 12.11.27 if thorium is an analyte of interest.

12.13.9 Elute neptunium into a clean labeled centrifuge tube with 15mL of 0.02N HNO_3/ 0.02N HF.

12.13.10 Proceed to step 12.15.5 for the Micro-Precipitation of Neptunium.

12.14 Method 8: Rapid Extraction of Am, Np, Pu, Th, U Using TEVA™ and TRU™ Columns

12.14.1 This method has been developed for use with the Eichrom vacuum box cartridge system, and should be used when a client specifies a quick turn for the above mentioned nuclide combination.

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12.14.1.1 This method may not be useful for soil samples over 1g, or other solids high in interfering elements,

12.14.1.2 This method is not economical for samples where only one or two isotopes are requested or the sample turnaround time is greater than 14 days.

12.14.1.3 This method should not be utilized unless specifically directed by the laboratory supervisor.

12.14.1.4 This method must not be used for the analysis of drinking waters.

12.14.2 Dissolve the sample residue in 12mL 3.0N HNO_3/ 1.0M $Al(NO_3)_3$ and add 0.5mL 1.5M sulfamic acid. Swirl the sample to mix the solution and wait five minutes for any reactions to subside. (Reactions will be minimal)

12.14.3 Add 2.0mL 1.5M ascorbic acid to the sample. Swirl the sample to mix the solution and wait five minutes for any reactions to subside. (Reactions will be minimal)

12.14.4 Add 1.0mL 4M sodium nitrite to the sample. Swirl the sample to mix the solution, wait until all reactions subside, and add an additional 1.0mL 4M sodium nitrite to the sample. Swirl the sample to mix the solution and wait five minutes for all reactions to subside. (This reaction will produce a lot of foaming. Care must be taken to eliminate sample losses due to foaming over. All reactions must subside prior to the addition of the extra 1.0mL of sodium nitrite solution.)

12.14.5 Stack a TEVA resin™ column onto a TRU resin™ column, and set them up on the vacuum box system as directed in the vacuum box instructions.

12.14.6 Precondition the columns on the system with 10mL of 3M HNO_3.

12.14.7 Load the samples onto the columns and catch all waste effluent in a disposal tray. Rinse the sample container with 5mL 3M HNO_3, and add the rinse to the appropriate column.

12.14.8 Rinse the sample cartridges with three subsequent 5mL 3M HNO_3 rinses. Catch all waste effluents and save them until after counts have been completed.

12.14.9 Separate the sample cartridges and place the TEVA™ columns on fresh tips for elution of the thorium, plutonium, and neptunium.

12.14.10 Elute the thorium from the TEVA™ column into a clean, labeled centrifuge tubes by

12.14.10.1 Adding 5mL 9N HCl to the column and allow it to drain,

12.14.10.2 Complete the elution with 25mL of 8N HCl.

12.14.10.3 Proceed to Steps 12.11.20 to 12.11.27.

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12.14.11 Elute the plutonium and neptunium from the TEVA column into a clean, labeled centrifuge tube with 20mL of the 0.1N HNO_3/ 0.05N HF/ 0.015M rongalite solution.

12.14.11.1 Proceed to Step 12.15.2 for the Micro-precipitation of Plutonium.

12.14.11.2 Note: Plutonium and neptunium can only be eluted, micro-precipitated, and counted as a single source if Pu-236 is used as a tracer rather than Pu-242 and Np-239.

12.14.12 Discard the TEVA columns and all tips.

12.14.13 Place the TRU columns on fresh tips for the americium and uranium elution.

12.14.14 Elute the americium into clean, labeled centrifuge tubes with 15mL 4N HCl.

12.14.14.1 Transfer the americium fraction of the sample to a clean, labeled glass beaker and add 2 drops of the iron carrier.

12.14.14.2 Place the sample on a hotplate and evaporate it to dryness.

12.14.14.3 Dissolve the residue in the beaker in 5mL 4N HCl, and transfer the solution to the centrifuge tube used for the initial elution with 15mL ASTM Type II DI water.

12.14.14.4 Proceed to Step 12.15.1 for the Micro-precipitation of Americium.

12.14.15 Elute the uranium into a clean, labeled centrifuge tube with 20mL 0.1M ammonium bioxalate.

12.14.16 Proceed to Step 12.15.3 for the Micro-precipitation of Uranium.

12.15 **Micro-precipitation of the Actinides**

12.15.1 Americium/Curium

12.15.1.1 Add 0.1mL of the 0.5 mg/mL neodymnium carrier to the sample. Swirl the sample to mix the contents.

12.15.1.2 Add 3mL conc. HF to the sample. Cap the centrifuge tube and shake the sample vigorously to mix the contents.

12.15.1.3 Allow the sample to sit for thirty minutes, then proceed with Step 12.15.6 for filtration.

12.15.2 Plutonium

12.15.2.1 Add 0.1mL 0.5mg/mL neodymnium carrier to the sample and swirl to mix.

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12.15.2.2 Add 12 drops of 25% dihydrazine dihydrachloride solution to each sample.

12.15.2.3 Swirl the solution to mix the contents, then allow the sample to sit for 5 minutes.

12.15.2.4 Add 3mL of conc. HF to the sample. Cap the sample and shake it vigorously to mix the contents.

12.15.2.5 Allow the sample to sit for thirty minutes.

12.15.2.6 Proceed to Step 12.15.6 for filtration.

12.15.3 Uranium

12.15.3.1 Add 0.1mL 0.5mg/mL neodymnium carrier to the sample and swirl to mix.

12.15.3.2 Add enough of the titanium chloride solution to the sample to maintain a light purple color when swirled (approximately 1-2mL).

12.15.3.3 Swirl the solution to mix the contents, then allow the sample to sit for a few minutes.

12.15.3.4 Add 3.0mL conc. HF to the sample. Cap the sample and shake it vigorously to mix the contents.

12.15.3.5 Allow the sample to sit for thirty minutes.

12.15.3.6 Proceed with Step 12.15.6 for filtration.

12.15.4 Thorium

12.15.4.1 Add 0.1mL 0.5mg/mL neodymnium carrier to each sample. Swirl the contents to mix.

12.15.4.2 Add 3.0mL conc. HF to the sample. Cap the sample and shake it vigorously to mix the contents.

12.15.4.3 Allow the sample to sit for thirty minutes.

12.15.4.4 Proceed with Step 12.15.6 for filtration.

12.15.5 Neptunium

12.15.5.1 Add 0.1mL 0.5 mg/mL neodymnium carrier to each sample. Swirl the contents to mix.

12.15.5.2 Add 3.0mL conc. HF to the sample. Cap the sample and shake it vigorously to mix the contents.

12.15.5.3 Allow the sample to sit for thirty minutes.

12.15.5.4 Proceed with Step 12.15.6 for filtration.

12.15.6 Filtration

12.15.6.1 Prepare the filtration unit by turning on the vacuum and rinsing each apparatus with severalmLs of ASTM Type II DI water.

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12.15.6.2 Carefully wash and rinse each of the filter funnels and set them aside.

12.15.6.3 Place a polypropylene filter onto each unit and ensure that it is centered.

12.15.6.4 (Carefully) Place the funnels on the filtration unit.

12.15.6.4.1 Do not rip the filters.

12.15.6.4.2 Rinse the sides of the funnels with 80% reagent grade alcohol.

12.15.6.4.3 If Tuffryn™ filters are used instead of polypropylene filters, add 5mL of the carbon substrate solution to each filter at this time.

12.15.6.5 When the sample has completely passed through the filter, rinse the sides of the funnel with a few mLs of the 0.1% HF solution.

12.15.6.6 Rinse the funnel and filter with a few mLs of 80% reagent grade alcohol.

12.15.6.7 When the rinses have completely passed through the filter, remove the filter funnels, turn off vacuum, and carefully remove the filter paper with tweezers.

12.15.6.8 Place the filter paper onto a labeled pre-taped metal disc for counting.

12.15.6.8.1 Allow the filter to completely dry prior to counting by placing it in a labeled petri dish, and storing it in the count room until ready to count.

12.15.6.9 Count the samples in an alpha spectrometry detector as instructed in the current revision of the instrument SOP, PGH-R-020.

12.15.6.10 Obtain instrument printouts and perform calculations as detailed in Attachment 1 of this SOP.

12.15.6.11 If plutonium-241 analysis is desired, the Pu counting source must be removed from the taped disk after alpha spectroscopy counting using a minimal amount of acetone.

12.15.6.12 Place the filter in a glass liquid scintillation vial. Cover the vial with aluminum foil and muffle it in an oven at 550°C for a minimum of 2 hours or until the filter has completely ashed away and there is no black residue left in the vial.

12.15.6.13 Remove the vial from the oven and discard the foil. Add 6 drops of saturated boric acid and 1mL of concentrated HCl to each sample and heat to dryness.

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12.15.6.14 Add 2.0mL 0.1N HCl to each sample to dissolve the residue and 15mL of Ultima Gold AB liquid scintillation cocktail. Cap the vial and shake it vigorously.

12.15.6.14.1 The samples should be free of any color.

12.15.6.15 Clean the outside of each vial with acetone followed by ASTM Type II DI water to remove any finger prints or residue.

12.15.6.16 Dark-adapt the samples for one hour prior to counting in a calibrated, liquid scintillation counter in accordance with the liquid scintillation instrument operating SOP, PGH-R-022, current revision.

13. Calculations

13.1 Refer to Attachment I of this SOP for all actinide analysis associated calculations.

14. Quality Control

14.1 Each analyst who performs this test must satisfactorily complete a Demonstration of Capability Study as documented in Section 3.4 of the most recent revision of the Quality Assurance Manual.

14.1.1 The DOC study results are evaluated against the LCS acceptance limits.

14.2 Daily instrument Quality Control checks for the alpha spectrometer must be completed following the instructions detailed in the current revision of Pace SOP PGH-R-020, “Alpha Spectroscopy Instrument Operations.”

14.3 Daily instrument Quality Control checks for the liquid scintillation counter must be completed following the instructions detailed in the current revision of Pace SOP PGH-R-022, “Liquid Scintillation Instrument Operations.”

14.4 Daily instrument Quality Control checks for the gas flow proportional counters must be completed following the instructions detailed in the current revision of Pace SOP PGH-R-002, “Gas Flow Proportional Instrument Operations.”

14.5 See Appendix II for performance indicator evaluation calculations and criteria. Numerical performance indicators may be used to assess QC for non-drinking water samples when the default assessment indicates a QC failure. The numerical performance indicator must be within +/- 3 for all other matrices. The z-score for precision assessment may be used for drinking waters with the approval of the Department Manager/Supervisor using the +/- 2 specification.

14.6 Sample Tracer Recovery/Tracer Peak Energy

14.6.1 Sample tracer is added to each sample and used to calculate sample recovery. Tracer recovery is required to be within 30%-110% for samples analyzed under jurisdiction of the DOD QSM.

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Pace's default acceptance criteria for tracer recovery requires recovery between 30%-110%; however, recoveries may be acceptable between 10% and as high as 130% with the documented permission of the Department Manager/Supervisor or specified designee.

14.6.2 Samples with tracer recoveries outside of this range should be re-prepped with direction from the Department Manager or Manager-specified designee after determining possible causes.

14.6.3 Sample tracer counts should be sufficient to minimize the expanded uncertainty of the count and any potential for tailing of the tracer counts into other regions of interest. A minimum of 400 tracer counts is recommended, however, in some instances, the sample matrices may prohibit achieving a minimum 400 tracer counts, and the sample data must be evaluated prior to extending or recounting samples solely to achieve a minimum 400 tracer counts.

14.6.4 Excluding samples analyzed for isotopic thorium content using Th-229 as a tracer, samples analyzed under jurisdiction of the DOD QSM, the tracer energy must be within 40 keV of the known tracer isotope peak energy.

14.6.5 For samples associated with the DOD QSM, if the tracer energy is not within 40 keV of the known peak energy, this may indicate an issue with the detector used for analysis. The sample may be reanalyzed using an alternate detector. If re-analysis results indicate an acceptable tracer energy peak location, results may be reported. If, following re-preparation and re-analysis, the tracer peak is not within 40 keV of the known peak energy, results may be reported with appropriate "J" flagging.

14.6.6 If the tracer is a non-Th-229 alpha emitter, its peak full width half maximum (FWHM) value must be evaluated and generally should be less than 100 keV. When the FWHM is greater than 100 keV the sample data must be inspected using professional judgment to determine if the detector was functioning properly and if the procedure was adequate. Data that has FWHM up to 125 keV may be reported with qualification, except for samples analyzed under the requirements of the DOD QSM. For DOD-associated samples, if the tracer FWHM exceeds 100 keV, the affected sample must either be re-prepared and re-analyzed or the alpha count source may be "re-purified" in accordance with the process outlined in this SOP. If count source re-purification is attempted but fails the FWHM criteria, the sample must be re-prepared and re-analyzed. If upon re-preparation and re-analysis the sample exhibits a tracer peak energy outside of established control criteria, analysis results may be reported with the appropriate "J" flag.

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14.6.7 Unlike other radioactive tracers used for yield monitoring, the alpha peak energies associated with Th-229 are of lower abundance and greater energy distribution over the region of interest associated with Th-229. For this reason, there is a greater uncertainty in calculating peak centroid energies and FWHM values when using spectroscopy systems that perform alpha spectral analysis of. When it is observed that the Th-229 centroid energy is calculated to be greater than 40 keV from the average Th-229 peak energy or when the Th-229 peak resolution is determined to be greater than 100 keV, analytical spectra must be reviewed and approved by the Department Manager or a Department Manager specified designee. For approval, analytical spectra must document clear de-markation between the Th-229 tracer and adjoining analyte regions of interest.

14.7 Method Blank (MB)

14.7.1 One MB must be prepared for each analytical batch. The purpose of the MB is to monitor for cross contamination during the analytical process. When available, the MB should be prepared from a similar matrix as samples contained in the analytical batch. If appropriate blank matrix material is not available, ASTM Type II DI water (Reagent Blank) must be carried through the procedure. A reagent blank may be used for sample correction purposes following approval of affected clients.

14.7.2 The MB result must be less than the MDC. If the method blank result is greater than MDC, individual sample results may still be reportable. PASI's default criteria allows reporting of sample results less than the CRDL (contract required detection limit) or greater than 10 times the blank result are still reportable. Relative sizes of the sample and blank aliquots must be factored when making this determination (raw counts).

14.8 Sample Duplicate (DUP)

14.8.1 One Duplicate Sample (DUP) must be randomly assigned within each batch. The purpose of the sample DUP is to measure precision of the analytical process. Laboratory duplicates are not intended to assess precision related to the sample collection process. Sample collection precision can only be assessed through collection of duplicate samples at the time of sample collection. The sample DUP is a duplicate volume of sample processed identically as other samples in the analytical batch.

14.8.2 For batches with drinking water samples originating from the state of Arizona, Duplicate Samples (DUP) must be randomly assigned within each batch at a frequency of no less than 10%. A batch of ten samples or fewer must contain at least one duplicate sample. A batch of greater than 10 samples up to 20

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samples must contain a minimum of two duplicate samples if the batch contains samples originating from Arizona.

14.8.3 Calculation

$$\%RPD = \frac{|R_S - R_D|}{(R_S + R_D)/2} \times 100$$ Where:

R_S = sample activity concentration
R_D = duplicate activity concentration

14.8.4 Duplicate sample performance is acceptable when the %RPD is <25%.

14.9 Sample Matrix Spikes (MS)

14.9.1 Because this analytical method requires the use of radiotracers for yield determination, PASI's default QC policy is that a sample matrix spike (MS) is not required for alpha spectrometry analyses except for drinking water analysis.

14.9.2 A matrix spike is prepared by spiking a known amount of spike solution (Am-241, Cm-244, Pu-239, Th-232, U-238, Np-237, etc.) into a portion of one sample in the batch, and it must be processed identically as for other samples. The purpose of the MS is to assess the effect of sample components on the analytical process. The volume of sample used for the MS must be equivalent to the volume used for sample analysis. The spike amount should be approximately 10 times the detection limit and not less than 20% of the anticipated sample concentration.

14.9.3 Matrix Spike Recovery Calculation

$$\%REC = \frac{(x - x_0)}{C} x100$$ Where:

x = measured concentration of the spiked sample
x_0 = measured concentration of the unspiked sample
c = spike concentration added

14.9.4 MS performance is acceptable when agreement of the measured value and the expected value is within ±25% of the true value.

14.10 Sample Matrix Spike Duplicates (MSD)

14.10.1 A sample Matrix Spike Duplicate (MSD) is not required for this analysis. When required by the customer/contract, a MSD must be prepared for each analytical batch. The MSD must be prepared as a duplicate of the MS.

14.10.2 For all matrices the MSD must pass the criteria established for the MS. Additionally, the MS and MSD must pass the criteria established for duplicate precision.

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14.11 Laboratory Control Sample (LCS)

14.11.1 One LCS must be prepared for each analytical batch and is a reference material that contains a known concentration of spike (Am-241, Cm-244, Pu-239, Th-232, U-238, Np-237, etc.) in a matrix that is similar to the samples within the batch. If this material is not available, a well-characterized material (WCM) may be used. If neither of these is available, DI may be spiked with a spike solution greater than 2 times the detection limit.

14.11.2 LCS Recovery calculations

$$\%REC = \frac{x}{C} x100$$ Where:

x = Analytical result of the LCS
c = Known concentration of the LCS

14.11.3 LCS performance is acceptable when the %REC is within ±25% of the known value.

14.12 Laboratory Control Sample Duplicate (LCSD)

14.12.1 A LCSD must be analyzed to measure batch precision whenever adequate sample volume is not available for sample DUP analysis. The LCSD must be prepared in an identical fashion as the LCS and processed identically as for other samples.

14.12.2 The LCSD must pass the criteria established for the LCS.

14.12.3 Additionally, the LCS and LCSD must pass the criteria established for duplicate precision.

14.13 Summary of QC related Activities:

Method Blank	One per Batch
Reagent Blank	One per Batch (as required by client)
Duplicate Sample	One per Batch (frequency of 1 per 10 samples for batches containing DW originating from AZ)
Matrix Spike	One per Batch (for drinking water analysis or as required by client)
Matrix Spike Duplicate	One per Batch (frequency of 1 per 10 samples for batches containing DW originating from AZ or as required by client)
Laboratory Control Sample	One per Batch
Laboratory Control Sample Dup	One per Batch for samples in the absence of Duplicate sample.

14.14 Corrective Actions for Out-Of-Control Data

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14.14.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.14.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.14.3 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and noted in the final report.

14.14.4 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.14.5 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.14.6 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.14.7 Laboratory Control Sample Duplicate (LCSD) – If an LCSD does not meet the recovery acceptance criteria, the entire analytical batch must be reanalyzed.

The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their the reporting limit, and duplicate precision meets the acceptance criteria.

14.14.8 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.15 Contingencies for handling Out-of-Control or Unacceptable Data

14.15.1 Method Blank (Reagent Blank): If the sample is exhausted, evaluate the usefulness of the data in the final report.

14.15.2 Duplicates: If the sample is exhausted, evaluate the usefulness of the data in the final report.

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14.15.3 Matrix Spike Recovery: If a Matrix Spike is analyzed and the spike recoveries are not comparable, and the sample is exhausted, evaluate the data usefulness in the final report.

14.15.4 Matrix Spike Duplicate: If a Matrix Spike Duplicate is analyzed and the spike recovery is not comparable to the Matrix Spike and the sample is exhausted, evaluate the data usefulness in the final report.

14.15.5 Tracer recovery: If the tracer recovery is less than 30% but greater than 10% with more than 400 tracer counts, the sample may be reported with supervisor permission. Tracer recovery above 110% but below 130% may be reported but must be narrated. Samples with tracer recovery below 10% or above 130% must be re-analyzed. If the sample is exhausted, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.2 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.3 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

15.4 Laboratory Control Samples are analyzed with each batch, the results are charted to monitor control limits and trending.

16. Pollution Prevention and Waste Management

16.1 Place radioactive waste into the appropriate receptacles.

16.2 Discard acidified samples and unusable standards into the proper waste drains.

16.3 Dispose of waste materials in accordance to type: (Non-hazardous, hazardous, non-radioactive, radioactive or mixed).

17. References

17.1 Bishop, C. T., et.al. “Radiometric Method for the Determination of Uranium in Water,” EPA 600/7-79-093, EMSL-LV, April 1979.

17.2 Edwards, K. W. “Isotopic Analysis of Uranium in Natural Waters by Alpha Spectrometry,” Radiochemical Analysis of Water, Geological Survey Water – Supply Paper 1696-F, U.S. Government Printing Office, Washington, D.C., 1968.

17.3 Krieger, H. L. and Whittaker, E. L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, “Uranium-Radiochemical Method,” Method 908.0, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, August, 1980.

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17.4 ASTM E181-93, Standard Test Methods for Detector Calibration and Analysis of Radionuclides, ASTM Standards, Vol. 12.02.

17.5 ASTM D-3972-90, Test Method for Isotopic Uranium in Water by Radiochemistry, ASTM Standards, Vol. 12.04.

17.6 Table of Radioactive Isotopes, Brown and Firestone, Shirley editor, John Wiley & Sons, 1986.

17.7 Currie, L., Limits for Quantitative Detection and Quantitative Determination, Analytical Chemistry, Vol. 40. No. 3, Pg 586-593, 1968.

17.8 Currie, L., Lower Limit of Detection: Definition and Elaboration of a Proposed Position for Radiological Effluent and Environmental Measurements, NUREG/CR - 4007, USNRC, 1984.

17.9 "American National Standard Calibration and Usage of Alpha/Beta Proportional Counters", ANSI N42.25-1997.

17.10 "Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)", July 2004, Final.

17.11 Eichrom Industries, Various Actinide Procedures. Darien, Illinois, 1995

17.12 EML Procedures Manual, HASL-300 28th Edition.

17.13 Pace SOP PGH-R-001, current revision (Analysis of Samples for Gross Alpha and Gross Beta content).

17.14 Pace SOP PGH-R-002, current revision (Gas Flow Proportional Counter Operation).

17.15 Pace SOP PGH-R-020, current revision (Alpha Spectroscopy Instrument Operations).

17.16 Pace SOP PGH-R-022, current revision (Liquid Scintillation Counter Operations).

17.17 Pace SOP PGH-R-024, current revision (Radiochem Sample Preparation).

17.18 Pace SOP PGH-C-027, current revision (Deionized Water Quality and Suitability).

17.19 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.20 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.21 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.22 Department of Defense (DOD), Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories; DOD QSM version 5.0, DOE Quality Systems for Analytical Services Version 3.0, July 2013.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Attachment No 1: Concentration Calculation & Counting Uncertainty

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18.2 Figure No 1: Analysis Flowchart for Sequential Analysis of Am, Pu, U, and Th

18.3 Figure No 2: Analysis Flowchart for Sequential Analysis for Am, Pu, U (Regular Water or Solids)

18.4 Figure No 3: Analysis Flowchart for Sequential Analysis of Am and Pu in Solids >1 Gram

18.5 Figure No 4: Analysis Flowchart for Sequential Analysis of U and Th in solid or water.

18.6 Figure No 5: Thorium Separation on UTEVA Resin

18.7 Figure No 6: Uranium Separation on UTEVA Resin

19. Method Modifications

19.1 This method for uranium in water is substantially compliant with ASTM Method D-3972-90 and HASL 300 Method U-02 for uranium with the following exceptions:

19.2 ASTM D3972-90 Modifications:

19.2.1 Ammonium iodide or HNO_3/H_2O_2 rinses have been substituted for the HI rinse to strip plutonium from the column prior to eluting uranium.

19.3 HASL U-02 Modifications:

19.3.1 U-02 foresees initial pre-concentration by simple evaporation. This can often lead to analyte loss due to poorly soluble residues. The method has been modified to employ a ferric hydroxide precipitation which both avoids formation of insoluble residues while providing additional decontamination.

19.3.2 Method HASL 300 U-02 specifies the use of AG 1X4 anion exchange resin. PASI utilizes AG 1X8 anion exchange resin due to increased loading capacity as well as enhanced selectivity in the separation of uranium from competing/interfering elements.

19.3.3 Method HASL 300 U-02 indicates the use of 7N HCL solution in the loading of uranium onto the anion exchange column with 1 N HCL as the eventual eluant for uranium. PASI utilizes a 9N HCL for loading and 0.1N HCL for elution to enhance analyte recovery.

19.3.4 Additionally, PASI utilizes intermediate stripping reagents to selectively remove plutonium (9N HCl / 0.05N NH_4I) and neptunium (6N HCl / 0.52N HF), if present in the samples.

19.3.5 Additional rinses have been added to HASL 300 U-02 to provide efficient decontamination from alpha emitting interferences.

19.3.6 Quality Control requirements have been modified to conform to PACE Analytical Services, Inc. QAP requirements and procedures.

19.4 This method for plutonium, americium and curium isotopes in all matrices and uranium in non-drinking water matrices is a PACE Analytical Services, Inc. proprietary method and is based in parts on EPA or other promulgated methods.

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20. Revisions

Document No.	Reason for Change	Date
PGH-R-008-6	1. Updated cover sheet to include Periodic Review. Updated Cover Page, Headers and Footers for this revision. Added periodic review signature lines to the cover page. 2. Updated Table of Contents section to include Attachments and Flowcharts. Made TOC updateable and linked to all the primary sections. 3. Updated Flow charts for the current thorium procedure after column separation. 4. Updated flowcharts with "Count to meet MDC and obtain 400 tracer counts", removing any suggested time requirement. 5. Section 12.7.6.6 – added to include addition of HCl to match flowchart directions. 6. Corrected section 12.8.7 to direct to the correct section for Pu analysis. 7. Section 14.4.3– expanded suggested minimum tracer counts requirements. 8. Section 15 – Removed annual MDL study requirement. Not performed for radiochemical methods. 9. Section 17 – Added TNI reference 10. Removed all references allowing approval of a "senior analyst" and replaced with "approval of Department Manager or Manager-specified designee."	31Dec2012
PGH-R-008-7	1. Updated cover page for this revision and to update the copy right footnote. Also updated to include the Methods Referenced 2. Section 1.3 corrected location of Method Deviations section. 3. Section 6: Updated to specify not targeting weights, recording observed measurements, and not removing sample from beakers once transferred from bottle. 4. Section 10: DI reference to ASTM Type II, and SOP reference. 5. Section 12: Updated to specify spiking and tracing preceding all chemical additions beyond initial preservation. 6. Section 17: Updated to include ASTM D 3972-90 and PASI-PGH QAM. 7. Section 19: Updated deviations from HASL 300 U-02 method.	07Nov2013
PGH-R-008-8	1. Annual SOP review and update. 2. Section 2 – Added references to applicable instrument operation SOPs. Included these references where instrumentation is discussed in other areas of the document. 3. Section 8.1.1 – Included pH verification requirements and recording. 4. Section 8.1.4 – Added maximum hold time requirement. 5. Section 9 – Included references to Pace SOP for instrument operations and listed instrumentation.	13Jul2014

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Document No.	Reason for Change	Date
	6. Section 12.1 – Clarified aqueous sample analysis amounts and instructions for diluting samples. 7. Section 12.6 – Urine samples measured with graduated cylinders not weighed. 8. Section 14.5 – Changed to be consistent with other SOPs for discussion of numerical indicator application. 9. Section 14 – Included duplicate requirement for Arizona drinking water samples in applicable sections. 10. Section 15 – added CDOC requirements 11. Section 17 – Added applicable instrument SOP references. 12. Reformatted document.	
PGH-R-008-9	1. Removed from section 5.1: Analysts must be trained as radiation workers and personal dosimeter worn. 2. Section 14 modified to add tracer peak quality control requirements for USDOD-related sample analysis. 3. Section 17 modified to add reference to the US DOD/DOE QSM version 5.0.	20Feb15
PGH-R-008-10	1. Annual review and update. 2. Updated section references throughout document. 3. Updated section 12.4.7 to discuss the process for treating highly oxidized solids to improve analyte recovery.	27Jul2015

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Attachment I - Calculations

The **radioactivity concentration** of a sample is calculated according to the following equations:

Eq. 1 $$A = \frac{(S_s / T_s)}{DENOM}$$

Eq. 2 $$E_T = R * E$$

Eq. 3 $$E_i = \frac{S_E}{T_E * C_E * F_E * D_E}$$

Eq. 4 *E = average of individual isotope efficiencies*

Eq. 5 $$D = e^{-\lambda T}$$

Eq. 6 $$\lambda = \frac{\ln 2}{T_{1/2}}$$

Eq. 7 $$Denom = E_T * V * .22 * D * F$$

Eq. 8 $$R = \frac{(S_T / T_S)}{(E * C)}$$

Where:

A = The radioactivity concentration for the radioisotope being measured in units of pCi per Liter, gram, filter, or sample. ***"Activity."***

S_S = Represents the background corrected net counts for the radioisotope being measured. ***"Peak Net Cts."***

B = Represents the Bkg Cts acquired in the applicable region of interest (ROI) referenced to the sample count time. "***Bkg Cts (ref to Sample ct time)".***

T_S = Represents the count time for the sample. ***"Sample time (min)."***

T_B = Represents the count time for the background. ***"Bkg Time (min)."***

E_T = Represents the total system efficiency for the counted sample. This represents the detector efficiency corrected for chemical recovery. ***"Total Eff."***

V = Represents the sample volume (in liters), mass (in grams), filter portion analyzed (fractional), or sample portion analyzed (fractional). ***"Aliquot."***

2.22 = Represents the factor to convert from disintegrations per minute (dpm) to picocuries (pCi). ***"Act. Conv. From dpm to pCi."***

D = Represents the fraction of analyte remaining after decay time T. ***"Fract. Remain."***

F = Represents the summed branching ratio for all alpha particles emitted in the region of interest. In most cases this is 100% (+/- 1%). If the branching ratio varies significantly (greater than associated uncertainty) from 100%, this correction should be applied. ***"abnd."***

R = Represents the analytical chemical recovery for the tracer analyte. ***"Chemical Yield."***

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S_T = Represents the background corrected net tracer peak counts in the applicable region of interest (ROI). Located in the **"Peak Net Cts"** column for the tracer nuclide row.

B_T = Represents the background counts for the tracer analyte acquired in the tracer region of interest (ROI) referenced to the sample count time. Located in the **"Bkg Cts (ref to Sample Ct time)"** column for the tracer nuclide row.

E = Represents the efficiency for the detector used for sample counting. The efficiency is a fixed number for each detector representing the fractional percent of radioactive events that are measured by the counting system. ***"Det. Eff. (cpm/dpm)."***

C = Represents the dpm of tracer (decay corrected to the time of sample counting) added to the sample. ***"Spike dpm."***

$T_{1/2}$ = Represents the half-life of the radionuclide being measured. ***"T1/2 (y)."***

t = Represents the elapsed time between the reference and count dates in the same units as $T_{1/2}$.

The sample specific **counting uncertainty** is calculated as follows.

Eq. 9 *Counting Uncertainty* $= \frac{1.96 * \sqrt{(S_S/T_S)/(T_S) + (B/T_S)/(T_B)}}{\text{Denom}}$

As summed background and analyte count rates approach zero, assumptions underlying the uncertainty calculation are violated and it will return an unrealistic value of zero (0) uncertainty when zero summed counts are observed. The following equation provides a more accurate estimate of count uncertainty at zero and near-zero count rates.

Eq. 10 $\text{ZeroUnc} = \frac{1.96 * \sqrt{zaf / T_S / T_S + zaf / T_B / T_B}}{DENOM}$

Where:

zaf = zero activity factor

and T_S, T_B, and Denom were previously defined

Note 1: Depending on sample type and contract requirements the zero activity factor may be either 3.0 or 2.71. PASI's default is 2.71 consistent with the current version of ANSI N42.23. Bioassay samples must be calculated using 3.0 to be consistent with ANSI N13.30.

Note 2: The Zero Count Uncertainty is compared to the count uncertainty above. The larger of the two is used as the counting uncertainty in subsequent total error calculations.

The error term is further evaluated to provide an estimate of total error hereafter referred to as the *Combined Standard Uncertainty* (CSU a.k.a. TPU).

Eq. 11 $\text{CSU (pCi/unit)} = \sqrt{\text{CountingUncertainty}^2 + (UE1 * A)^2 + (UE2 * A)^2 + (UE3 * A)^2 + (UE4)^2}$

UE1, UE2, UE3, and UE4 represent partial derivatives estimating the relative uncertainty at the ***95% confidence interval*** for various factors in the activity calculation as follows:

UE1 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with preparation (e.g., sample aliquot or transfers and splits prior to addition and equilibration of tracer).

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UE2 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with analysis (e.g., peak integration, peak overlap, tracer contaminants).

UE3 represents combined factors estimating relative uncertainty (fractional) associated with yield correction (e.g., count uncertainty for tracer peak, SRM known value, tracer volume or mass aliquot, tracer equilibration efficiency).

UE4 represents the factor estimating additional uncertainty (activity) associated with an individual sample -- to be used in exceptional circumstances with approval of the Department Manager or Manager-specified designee and with appropriate documentation and narration only.

The Minimum Detectable Concentration (MDC), Decision Level (DL) activity and Critical Level are calculated per guidance of ANSI N42.23 and N13.30 as:

Eq. 12 $$MDC = \frac{4.65 * \sqrt{(B/Ts) * T_S} + ZeroActFac_T}{Ts * Denom}$$

The Critical Level (LC), is calculated per guidance of ANSI N42.23 as:

Eq. 13 $$LC = \frac{1.65 * \sqrt{(B/Ts) * (1/T_S + 1/T_B)}}{Denom}$$

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Attachment II - (Numerical Performance Indicators)

1. **Method Blank (MB)**

1.1 The numerical performance indicator for the method blank is calculated by:

$$Z_{Blank} = \frac{x}{u(x)}$$

Where:
x = Measured blank activity
u(x) = Combined standard uncertainty (1 sigma) in the blank measurement

1.2 MB performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. MB performance indicator values should be recorded on a control chart.

2. **Laboratory Control Sample (LCS)**

2.1 The numerical performance indicator for a laboratory control sample is calculated by:

$$Z_{LCS} = \frac{x - c}{\sqrt{u^2(x) + u^2(c)}}$$

Where:

x = Analytical result of the LCS
c = Known concentration of the LCS
$u^2(x)$ = Combined standard uncertainty (1 sigma) of the result squared.
$u^2(c)$ = Combined standard uncertainty (1 sigma) of the LCS value squared.

2.2 LCS performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. Performance indicator values should be recorded on a control chart.

3. Duplicates (DUP)

3.1 These criteria are applicable for the evaluation of the Duplicate, Matrix Spike Duplicate and Laboratory Control Sample Duplicates.

3.2 The numerical performance indicator for laboratory duplicates is calculated by:

$$Z_{Dup} = \frac{x_1 - x_2}{\sqrt{u^2(x_1) + u^2(x_2)}}$$

Where:
x_1, x_2 = Two measured activity concentrations
$u^2(x_1)$, $u^2(x_2)$ = The combined standard uncertainty (1 sigma) of each measurement squared.

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3.3 Duplicate sample performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. DUP performance indicator values should be recorded on a control chart for each QC sample type (Dup, MSD, LCSD)

4. **Matrix Spike/Matrix Spike Duplicate (MS/MSD)**

4.1 The numerical performance indicator for a matrix spike sample is calculated by:

$$Z_{MS} = \frac{x - x_0 - c}{\sqrt{u^2(x) + u^2(x_0) + u^2(c)}}$$

Where:
x = measured concentration of the spiked sample
x_0 = measured concentration of the unspiked sample
c = spike concentration added
$u^2(x)$, $u^2(x_0)$, $u^2(c)$ = the squares of the respective combined standard uncertainties (1 sigma) of these values.

4.2 MS performance for all matrices is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. MS performance indicator values should be recorded on a control chart.

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Figure 1. Analysis Flowchart for Sequential Analysis of Am, Pu, U, and Th

BOX 1___Precondition a small anion column with 20mL 8N HNO_3 – discard
___Dissolve sample in 15mL 8N HNO_3 - heat to aid in dissolution as necessary – samples must be clear – centrifuge if suspended solids are present
___Load sample onto conditioned columns – collect in clean c-tubes labeled **ALL**
___Rinse sample c-tube with 15mL 8N HNO_3 and add to columns – collect for **ALL**
___Rinse column with 15mL 8N HNO_3 – collect for **ALL**
___Pour contents of **ALL** c-tubes into clean glass beakers and heat to dryness. **Proceed to Box 3.**
___Place new c-tubes under columns labeled **TH** – elute and collect thorium by adding 25mL 9N HCl to columns. **Proceed to Box 2.**
___Save columns for re-use

BOX 2___Transfer **TH** fraction to new labeled 250mL disposable cup.
___Add 0.80ml of iron carrier and dilute to the 220mL mark with DI water
___Precipitate the thorium as a hydroxide by adding 22mL of NH4OH and stirring with a disposable pipette.
___Stir the samples vigorously after 15 minutes.
___Allow the precipitate to settle for 30 minutes, decant the supernate, and transfer the rest to the original c-tube with pH 10 DI water.
___Centrifuge and discard the supernate.
___Dissolve **TH** residue in 3mL 9N HCl
___Dilute the dissolved **TH** with DI water to a final volume of 25mL
___Microprecip **TH** with Neodymnium and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 3___Add 15mL conc HCl to beakers labeled **ALL** and heat to dryness
___Dissolve contents of beakers labeled **ALL** in 15mL 9N HCl / 0.1% H_2O_2 – heat to aid in dissolution
___Load samples onto columns previously used – collect in c-tubes labeled **AM**
___Rinse **ALL** beakers with 10mL 9N HCl / 0.1% H_2O_2 and pour on columns – collect for **AM**
___Rinse columns with 20mL 9N HCl – collect for **AM. Proceed to Box 4**
___Place new c-tubes under columns labeled **PU –** elute and collect plutonium by adding 20mL 9N HCl / 0.05N NH_4I. **Proceed to Box 5**
___Rinse columns with 15mL 6N HCl / 0.52N HF – discard to waste
___Rinse columns with 10mL 9N HCl – discard
___Elute uranium into c-tubes labeled **U** by adding 20mL 0.1N HCl
___Microprecip **U** with neodymnium, titanous chloride to persistent purple color, and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 4___Transfer contents of c-tubes labeled **AM** to new glass beakers, add 3 drops Fe carrier and heat to dryness
___Add 5mL conc HNO_3 and heat to dryness
___Prepare Tru resin columns with pre-filter resin on bottom
___Condition columns with 5mL 2N HNO_3 - discard
___Dissolve contents of beaker in 10ml 2N HNO_3 / 0.5N $AlNO_3$
___Add 1 drop KSCN indicator and 6-8 drops of fresh 1N ascorbic acid – samples should be clear
___Pour sample onto columns – discard
___Rinse sample beaker with 5mL 2N HNO_3 – add to column - discard
___Rinse with 5mL 2N HNO_3 - discard
___Rinse with 5mL 2N HNO_3 - discard
___Elute AM into c-tubes with 2mL 9N HCL followed by 10mL 4N HCl
___Transfer to beakers and heat to dryness
___Add 1.0mL formic acid – heat to dryness
___Condition TEVA columns with 5mL fresh 3N Ammonium Thiocyanate / 0.1N Formic acid
___Dissolve samples in 15mL 3N AThio/ 0.1N formic
___Load sample onto columns – discard
___Rinse columns with 2mL 1N AThio/ 0.1N formic – discard
___Rinse with 3mL 1N AThio/ 0.1N formic – discard
___Rinse with 5ml 1N AThio/ 0.1N formic – discard
___Elute **AM** into new c-tubes with 15mL 2N HCl
___Microprecip **AM** with neodymnium and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 5___Transfer **PU** fraction to new glass beakers
___Add 10mL conc HNO_3 and 3 drops iron carrier
___Heat until reactions subside
___Add H_2O_2 dropwise to destroy NH_4I – about 15 drops
___Heat to dryness
___Add 5mL conc HCl
___Heat to dryness
___Dissolve **PU** residue in 10mL 9N HCl
___Transfer to new c-tubes with DI water to a final volume of 20mL
___Microprecip **PU** with neodymnium, 10-12 drops 25% dihydrazine dihydrochloride, and HF
___Count to meet MDC and obtain 400 tracer counts.

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Figure 2: Analysis Flowchart for Sequential Analysis for Am, Pu, U (Water or Solids)

Box 1___Prepare samples in accordance with the applicable section based on the matrix (12.1 for aqueous samples, 12.4 for solid samples). Solids must undergo complete digestion with HF.
___Condition prepared anion columns with 10mL 9N HCl.
___**Proceed to Box 2.**

BOX 4___Transfer **PU** fraction to new glass beakers
___Add 10mL conc HNO_3 and 3 drops iron carrier
___Heat until reactions subside
___Add H_2O_2 dropwise to destroy NH_4I – about 15 drops
___Heat to dryness
___Add 5mL conc HCl
___Heat to dryness
___Dissolve **PU** residue in 10mL 9N HCl
___Transfer to new c-tubes with DI water to a final volume of 20mL
___Microprecip **PU** with neodymnium, 10-12 drops 25% dihydrazine dihydrochloride, and HF
___Count for to meet MDC and obtain 400 tracer counts.

BOX 2___Dissove sample residue/precipitate in 15mL 9N HCl / 0.1% H_2O_2 – heat to aid in dissolution
___Centrifuge samples if necessary
___Load samples onto columns collect in c-tubes labeled **AM**
___Rinse sample c-tube with 10mL 9N HCl / 0.1% H_2O_2 and pour on columns – collect for **AM**
___Rinse columns with 20mL 9N HCl – collect for **AM.**
Proceed to Box 3
___Place new c-tubes under columns labeled **PU –** elute and collect plutonium by adding 20mL 9N HCl / 0.05N NH_4I. **Proceed to Box 4**
___Rinse columns with 15mL 6N HCl / 0.52N HF – discard to waste
___Rinse columns with 10mL 9N HCl – discard
___Elute uranium into c-tubes labeled **U** by adding 20mL 0.1N HCl
___Microprecip **U** with neodymnium, titanous chloride to persistent purple color, and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 3___Transfer contents of c-tubes labeled **AM** to new glass beakers, add 3 drops Fe carrier and heat to dryness
___Add 5mL conc HNO_3 and heat to dryness
___Prepare Tru resin columns with pre-filter resin on bottom
___Condition columns with 5mL 2N HNO_3 - discard
___Dissolve contents of beaker in 10ml 2N HNO_3 / 0.5N $AlNO_3$
___Add 1 drop KSCN indicator and 6-8 drops of fresh 1N ascorbic acid – samples should be clear
___Pour sample onto columns – discard
___Rinse sample beaker with 5mL 2N HNO_3 – add to column - discard
___Rinse with 5mL 2N HNO_3 - discard
___Rinse with 5mL 2N HNO_3 - discard
___Elute AM into c-tubes with 2mL 9N HCL followed by 10mL 4N HCl
___Microprecip **AM** with neodymnium and HF
___Count to meet MDC and obtain 400 tracer counts.

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Figure 3: Analysis Flowchart for Sequential Analysis of Am and Pu in Solids >1g

Box 1___1. Aliquot 3-4 grams of dry pulverized solid into clean labeled ceramic crucible.
___2. Add 1.0mL of iron carrier. Add tracers to all samples, and spike solution to LCS and MS.
___3. Cover sample with crucible lid and place in oven at 550C overnight (minimum of 4 hours).
___4. Remove samples from oven, re-label, and carefully loosen solid with a disposable pipette.
___5. Transfer loosened solid to a labeled glass beaker with a minimal amount of 8N HNO_3.
___8. Add 5mL 16N HNO_3 and 5mL 12N HCl to the crucible and place on hotplate at medium heat to loosen/remove the remaining solid.
___9. Transfer this solution to the appropriate glass beaker with 9N HCl. Repeat the above step as necessary to remove solid from the crucible.
___10. __ __Add 15mL 16N HNO_3 and 15mL 12N HCl to each sample beaker.
___11. __ __Cover sample with a watch glass and leach for 30 minutes on hotplate at medium heat.
___12. __ __Cool sample and transfer to a centrifuge tube using DI water. Centrifuge the sample.
___13. __ __Transfer the supernate to a clean labeled glass beaker and heat to dryness.
___14. __ __Transfer the solid back to the original beaker with 9N HCl.
___15. Repeat steps 10-14 two additional times adding the supernate from each centrifuge cycle to the beaker in step 13. The solid should be lighter in color indicating complete leaching of iron metal from the sample.
___16. Heat the supernate to dryness.
___17. Add 10mL 12N HCl to each sample beaker and heat to dryness. **Proceed to Box 2.**

BOX 4___Transfer **PU** fraction to new glass beakers
___Add 10mL conc HNO_3 and 3 drops iron carrier
___Heat until reactions subside
___Add H_2O_2 dropwise to destroy NH_4I – about 15 drops
___Heat to dryness
___Add 5mL conc HCl
___Heat to dryness
___Dissolve **PU** residue in 10mL 9N HCl
___Transfer to new c-tubes with DI water to a final volume of 20mL
___Microprecip **PU** with neodymnium, 10-12 drops 25% dihydrazine dihydrochloride, and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 2___Precondition small anion column with 10mL 9N HCl.
___Dissolve contents of beakers in 15mL 9N HCl / 0.1% H_2O_2 – heat to aid in dissolution – centrifuge sample
___Load samples onto columns – collect in c-tubes labeled **AM**
___Rinse beakers/c-tubes with 10mL 9N HCl / 0.1% H_2O_2 and pour on columns – collect for **AM**
___Rinse columns with 20mL 9N HCl – collect for **AM.**
Proceed to Box 3
___Place new c-tubes under columns labeled **PU –** elute and collect plutonium by adding 20mL 9N HCl / 0.05N NH_4I.
Proceed to Box 4
___Rinse columns with 15mL 6N HCl / 0.52N HF – discard to waste
___Rinse columns with 10mL 9N HCl – discard
___Elute uranium into c-tubes labeled **U** by adding 20mL 0.1N HCl
___Microprecip **U** with neodymnium, titanous chloride to persistent purple color, and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 3___Transfer contents of c-tubes labeled **AM** to new glass beakers, add 3 drops Fe carrier and heat to dryness
___Add 5mL conc HNO_3 and heat to dryness
___Prepare Tru resin columns with pre-filter resin on bottom
___Condition columns with 5mL 2N HNO_3 - discard
___Dissolve contents of beaker in 10ml 2N HNO_3 / 0.5N $AlNO_3$
___Add 1 drop KSCN indicator and 6-8 drops of fresh 1N ascorbic acid – samples should be clear
___Pour sample onto columns – discard
___Rinse sample beaker with 5mL 2N HNO_3 – add to column - discard
___Rinse with 5mL 2N HNO_3 - discard
___Rinse with 5mL 2N HNO_3 - discard
___Elute AM into c-tubes with 2mL 9N HCL followed by 10mL 4N HCl
___Transfer to beakers and heat to dryness
___Add 1.0mL formic acid – heat to dryness
___Condition TEVA columns with 5mL fresh 3N Ammonium Thiocyanate / 0.1N Formic acid
___Dissolve samples in 15mL 3N AThio/ 0.1N formic
___Load sample onto columns – discard
___Rinse columns with 2mL 1N AThio/ 0.1N formic – discard
___Rinse with 3mL 1N AThio/ 0.1N formic – discard
___Rinse with 5ml 1N AThio/ 0.1N formic – discard
___Elute **AM** into new c-tubes with 15mL 2N HCl
___Microprecip **AM** with neodymnium and HF
___Count to meet MDC and obtain 400 tracer counts.

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Figure No 4: Analysis Flowchart for Sequential Analysis of U and Th in solid or water utilizing Anion Resin.

BOX 1___Precondition a small anion column with 20mL 8N HNO_3 – discard
___Dissolve sample in 15mL 8N HNO_3 - heat to aid in dissolution as necessary – samples must be clear – centrifuge if suspended solids are present. An extra 5mL of 8N HNO_3 may be used if transferring solids to a centrifuge tube.
___Load sample onto conditioned columns – collect in clean c-tubes labeled **U**
___Rinse sample c-tube with 15mL 8N HNO_3 and add to columns – collect for **U**
___Rinse column with 15mL 8N HNO_3 – collect for **U**
___Pour contents of **U** c-tubes into clean glass beakers and heat to dryness. **Proceed to Box 3.**
___Place new c-tubes under columns labeled **TH** – elute and collect thorium by adding 25mL 9N HCl to columns. **Proceed to Box 2.**
___Save columns for re-use

BOX 2___Transfer **TH** fraction to new labeled 250mL disposable cup.
___Add 0.80ml of iron carrier and dilute to the 220mL mark with DI water
___Precipitate the thorium as a hydroxide by adding 22mL of NH4OH and stirring with a disposable pipette.
___Stir the sample vigorously after 15 minutes.
___Allow the precipitate to settle for 30 minutes, decant the supernate, and transfer the rest to the original c-tube with pH 10 DI water.
___Centrifuge and discard the supernate.
___Dissolve **TH** residue in 3mL 9N HCl
___Dilute the dissolved **TH** with DI water to a final volume of 25mL
___Microprecip **TH** with Neodymnium and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 3___Add 5mL conc HCl to beakers labeled **U** and heat to dryness
___Dissolve contents of beakers labeled **U** in 15mL 9N HCl– heat to aid in dissolution
___Load samples onto columns previously used
___Rinse **U** beakers with 10mL 9N HCl and pour on columns
___Rinse columns with 20mL 9N HCl
___Rinse columns with 20mL 6N HCl / 0.52N HF – discard to waste
___Rinse columns with 10mL 9N HCl – discard
___Elute uranium into c-tubes labeled **U** by adding 20mL 0.1N HCl
___Microprecip **U** with neodymnium, titanous chloride to persistent purple color, and HF
___Count to meet MDC and obtain 400 tracer counts.

Figure No 5: Thorium Separation on TEVA Resin

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BOX1 Prepare a labeled 2cm column with 3.5mL prepared (0.7 grams) TEVA resin. Allow the excess water to drain away.
_____Condition the column with 5mL of 3N HNO3.
_____Dissolve the sample in 10-20mL of 3N HNO3/1.0M Al(NO3)3
_____Centrifuge the samples to remove any solids prior to loading the sample onto the column.
_____If sequential uranium analysis is desired, place a clean labeled centrifuge tube beneath each column to collect the sample load solution.
_____Load the samples onto the column. Discard the effluent unless sequential uranium is desired, proceed to Box 2.
_____Rinse the sample container with 10mL of 3N HNO3.
_____When the sample has passed through the column, pour the sample rinse onto the column. Discard the effluent unless sequential uranium is desired, proceed to Box 2.
_____Rinse the column with an additional 20mL of 3N HNO3 after the first rinse has completely passed through. Discard the effluent.
_____Place a clean, labeled centrifuge tube under each column and elute the thorium from the column with 20mL of 9N HCl.
_____Collect any residual thorium from the column by rinsing with an additional 5mL of 6N HCl.
_____Transfer the thorium fraction to a 250mL labeled disposable plastic cup.
_____Add 0.8mL iron carrier (10mg/mL) to each sample.
_____Dilute the sample to the 220mL mark and add 22mL NH4OH to each sample.
_____Stir the samples vigorously with a glass stir rod. Allow the samples to sit for 15 minutes, and stir them again.
_____Remove the stir rod and allow the samples to settle for a minimum of 30 minutes.
_____Decant the excess supernate and transfer the precipitate back into the original collection c-tube from step 8/9.
_____Dilute the samples to the 50mL mark with DI water and centrifuge for 10 minutes. Decant the supernate.
_____Dissolve the precipitate in 3mL of 9N HCl. Dilute the sample to a final volume of 25mL with DI water.
_____Proceed to Step 12.14.4 for the Micro-Precipitation of Thorium.

Figure No 6: Uranium Separation on UTEVA Resin

BOX 2 Prepare a labeled 2cm column with 3.5mL prepared (0.7 grams) UTEVA resin. Allow the excess water to drain away.
_____Condition the column with 5mL of 3N HNO3.
_____Dissolve the sample in 10-20mL of 3N HNO3/1.0M Al(NO3)3 or collect the load solution passed through the TEVA columns during thorium analysis.
_____If necessary, centrifuge the load solution and load the sample onto the column. Discard the effluent.
_____Rinse the sample container or centrifuge tube with the 10mL of 3N HNO3 and add this rinse to the column. This would also have been collected during the TEVA thorium analysis if run sequentially. Discard the effluent.
_____Convert the column to chloride form by rinsing with 5mL of 9N HCl.
_____Remove polonium and residual thorium by rinsing with 15mL 5N HCl/0.05 M oxalic acid.
_____Rinse the oxalic acid from the column with 10mL of 6N HCl.
_____Pipette 2mL of 6N HCl into each clean, labeled centrifuge tube and place the tubes under each column.
_____Elute uranium from the column with 20mL of 0.01N HCl.
_____Proceed to Step 12.14.3 for the Micro-Precipitation of Uranium.

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STANDARD OPERATING PROCEDURE

Gamma Spectroscopy Instrument Operations

Method: EPA 901.1

SOP NUMBER:	PGH-R-023-9
REVIEW:	R. Kinney
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-R-023-8
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager — Date: 12/03/15

Senior Quality Manager — Date: 12/03/15

Department Manager/Supervisor — Date: 12/03/15

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date

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1. Purpose

This procedure describes the general operation and maintenance of the gamma spectroscopy instrumentation utilized by the Pace Analytical Services, Inc. For additional operational details not discussed in this SOP, the user should consult the instrument and software operations manuals referenced in Section 17. These documents are located in the gamma instrument room.

2. Scope and Application

2.1 Pace SOP PGH-Q-038, current revision (Laboratory Equipment) addresses general requirements regarding the purchase, installation, operation, maintenance, and disposition of laboratory equipment.

2.2 This procedure addresses the process for analyzing sample sources generated as the product of current revision analytical SOPs: PGH-R-027 (Analysis of Neutron Dosimeter Wires by Gamma Spectroscopy), PGH-R-028 (Analysis of Neutron Dosimeter Capsules for Cesium-137), and PGH-R-030 (Iodine-129 Analysis).

2.3 Samples for non-destructive gamma spectroscopy analysis are prepared using the current revision of Pace SOP PGH-R-040.

2.4 This procedure applies to the measurement of gamma particles emitted from a variety of sample types. Several detection systems are utilized, but all analysis, data processing, storage, and reporting can be performed using different software commands within one flexible user interface for each system type. Each system type has an independent user platform consisting of a computer and detector-specific software that controls instrument operation, spectral analysis, and calculations.

2.5 Sample specific preparation is not discussed in this SOP. The final sample geometry must conform to one of the existing calibration geometries at the time of counting. Deviations in sample geometry from the calibration geometry require a new calibration.

2.6 This procedure describes the performance of the gamma detector efficiency, energy, and FWHM calibration; monthly background determination; and daily or prior to use (PTU) continuing calibration verification checks. Also discussed are the general systems operating requirements and maintenance.

2.7 This procedure is applicable to gamma spectroscopy detectors of HPGe “p” type, HPGe “n” type, or LeGe (LEPS) type, utilizing multiple software components.

3. Summary of Method

3.1 The system is calibrated for efficiency, energy, and resolution full width-half max (FWHM) for all new counting geometries. Sources may be commercially available or laboratory prepared with NIST traceable materials and equipment. Long backgrounds (minimum of 1000 minute duration) are performed within 30 days prior to all sample analyses or more frequently as necessary. Daily (or PTU) checks of the efficiency, energy, FWHM, and background are performed to ensure detector function prior to use.

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3.2 Samples are counted upon completion of a daily check, utilizing the system software available, on a detector capable of detecting the nuclides of interest in the sample. Once counting is complete on Canberra system, the system software automatically processes the data, and the primary count analyst must review spectra and enter the data into LIMS for client delivery. For the Ortec system, the user must manually process data.

4. Interferences

4.1 Sample counting geometries must be of uniform consistency for accurate results. Phase separations in liquid samples or grading in solid samples may bias sample results.

4.2 In order to prevent possible detec tor contamination, aqueous samples should be contained in a plastic bag or other suitable device to ensure secondary containment, with the first container being the durable sample container such as a Marinelli beaker or plastic "jar." In the event of a spill, the detector must be cleaned immediately, and backgrounds must be measured.

4.3 High activity samples may cause excessive dead time in detectors and should be analyzed utilizing a geometry that increases the sample to detector distance, thereby decreasing the observed count rate.

4.4 Detector electronics must be kept cool while counting is in progress. Liquid nitrogen is stored in a dewar at the base of the instrument for this purpose. The level must be maintained by regularly filling the dewar with liquid nitrogen. System performance is greatly affected by temperature fluctuations, and damage to detectors can result from operating without proper cooling.

4.5 Many radioisotopes emit gamma rays that are indistinguishable (by energy) from other gamma-emitting radioisotopes. One such example, Ra-226, emits a predominant gamma ray very near that of a gamma ray emitted by U-235. Common gamma spectroscopy systems cannot easily identify the source of the gamma ray. For this reason, interfering gamma rays should be excluded from use for quantitation. Alternatively, if the interfering gamma rays are used for quantitation, the results must be qualified as potentially biased due to conflicts with other radionuclides.

5. Safety

5.1 Procedures must be carried out in a manner that protects the health and safety of all personnel. Since this analysis is for a radioactive constituent, the sample must be treated as radioactive. .

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves will be cleaned immediately.

5.3 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye protection, gloves, and lab coat must be worn.

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5.4 Exposure to radioactivity and chemicals must be maintained as low as reasonably achievable therefore, unless they are known to be non-hazardous and/or non-radioactive, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 In order to minimize the potential for cross contamination of high and low levels of radioactive samples, good housekeeping and good laboratory practices are essential and must be strictly adhered to.

5.6 Organic samples of unknown content must be handled with extreme caution and under the direct instruction of a senior analyst. Direct treatment of organic matrices with strong oxidizing chemicals such as nitric acid and/or hydrogen peroxide is strictly prohibited.

5.7 Hydrofluoric acid is particularly hazardous because a serious skin exposure may cause no immediate sensation of pain. The acid penetrates the skin and spreads internally, causing tissue damage deep under the skin. The resulting burn is painful, difficult to treat, and easily infected. Gloves must be checked for pinhole leaks before use. They must be rinsed before they are removed and must be discarded after use. HF burn gel shall be put on suspected HF burns after flushing (except the eyes) until medical help can be obtained. Medical attention shall be sought even if suspicions arise after working hours. Contact the group leader immediately for further information if an HF burn is suspected.

5.8 In addition, HF vapors are also hazardous. Exposure can cause permanent damage. Breathing HF vapors even for a short time and at a low temperature can be injurious to the respiratory system, and even fatal. All such direct contact must be avoided.

5.9 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the SDS files maintained in the laboratory.

5.10 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.11 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.12 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Hardware equipment and software terms are defined in the applicable operating manuals by the equipment and/or software manufacturer.

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6.2 Refer to the current Quality Manual for definitions.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

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8.1 Refer to the applicable SOP and certified test method for sample collection and preservation requirements. The list of applicable SOPs and reference methods is located in Sections 2.2 and 2.3.

8.2 Aqueous samples should be bagged to prevent leaking that may contaminate detectors.

8.3 Solid samples should be sealed in order to prevent detector contamination in the event that the sample is dropped.

9. Equipment and Supplies

9.1 High Purity Germanium (HPGe) “p” type, “n” type and Low-Energy Germanium (LeGe) or Low-Energy Photon Spectrometer (LEPS) type detectors.

9.2 Computer Data Analysis system run on a Canberra instrument-compatible computer. Canberra utilizes multiple software applications joined together to form the Genie 2000/Procount software package. For issues/processes not addressed within this SOP, refer to the instrument manual current revision.

9.3 Ortec GammaVision® software. Ortec GammaVision®-compatible computer. For issues/processes not addressed within this SOP, refer to the instrument manual current revision.

9.4 Front End Electronic components:

9.4.1 High Voltage Power Supply: supplies power to detectors.

9.4.2 Analog to Digital converter: converts analog voltage from crystal to digital readout.

9.4.3 Multi Channel Analyzer (MCA): Detector acquisition and control is performed through an MCA. The MCA is supported through a combination of hardware and software and functions as the analyzer. It is the link between spectra and the computer system.

9.5 Kim wipes® or lint free cloths.

9.6 Plastic bags.

10. Reagents and Standards

10.1 Reagents should be prepared from reagent grade chemicals, unless otherwise specified below. Reagent (DI) water must be at least ASTM Type II quality or better. NOTE: Consult Safety Data Sheets for the properties of these reagents, and how to work with them.

10.2 Distilled or deionized water, ASTM Type II generated as specified in Pace SOP PGH-C-027, current revision.

10.3 Liquid nitrogen, ACS grade, for detector cooling.

11. Calibration and Quality Control

Note: Refer to the instrument operations manual for instructions regarding specific system setup options.

11.1 Daily Checks

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11.1.1 Daily or prior to use, a continuing calibration verification (CCV) check source is counted for five minutes to determine detector function, assessing the energy, efficiency (activity), and resolution (FWHM) calibrations.

11.1.2 High Purity Germanium Detectors with associated electronics are sensitive to temperature variations within the count room environment. The probable effect of variations in temperature is the slight drifting of gamma peaks in the high-energy range (>1MeV) of the analytical spectrum. Marginal shifts in the ambient temperature do not cause spectral shifts that would negatively impact analytical results. In order to optimize gamma spectral analysis, the system fine amplifier gain may be adjusted to correct for minor peak drifting. This process applies exclusively to Ortec gamma detectors.

11.1.3 Gain Adjustment

11.1.3.1 Place the check source used for instrument performance checks on the endcap of the applicable detector. Perform a manual count of the check source while observing the spectral location of the 1332.5 keV peak of Co-60. Adjust the system fine gain incrementally in order to position the peak at channel 5330. Record the fine gain adjustment value in the detector Maintenance Logbook.

11.1.3.2 Clear the analysis spectrum and re-start the qualitative count of the check source. Confirm the location of the 1332.5 keV peak to be centered at channel 5330. Clear the analysis spectrum and perform performance checks as documented below.

11.1.4 Each energy, efficiency (activity), and resolution (FWHM) is assessed using defined tolerances for each parameter. For the efficiency (activity) assessment, the defined tolerance is used as a total allowable deviation for the count source. For control purposes, the tolerance is divided by 3.0 to generate a standard tolerance deviation. Warning limits are set at +/- 2.0 standard tolerance deviations and control limits are set at +/- 3.0 standard tolerance deviations. The assessments of peak energy and resolution (FWHM) are not statistical measurements. For these variables, tolerances have been set based on manufacturer's recommendations. Limits have been set to establish a warning and control boundaries.

11.1.5 The tolerance for efficiency (activity) has been established at 5%. This tolerance was chosen based upon combined uncertainties for the source count including count uncertainty and variability in source placement.

11.1.6 The low warning limit for energy has been established as -0.25 keV difference from the known peak energy. The low control limit has been established as -0.50 keV from the known peak energy. The high

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warning limit and high control limit for energy have been established as 0.25 keV and 0.50 keV, respectively.

11.1.7 The control assessment for resolution is measured as a ratio of the source check peak resolution versus the calibration-defined resolution. The low warning limit for resolution (FWHM) has been established at 0.9 with a low control limit at 0.8. The high warning limit and high control limit for resolution (FWHM) have been established as 1.2 and 1.5 respectively.

11.1.8 A minimum five minute daily background of the empty shield is conducted and compared to the running median background counts to determine if the detector shield has been contaminated.

11.1.8.1 The control limit for the daily background count has been established statistically using a representative population of background counts. Warning and control limits have been established for each detector system with warning limits established at +/- 2.0 standard deviations of the system total background count rate in units of counts per second and control limits set at +/- 3.0 standard deviations of the system total background count rate in units of counts per second.

11.1.9 To perform the daily check, place the designated check source in the sample holder onto the shield, and close the cover. For the Canberra system: Select QC, then CALIBRATION CHECK. Choose the appropriate detector from the dropdown list. Select QCC-A (or the appropriate detector-specific file), then Control Det A (or the appropriate detector-specific control program), followed by OK to initiate the five-minute count. For the Ortec system: Double-click appropriate desktop icon (Det "#" QA Daily Check). Click "OK" at the following prompt.

11.1.10 Upon completion, the QC report will automatically be generated. QC reports are stored electronically and may be retrieved for performance troubleshooting. Data from each QC assessment are automatically loaded into the QA database for automated assessment and charting.

11.1.11 The analyst must verify that the detector meets the control criteria. To determine system acceptance for use, review the instrument check printouts for the assessment criteria OR review the control chart for each performance parameter monitored. QA assessment is software controlled within each counting system type. Control limits are statistical for activity assessments and are based on generally recognized tolerances for resolution and peak location.

11.1.12 Any daily check not meeting the control criteria must be recounted. Check the positioning of the source within the detector and verify the correct placement of the check source prior to initiating a recount. Two consecutive acceptable recounts are required for the

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detector to be in service. If the recount is unsuccessful, the detector must be locked out until a successful daily check is performed. If a detector fails several consecutive daily checks, the cause must be investigated. Consult with a senior analyst on how to proceed.

11.2 Monthly Background Measurement

11.2.1 Every month, at a minimum, (or within thirty days of sample analysis, at a minimum) an extended background count is completed for use in sample analysis. Additionally, backgrounds must be re-acquired following calibration, detector cleaning due to confirmed contamination, or maintenance. Typically, extended background counts are performed weekly. For all sample analyses, the prior (but most recent) background must be used for sample analysis.

11.2.2 Clean the detector shields prior to counting backgrounds with a lint free cloth dampened with ASTM Type II DI water.

11.2.3 Ensure daily checks have been performed and detectors have passed control criteria prior to performing background counts.

11.2.4 Canberra System:

11.2.4.1 For the Canberra system: Start counts by selecting COUNT and Start A LONG BACKGROUND COUNT. Choose the appropriate detector when prompted, followed by LONG BKG and NO SPECIFIC GEOMETRY. Select OK to begin the acquisition. Select OK in the following window, since all of the criteria has been pre-selected. The detector will begin counting. The shield cover must remain closed during the count.

11.2.4.2 When counting is complete, a background report will automatically be generated.

11.2.5 Ortec System:

11.2.5.1 For the Ortec system, ensure that the detector shield is empty. Perform step 12.1.5 as indicated below, acquiring an empty chamber count using a count time of 1000 minutes (60,000 seconds). The convention for naming the background count is LB (Long-background) Detector Number (DX), date of counting (MMDDYY). A background count performed for detector 2 on June 1, 2015 would be named, “LBD2060115.”

11.2.5.2 The Ortec Background Spectrum must be analyzed using each combination of detector/geometry calibration/library to be used for sample analysis.

11.2.5.3 Upon completion of the background count, recall the background spectrum into the processing “buffer.” To apply the appropriate calibration file: from GV toolbar (Fig 1. below), click CALIBRATION and select RECALL

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CALIBRATION. From the list of archived calibration files, select the file for the appropriate geometry for which to create the background analysis file. Next, select the appropriate nuclide library. From the GV toolbar, click LIBRARY and click SELECT.

11.2.5.4 Click ANALYZE, place cursor over SETTINGS and select SAMPLE TYPE. A new window will appear into which sample data will be entered. From the SAMPLE tab (Fig 2.), click BROWSE, near the file entry blank, and select the appropriate .sdf file. Also from the SAMPLE tab, select the appropriate library and calibration files.

11.2.5.5 For the background spectral analysis, the sample size and decay correction date are not necessary. The "Peak-Background Correction" (PBC) file created for the background analysis only requires the energy calibration file which relates peak channel to energy and the library file which relates peak energy to detected analyte. At the bottom of the window select CLOSE and click YES, when prompted to save.

11.2.5.6 Lastly, from the GV toolbar, click ANALYZE and ANALYZE ENTIRE SPECTRUM IN MEMORY. If the printer output has been selected, the analyzed report will be printed.

11.2.5.7 To create the individual "Peak-Background-Correction" (PBC) files, click "ANALYZE" on the GV menu bar. Select "SETTINGS". Select "Peak Background Corrections", then "Select PBC" Choose the file for a recently-completed PBC file and select "OPEN."

11.2.5.8 Using the cursor, depress the "Cut" button repeatedly until all analytes have been removed from the active PBC file. Once all analytes have been removed, select the window in the very upper left-hand corner of the PBC box. Select the "Show Background Analysis" option.

11.2.5.9 The system will show all of the available un-formatted output "UFO" files for each sample spectrum previously analyzed. Find and choose the .UFO file for the analyzed background file you wish to create the PBC file from. The .UFO file will have the name of the background spectrum with a .UFO extension. For the example cited in section 11.2.5.1 above the .UFO file will correspond as "LBD2060115.UFO."

11.2.5.10 Once the .UFO file has been high-lighted, select the window in the very upper left-hand corner of the PBC window. Select, "Save PBC table as"…." Type in the name for the new detector/geometry/library PBC combination and select, "Save."

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11.2.6 For each detector platform, the analyst must check the report and compare it to previous long backgrounds to determine if contamination is present.

11.2.7 Background changes must be tracked to determine if detectors need more vigorous cleaning. All detectors which do not pass the control criteria must be locked out to prevent accidental use during sample analysis.

11.2.8 The background count for detectors failing control criteria may be re-acquired following maintenance to improve background performance, including reassessment of potential contamination sources and re-cleaning of the detector shields.

11.3 Detector Calibration

11.3.1 Efficiency, energy, and FWHM calibrations for specific counting geometries must be completed initially or following major system maintenance, such as detector replacement. Calibration for specific counting geometries must be performed following major analytical SOP changes that would change the final geometric configuration of the final counting source. For example, an analytical change resulting in counting an aqueous sample in a 1.0L Marinelli beaker to counting an aqueous sample in a 0.5L Marinelli beaker requires calibration for the additional geometry.

11.3.2 Calibrations must be performed using the same protocols as used in sample analysis, with adjustment to sample count time being the only factor to change. Calibration instructions for each analysis type are included in the current revision of each applicable SOP. The list of applicable SOPs and reference methods is located in Sections 2.2 and 2.3 of this SOP.

11.3.3 Gamma Spectroscopy Instrument Calibration Requirements

11.3.3.1 Energy calibrations are performed prior to geometry-specific efficiency calibrations. The energy calibration documents the peak channel number to the peak energy. Geometry efficiency calibrations relate the peak energy to the detector response as percent of emissions observed versus emitted.

11.3.3.2 A minimum of 10000 net counts for each nuclide of interest utilized in the calibration source must be obtained. Nuclides of interest should be chosen in order to encompass various energy ranges consistent with those encountered in routine sample counting. Typically, a minimum of ten nuclides, are utilized in a calibration source. For each geometry-specific efficiency calibration performed, a known standard reference material (SRM) in an identical configuration is counted and assessed using the statistical control limits used for Laboratory Control Samples (LCS) in the related Gamma analysis SOP.

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Sources used for calibration verifications must incorporate the use of a SRM that is not related to the calibration source parent solution.

11.3.3.3 Data are analyzed by the Genie 2000/Procount® or Ortec GammaVision® software package.

11.3.3.4 Calibrations must be verified annually for all aqueous geometries, including those used for drinking water analysis. The same source utilized for the initial calibration must be used for verifying the calibration. A minimum of three of the nuclides used in the initial calibration must be used to verify the calibration. The three nuclides should span the energy range (low, mid, high) of the initial calibration, for example Am-241, Co-60, and Cs-137. The verification source result for all three nuclides must be within 10% of the known nuclide concentration for the verification to be acceptable.

11.3.3.5 For all other calibration geometries, calibrations must be verified annually. Calibration standard reference materials (SRMs) such as spiked soils are purchased in limited quantities that do not allow simultaneous creation of all solid calibration sources used by the lab. For this reason, SRM material is often recycled to perform all of the necessary geometry calibrations. Calibration verification should be performed with the original calibration material, however, source material may be re-prepared in a matching geometry. A minimum of three of the nuclides used in the initial calibration must be used to verify the calibration. The three nuclides should span the energy range (low, mid, high) of the initial calibration, for example Am-241, Co-60, and Cs-137. The verification source result for all three nuclides must be within 10% of the known nuclide concentration for the verification to be acceptable.

12. Operating Procedures

12.1 Sample Counting and Processing

12.1.1 Before beginning any counts, the detector run log information must be completed. This information includes: the date, analyst, and passing detectors.

12.1.2 Prior to counting, ensure that daily checks have been completed satisfactorily and the detector is free of check sources and contamination.

12.1.3 Insert the sample to be counted and record the detector in which it will be counted in the gamma instrument run log. Record all sample information in the run log. Place sample into the detector and close the shield lid.

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12.1.4 For the Canberra system: select COUNT and START AND COUNT from the Procount-ESP Screen. Select the detector, then choose the ANALYTICAL SEQUENCE FILE (ASF), which will determine the criteria by which the sample will be analyzed. Choose the geometry, then select OK to start the acquisition. Complete the sample information form, and select OK. A report will be generated automatically upon count completion.

12.1.5 For the Ortec system: Double-click the appropriate desktop icon (Det "#" Sample). When prompted, enter the requested sample information. After entering the time, in seconds, select CLOSE. Finally, click OK on the following popup. Upon completion of sample counting, the user will be required to manually process data

Fig 1. (GV toolbar)

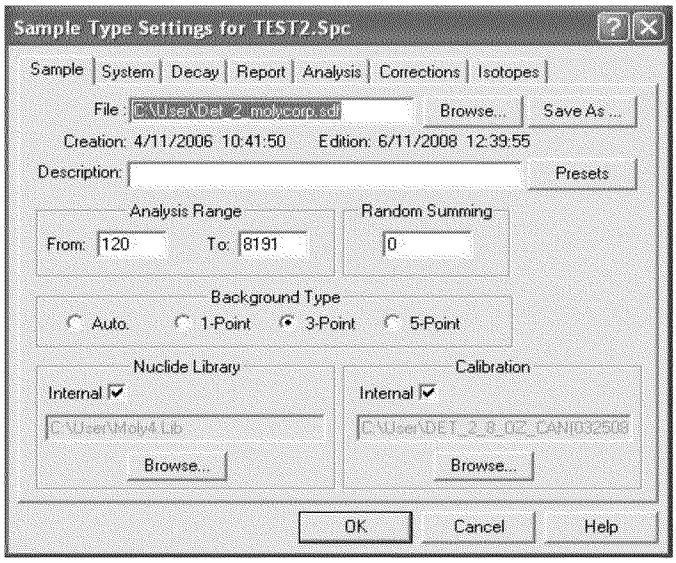

Fig 2. (Sample Tab)

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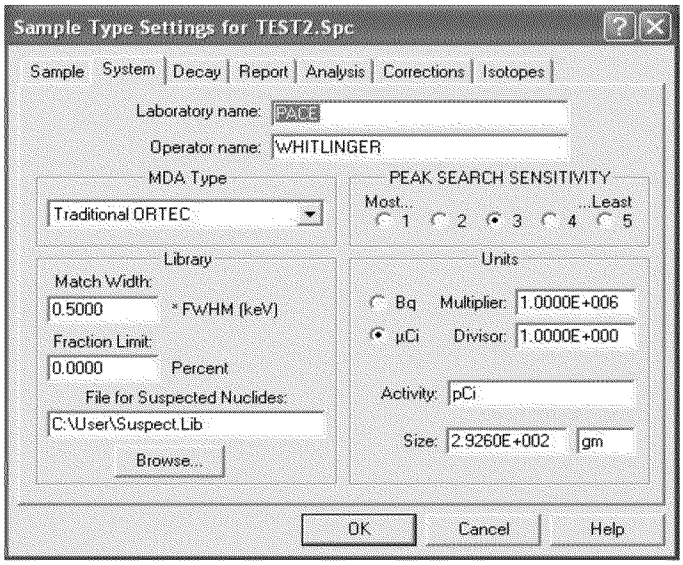

Fig 3. (Sample Tab)

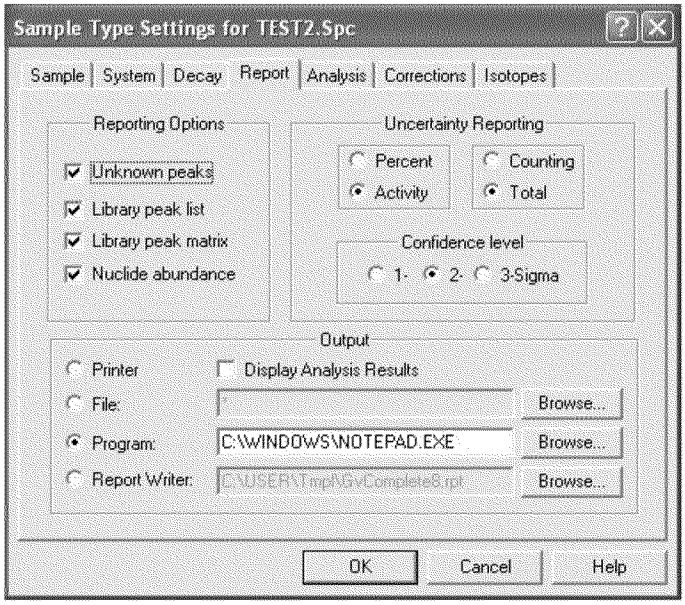

Fig 4. (Report Tab)

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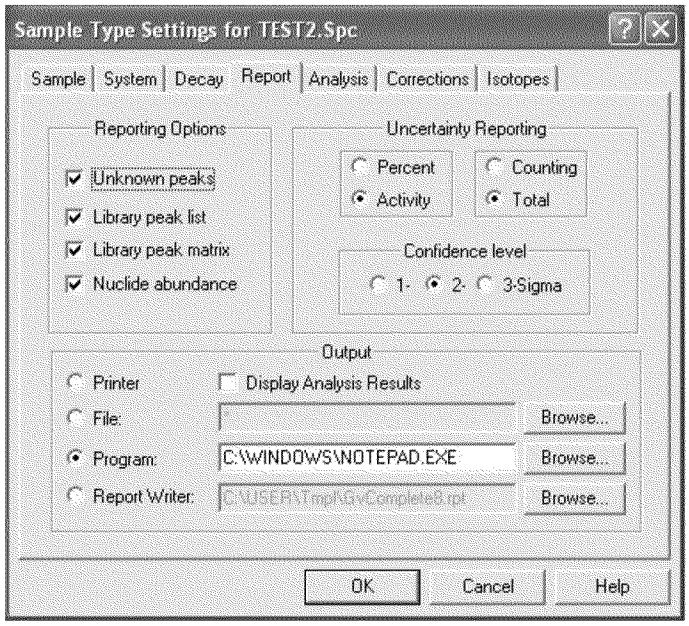

Fig 5. (Report Tab)

12.1.6 To process data from the Ortec system, the analyst must first recall the desired spectrum, using the GammaVision(GV)® program. To apply the appropriate calibration file: from GV toolbar (Fig 1.), click CALIBRATION and select RECAL INFORMATION. From the list of archived calibration files, select the most recent file for the appropriate geometry. Next, select the appropriate nuclide library. From the GV toolbar, click LIBRARY and click SELECT.

12.1.7 Click ANALYZE, place cursor over SETTINGS and select SAMPLE TYPE. A new window will appear into which sample data will be entered. From the SAMPLEtab (Fig 2.), click BROWSE, near the file entry blank, and select the appropriate .sdf file. Also from the SAMPLE tab, select the appropriate library and calibration files.

12.1.8 From the “System” tab (Fig 3.), enter the sample size, in grams. From the “Decay” tab (Fig 4.), enter the sample date and time. From the “Report” tab, select the output option, printer or file. At the bottom of the window select CLOSEand click YES, when prompted to save.

12.1.9 Finally, from the GV toolbar, click ANALYZE and ANALYZE ENTIRE SPECTRUM IN MEMORY. If the printer output has been selected, the analyzed report will be printed.

12.1.10 The gamma report must be reviewed by the analyst, and the spectrum must be viewed and compared to the report. Sign the report and enter the calculated activities into LIMS for the final report.

12.2 Maintenance

12.2.1 Detector

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12.2.1.1 Detectors can be cleaned and maintained with ASTM Type II DI water and lint free cloths, or KImwipes®.

12.2.1.2 Removal and replacement of any detector requires a new calibration be established and must be recorded in the equipment maintenance logbook.

12.2.1.3 Detector temperature must be maintained with liquid nitrogen. Maintaining the level of liquid nitrogen in the dewar under each detector is crucial for system operation.

12.2.2 Major Instrument Maintenance

12.2.2.1 Consult with a senior analyst prior to performing troubleshooting steps to identify the source of system problems. Refer to the instrument manual for guidance on diagnosing system problems.

12.2.2.2 Consult with the manufacturer for troubleshooting major system problems.

12.3 All maintenance functions involving power disruptions to the instrument must be documented in the appropriate instrument maintenance logbook at the time of occurrence. Calculations

12.4 Refer to the Canberra "Spectroscopy Applications Algorithms and Software Verification and Validations Manual 07-0368, September 1991" for analysis calculation documentation.

13. Quality Control

13.1 See Section 11.0 of this SOP for system calibration and for system Quality Control requirements.

13.2 Analytical batch Quality Control is documented for each analyte in the applicable SOP. The list of applicable SOPs and reference methods is located in Section 2.2 and 2.3.

13.3 Corrective Actions for Out-Of-Control Data

13.3.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

13.3.2 Duplicate (DUP) – The duplicate sample is typically a duplicate count of the Laboratory Control Sample (LCS) DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

13.3.3 Matrix Spike Recovery (MS) – MS samples are not typically analyzed for gamma spectral content due to inability of the lab to homogenize spike material with sample media. If performed, MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is

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also analyzed and the recovery is comparable to the MS, the results are reported and noted in the final report.

13.3.3.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

13.3.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

13.3.5 Laboratory Control Sample (LCS) – The LCS used for gamma-spectral analysis is a static source of relative consistent content of project samples, matching the geometric configuration of prepared project samples. If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

13.3.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

13.3.6 Laboratory Control Sample Duplicate (LCSD) – The LCSD is typically a replicate count of the static LCS source described in section 13.3.5. If a LCSD does not meet the recovery acceptance criteria, the entire analytical batch must be reanalyzed.

13.3.6.1 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit, and duplicate precision meets the acceptance criteria.

13.3.7 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14. Method Performance

14.1 Laboratory control samples (LCS) are analyzed with each batch; the results are charted to monitor control limits and trending.

14.2 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

14.3 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

14.4 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

15. Pollution Prevention and Waste Management

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15.1 Place radioactive waste into appropriate receptacles.

15.2 Discard acidified samples and unusable standards into proper waste drains.

15.3 Dispose of waste materials in accordance to type: Non-hazardous, hazardous, non-radioactive, radioactive or mixed.

16. References

16.1 ASTM E181-93, Standard Test Methods for Detector Calibration and Analysis of Radionuclides, ASTM Standards, Vol. 12.02.

16.2 User's Manual, Model 480726 Genie-ESP System, September, 2000.

16.3 Advanced Concept's Manual, Model 480198 Genie-VMS Spectroscopy System, September 2000.

16.4 Command Descriptions Manual, Model 480198 Genie-V<MS Spectroscopy System, September, 2000.

16.5 Crystal Reports, Version 8.5, Seagate, 2001.

16.6 User's Manual, Model 480206 Genie-VMS Quality Assurance Software, September, 2000.

16.7 User's manual, Model 480720 PROcount-ESP, September, 2000.

16.8 User's Manual Maestro-32 MCA Emulator, Ortec, Version 6.05, 2002.

16.9 Programmer's Guide, Model 480198 Genie-VMS Spectroscopy System, September, 2000.

16.10 Nuclide Identification Algorithms and Software Verification and Validation Manual, 07-0464-02, Canberra Industries, November 1993.

16.11 Peak Search Program Algorithm Manual, 07-0064, Canberra Industries, March 1985.

16.12 Spectroscopy Applications Algorithms and Software Verification and Validation Manual, 07-0368, September 1991.

16.13 Table of Radioactive Isotopes, Brown and Firestone, Shirley editor, John Wiley & Sons, 1986.

16.14 Krieger, H. L. and Whittaker, E. L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, "Gamma Emitting Radionuclides in Drinking Water," Method 901.1, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, August, 1980.

16.15 "Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)", July 2004, Final.

16.16 Department of Defense Quality System Manual for Environmental Laboratories (DoD QSM), current version.

16.17 *EML Procedures Manual*, HASL-300, 27th Edition, Volume 1, 1990, Method 4.5.2.3 – Gamma.

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16.18 Pace SOP PGH-Q-038 (Laboratory Equipment), current revision.

16.19 Pace SOP PGH-R-040 (Gamma Spec Prep), current revision.

16.20 Pace SOP PGH-R-027 (Neutron Dosimetry), current revision.

16.21 Pace SOP PGH-R-028 (Cs-137 Dosimeter), current revision.

16.22 Pace SOP PGH-R-030 (I-129), current revision.

16.23 Pace SOP PGH-C-027, current revision (Deionized Water Quality and Suitability).

16.24 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

16.25 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

16.26 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17. Tables, Diagrams, Flowcharts, Appendices, etc.

17.1 See the operations manual supplied by the manufacturer for diagrams and tables associated with the operation or maintenance of gamma spectroscopy detectors.

18. Method Modifications

18.1 Not Applicable.

19. 20. Revisions

Document Number	Reason for Change	Date
PGH-R-023-5	1. Table of contents added. 2. Section 1 modified to specify location of referenced documents. 3. Section 2 modified to specify hardware and software as required by DOD QSM. 4. Section 3 modified to incorporate “resolution” term in conjunction with FWHM calibration. Long Background count time corrected to minimum of 1000 minutes. Long Background frequency defined to reflect specific requirements. 5. Section 4.2 modified to clarify secondary containment of aqueous count geometries for prevention of cross-contamination. 6. Section 6 Revised to discuss the location of definitions for terms related to the equipment hardware and system software. 7. Section 8 modified to remove extraneous analysis sample analysis protocols. Specification that geometries containing solid sample should be sealed. 8. Section 9 modified to describe computer requirements for the two analysis platforms used currently 9. Section 11 modified to cite requirement for daily performance	18May2012

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Document Number	Reason for Change	Date
	check assessment by analyst. Also, order of calibrations is documented to require energy calibration prior to geometry-specific efficiency calibrations. 10. Section 15, 19 and 20 added. 11. Section 15 renamed as Method Performance. Method performance requirements added. 12. Section 17: Added Method 901.1 reference 13. Section 19 renamed as Method Modifications	
PGH-R-023-6	1. Annual Review and Update (2013). 2. Added specifications for DI water as ASTM Type II DI water and included reference to SOP PGH-C-027, the SOP that documents the DI water production and testing process. 3. Section 11.1.2 Specified the requirement of a minimum five minute daily background check for gamma instruments. 4. Section 11.2.1 specified that extended background counts used for sample analyses are performed monthly at a minimum but specified that backgrounds are typically run weekly. 5. Section 11.3.3.3 added Ortec GammaVision software to the list of software used for calibration calculations. 6. Section 17.19 Added reference to *EML Procedures Manual*, HASL-300, 27th Edition, Volume 1, 1990, Method 4.5.2.3 – Gamma.	25Jun2013
PGH-R-023-7	1. Annual SOP Review (2014) 2. Section 2.2 and 2.3 - Included reference to Pace SOPs and methods for analyses performed by gamma counting. 3. Section 11 – Updated for verification procedure and acceptance criteria. 4. Section 11 – Updated to include aqueous and Drinking Water calibration and other geometry calibration verification requirements. 5. Document updated to include reference to all applicable Pace SOP and method references for analyses where a gamma detector/system is utilized. 6. Section 17 – Updated to include Pace SOP and method references related to gamma spectroscopy counting. 7. Reformatted document.	13Jul2014
PGH-R-023-8	1. Section 11 (11.1.2) updated to include process for amplifier gain adjustments for Ortec gamma detectors.	20Feb2015
PGH-R-023-9	1. Corrected formatting in Section 8. 2. Section 9.1, defined Gamma Detector Types. 3. Section 9.2 and 9.3, added suggestion to consult the respective instrument manuals for issues not covered by this SOP. 4. Section 11.1.5, revised SOP to indicate that hard-copy performance check data are being stored electronically. Printouts are no longer stored. 5. Section 11.2.5, added procedure for performing long background counts on the Ortec system. 6. Section 13.3, added clarifying information regarding the LCS	03Dec2015

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	and duplicate counts.	

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STANDARD OPERATING PROCEDURE

Analysis of Water Samples for Radium-226

Methods: EPA 903.1, SM7500-Ra C

SOP NUMBER:	PGH-R-007-16
REVIEW:	R. Kinney
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-R-007-15
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager	12/14/15 Date
Senior Quality Manager	12/14/15 Date
Department Manager/Supervisor	12/14/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date

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1. Purpose

1.1 This SOP documents the analytical procedure to be used for analysis drinking water and other aqueous samples for radium-226.

2. Scope and Application

2.1 This procedure covers the measurement of radium-226 in drinking water samples and should be employed after the gross alpha or gross radium alpha screening technique had indicated possible non-compliance with the alpha radioactivity limits set forth in the Safe Drinking Water Act, PL 93-523. 40 FR 34324.

2.2 Additionally, this SOP is applicable to the analysis of other aqueous sample types without modification.

2.3 This procedure is specific for radium-226, and is based on the emanation of radon-222, a daughter product of radium-226. Radium-226 concentration is determined by scintillation counting of radon-222, polonium-218, and polonium-214 (daughters of radon-222).

2.4 The detection limit for this procedure assures measuring radium-226 concentrations lower than 1.0pCi/L and potentially as low as 0.1pCi/L.

2.5 Without qualification, this procedure, as written, is compliant with Method 903.1 of "*Prescribed Procedures for Measurement of Radioactivity in Drinking Water*, EPA-600/4-80-032". Deviations from the promulgated methods are discussed in Section 18 of this SOP.

2.6 Pace Analytical applies isotope decay correction only in instances where the total impact in the analysis result is 2% or greater. Assuming a maximum hold time of 180 days, a 2% isotope decay would occur only for radioisotopes with a half-life of 17.14 years or less. The parameters reported in this SOP are not affected by this policy. Decay correction has not been applied to the parameters measured by this SOP.

3. Summary of Method

3.1 The radium-226 in the drinking water sample is concentrated and separated by co-precipitation on barium sulfate. The precipitate is dissolved in EDTA reagent and placed in a sealed bubbler. Radon-222 is flushed from the sample using inert helium or nitrogen gas. The bubbler is stored for ingrowth of radon-222. After ingrowth, the gas is purged into a scintillation cell. When the short-lived radon-222 daughters are in equilibrium with the parent, the scintillation cell is counted for alpha activity.

3.2 The absolute measurement of radium-226 is ensured by calibrating the scintillation cell system with a standard solution of radium-226.

4. Interferences

4.1 There are no radioactive interferences in this method.

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4.2 To prevent possible cross contamination during the emanation of multiple samples through the same apparatus, apply vacuum intermittently to the apparatus and attached drying tube. This will allow the drying tube and apparatus to be flushed with room air.

4.3 To prevent contamination of bubblers, samples with visible suspended material must be centrifuged prior to transfer to the bubbler for ingrowth.

5. Safety

5.1 Procedures must be carried out in a manner that protects the health and safety of all personnel. Since this analysis is for a radioactive constituent, the sample must be treated as radioactive.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves will be cleaned immediately.

5.3 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye-protection, gloves, and lab coat must be worn.

5.4 Exposure to radioactivity and chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous and/or non-radioactive, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 In order to minimize the potential for cross contamination of high and low levels of radioactive samples, good housekeeping and good laboratory practices are essential and must be strictly adhered to.

5.6 Organic samples of unknown content must be handled with extreme caution and under the direct instruction of a Department Manager/Supervisor or Department Manager/Supervisor's specified designee. Direct treatment of organic matrices with strong oxidizing chemicals such as nitric acid and/or hydrogen peroxide is strictly prohibited.

5.7 Hydrofluoric acid is particularly hazardous because a serious skin exposure may cause no immediate sensation of pain. The acid penetrates the skin and spreads internally, causing tissue damage deep under the skin. The resulting burn is painful, difficult to treat, and easily infected. Gloves must be checked for pinhole leaks before use. They must be rinsed before they are removed and must be discarded after use. HF burn gel shall be put on suspected HF burns after flushing (except the eyes) until medical help can be obtained. Medical attention shall be sought even if suspicions arise after working hours. Contact your group leader immediately for further information if a HF burn is suspected.

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5.8 In addition, HF vapors are also hazardous. Exposure can cause permanent damage. Breathing HF vapors even for a short time and at a low temperature can be injurious to the respiratory system and even fatal. All such direct contact must be avoided.

5.9 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory.

5.10 Refer to the Pace Analytical Services, Inc. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.11 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.12 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 See the glossary section of the most recent revision of the Pace Analytical Services Inc. Quality Assurance Manual for commonly used laboratory terms.

6.2 Batch: For all matrices, an analytical batch contains 20 or fewer samples of a similar matrix, prepared at the same time, by the same analyst, using the same reagents.

6.3 Throughout this procedure, approximate weights and measures will be designated by the use of whole numbers when referring to masses exceeding 1g or volumes in excess of 1mL. Measurements of weights and volumes so designated can be made with top loading balances, graduated cylinders, etc. For approximate measures below 1g or 1mL, the word "approximately" must be used prior to the described mass or volume.

6.4 Throughout this procedure, exact or critical masses and volumes will be designated by the use of one or more decimal places. Measurements of masses and volumes so designated should be made with accurate analytical instruments such as analytical balances, calibrated pipettes, etc.

6.5 Observed masses must be recorded in logbooks to the lowest weight indicated on the balance. Sample aliquot masses cannot be targeted. Once sample is aliquotted, it cannot be removed from the beaker.

6.6 The method employed to measure the sample, whether it be by balance, pipette, or graduated cylinder, must be clearly documented in the preparation logbook.

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7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Plastic or glass containers may be used for sample collection.

8.1.1 Containers used for sample collection must never be re-used.

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8.2 Aqueous samples must be preserved at the time of collection by adding enough concentrated (16N) HNO_3 to the sample to make the sample pH <2. Typically, 2mL of 16N HNO_3 per liter of sample is sufficient to obtain the desired pH. Samples must be preserved within five days of collection. If samples are collected without preservation, they must be received by the laboratory and preserved within five days of collection. Following preservation with acid, samples must be held in the original container for a minimum of 16 hours before analysis or transfer of sample. Samples preserved upon receipt at the laboratory, must be re-checked by laboratory personnel a minimum of 16 hours after preservation. The pH re-check date and time, the initials of the analyst verifying the pH, as well as any adjustments or notes regarding the preservation must be recorded in the pH Verification Logbook.

8.2.1 For dissolved analysis, samples must be filtered through a 0.45□m membrane filter and preserved to a pH <2.

8.2.2 For total analysis, the sample is not filtered, but is preserved.

8.3 Refrigeration is not required for aqueous samples.

The maximum hold time for samples analyzed by this SOP is 180 days from collection to analysis.

9. Equipment and Supplies

9.1 Scintillation Cell system.

9.2 Radon emanation apparatus consisting of 1) radon bubbler, 2) scintillation cell and 3) a drying tube.

9.3 Electric hot plate.

9.4 Centrifuge and disposable 50mL centrifuge tubes.

9.5 Membrane filters, 0.45 □m, 47mm, Metricel® or equivalent.

9.6 Glassware, various sizes.

9.7 Analytical balance.

9.8 Vacuum manifold.

9.9 Vortex mixer

9.10 Hot water bath.

10. Reagents and Standards

10.1 Reagents should be prepared from reagent grade chemicals, unless otherwise specified below. NOTE: Consult the Safety Data Sheets for the properties of these reagents, and how to work with them.

10.2 Distilled or deionized (DI) water. ASTM Type II as produced using the specifications documented in SOP PGH-C-027, current revision.

10.3 Acetic acid, 17.4N: glacial CH_3COOH (conc.), sp. Gr. 1.05, 99.8%.

10.4 Ammonium hydroxide, 15N: NH_4OH (conc.), sp. gr. 0.90, 56.6%.

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10.5 Ammonium sulfate, 200mg/mL: Dissolve 20 g $(NH_4)_2SO_4$ in water and dilute to 100 mL.

10.6 Anti-foaming agent, Anti-foam B, or equivalent.

10.7 Ascarite, drying reagent: 8-20 mesh.

10.8 Barium carrier, 16 mg/mL, standardized. Dissolve 28.46 g $BaCl_2 \cdot 2H_2O$ in water, add 5.0 mL 16N HNO_3, and dilute to 1.0L with ASTM Type II DI Water.

10.9 Citric acid, 1M: Dissolve 192 g of $C_6H_8O_7 \cdot H_2O$ in water and dilute to 1.0L with ASTM Type II DI water.

10.10 EDTA reagent, basic, (0.25M): Dissolve 20 g NaOH in 750mL water, heat, and slowly add 93g disodium ethylenedinitriloacetate dihydrate, $(Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O)$ while stirring. After the salt is in solution, dilute to 1L with ASTM Type II DI Water.

10.11 Helium Gas, ultra high purity.

10.12 Nitrogen gas, ultra high purity.

10.13 Lead carrier, 150mg/mL: Dissolve 239.7 g $Pb(NO_3)_2$ in ASTM Type II DI water, add 5.0mL 16N HNO_3 and dilute to 1.0L with ASTM Type II DI water.

10.14 Methyl Orange Indicator, 0.1%: Dissolve 0.1g methyl orange indicator in 100mL ASTM Type II DI water.

10.15 Nitric acid, 16N: HNO_3 (conc.), Sp. Gr. 1.42, 70.4%.

10.16 Magnesium perchlorate, $Mg(ClO_4)_2$: reagent grade.

10.17 Radioactivity standard solutions: radium-226 may be utilized for batch control spike samples or instrument calibrations and barium-133 may be used for radio-tracer yield determinations. All radioactive standards must be NIST traceable.

10.18 Sodium hydroxide, 10N: Dissolve 400 g NaOH in 500 mL deionized water, cool, and dilute to 1.0L with ASTM Type II DI Water.

10.19 Sulfuric acid, 18N: Cautiously mix 1 volume 36N H_2SO_4 (conc.) with 1 volume of ASTM Type II DI water in a tub of ice or cool water. As water evaporates, replace with ASTM Type II DI water to desired final volume.

10.20 Yttrium carrier, 18 mg/mL: Add 22.85g Y_2O_3 to an Erlenmeyer flask Add 50mL of ASTM Type II DI water. Carefully add 40mL of concentrated nitric acid. Heat the mixture to boiling while stirring on a magnetic stirring hotplate. The solution must heat to boiling. Additional water and nitric acid may be added as necessary to aid in dissolution. Measure the additions of Type II DI water and concentrated nitric acid and record the reagent volumes added into the reagent preparation logbook. Scrape the bottom of the Erlenmeyer flask with a Teflon® scraper if the yttrium oxide is caked onto the glass to enhance dissolution. Once the yttrium oxide has completely dissolved, add a quantity of concentrated nitric acid so

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that the total volume of concentrated nitric acid added is 100 mL. Do not add more than 100mL of nitric acid total. Upon complete dissolution, remove the beaker from the hotplate and cool completely. Dilute to 1L with ASTM Type II DI water.

11. Calibration

11.1 Cell/Detector calibrations are performed uniformly, independent of sample analysis matrix type. The calibration values determined by application of this process are applied universally for all matrices for which the analytical process is defined in this SOP.

11.2 Cell/Detector calibrations must be performed on an annual basis.

11.3 Transfer between 500 to 1500 dpm of radium-226 (25mL volume) standard into a bubbler that has been designated for calibration purposes only.

11.4 Note: The specified calibration source activities have been optimized to allow manageable count times for individual sources.

11.5 Attach the bubbler to the radon assembly.

11.6 With the scintillation cell disconnected, bubble helium (or nitrogen) gas through the solution for 20 minutes to remove all Rn-222.

11.7 Close both stopcocks on the bubbler to establish zero time for ingrowth of Rn-222. Record the date and the time of the calibration source flushing on the appropriate bench sheet. Store the bubbler to allow ingrowth of Rn-222.

11.8 Following adequate ingrowth time for the calibration source, proceed with steps 12.12 through 12.18, Radon Emanation Technique.

11.8.1 EPA Method 903.1, “Radium-226 in Drinking Water Radon Emanation Technique” requires a minimum of 18 hours of ingrowth for the calibration. Pace has adopted a minimum ingrowth period of four days for calibrations and samples.

11.9 The calibration constant includes the de-emanation efficiency of the system, the counting efficiency of the cell, and the alpha activity contributed by Po-218 and Po-214, which will be in equilibrium with Rn-222 when the sample is counted approximately 4 hours (minimum of 3 hours) after the de-emanation. Calibration sources must be counted until a minimum of 10,000 counts has been obtained.

11.10 Proceed to Section 13 to determine the cell calibration constant.

11.11 Following the cell counting, flush the cell by alternating vacuum and room air to remove Rn-222 from the cell. Store the cell for a minimum of 24 hours prior to use for samples. This delay allows adequate decay of Rn-222 daughters. Lucas cells must be counted for a minimum of ten minutes to determine the cell background prior to use for sample analysis.

11.12 The bubbler used for Ra-226 calibration should not be used for sample analysis. It should be set aside and retained for future calibrations. The

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cell/detector combination must be calibrated annually. Additionally, calibrations must be performed if either the cell or the detector undergo any major maintenance. New cells and cells returned from a repair facility must be given a new ID.

11.13 For cells previously successfully calibrated, the new cell constant should be within 10% of the previously acceptable cell constant (CAL A) counted in the same detector. Typical cell constants will be around 2.2 to 2.5, and may vary for the same cell among each individual detector. For a new calibration attempt (CAL B), any deviation outside of the 10% rule may indicate a problem during calibration (CAL B) and the calibration should be re-performed using a different calibration source (bubbler). If the new calibration value (CAL C) is within 5% of the most recent calibration value (CAL B), the newest calibration value (CAL C) should be used as the cell/detector calibration value. If the new calibration value (CAL C) is greater than 5% of the most recent calibration value (CAL B) but within 10% of the previously-implemented calibration value (CAL A), this indicates that the process in performing CAL B was compromised. In this case, the newest calibration value (CAL C) should be used as the cell/detector calibration value. Cells for which calibration values do not comply with the listed requirements must be removed from future service until appropriate corrective action has been applied and documented. At a minimum, prior to repeating the calibration process, check the cell for damage, especially around the stopcock, base of the stem, and the window, which could cause gas loss during calibration.

11.14 Cell constants will vary slightly based on the imperfect mechanism of applying the zinc sulfide interior coating, as well as minor differences in cell volume. Cells which cannot be calibrated should be sent out for repair which will include resealing the stopcock stem, re-applying the zinc sulfide coatings, and cleaning and replacing the glass surface.

12. Procedure

Unless specified otherwise, the documented analysis process must be followed, as written, including the order of analytical process and the addition of chemicals

12.1 Weigh approximately 500g of aqueous sample into an appropriately sized glass beaker. Record the observed mass of the sample added to the beaker (do not remove any sample from the beaker). The actual amount of sample used may vary based on sample availability and expected or possible matrix interferences, but the routine amount is approximately 500 grams. When using < 500g, samples should be diluted with ASTM Type II DI water to the 500 ml mark on the beaker, and acidified with nitric acid.

12.2 Prepare a Method Blank (MB), Laboratory Control Sample (LCS), and Laboratory Control Sample Duplicate (LCSD), by weighing about 500g of ASTM Type II DI water into a labeled beaker, and record the actual mass observed in the logbook. Add 2.0 ml of concentrated nitric acid to the MB, LCS, and LCSD. Add the appropriate amount of Ra-226 spike

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solution to the LCS and LCSD based on the requirements listed in Section 14.6.3 of this SOP.

12.3 If a Matrix Spike (MS) is prepared (MS is required when analyzing drinking water samples or when specified by the client), add the appropriate amount of spike solution to the MS sample based on the requirements of Section 14.9.2 of this SOP.

12.4 To all samples including the QC samples, add 5mL 1N citric acid solution and a few drops methyl orange indicator. The solution should be red. If the solution is not red, check the solution pH with pH indicator strips capable of determining pH 0-14. The sample pH must be <2.0. Otherwise, refer to Section 8.2 regarding sample preservation requirements.

12.5 Add 1mL lead carrier (150 mg/mL), 1mL yttrium carrier (18 mg/mL) and 2.0mL barium carrier (16 mg/mL). Add a suitable amount of barium-133 tracer based on the guidance in section 14.11 if yield determination is to be made by radio-tracer counting. Stir well. Heat to incipient boiling and maintain at this temperature for 30 minutes.

12.6 Add a few drops methyl orange indicator again as it is destroyed upon prolonged heating. Add 15N NH_4OH until a definite yellow color is obtained, then add a few drops excess. Precipitate lead and barium sulfates by adding 18N H_2SO_4 until the red color reappears, then add 0.25mL excess. Add 5mL $(NH_4)_2SO_4$ (200 mg/mL) and stir vigorously until a precipitate forms. Allow the solution to heat for a minimum of 30 minutes, and then remove the samples from the hot plate to cool.

12.7 Allow the sample precipitate to settle overnight or for a minimum of 2 hours until completely clear; then siphon most of the supernatant liquid and discard, saving the precipitate.

12.8 Transfer the precipitate with the aid of 0.1N H_2SO_4 to a 50mL disposable centrifuge tube; centrifuge, and discard the supernatant liquid.

12.8.1 For wastewater samples or samples containing suspended solids, add 20mL of 16N HNO_3 to each centrifuge tube and heat in a hot water bath for 30 minutes. This step will aid in the removal of interfering element components.

12.8.2 Centrifuge and discard acid solution into an appropriate waste stream. Rinse the precipitate in 20mL 16N HNO_3. Shake to mix, centrifuge, and discard acid rinses into an appropriate waste stream.

12.8.3 Rinse the precipitate two times with 10mL aliquots of 0.1N H_2SO_4. Add the acid to the precipitate in the centrifuge tube, cap and vortex to rinse. Centrifuge and discard the supernate into the appropriate waste stream.

12.9 Add 25mL 0.25M EDTA solution to the sulfate precipitate. Vortex the samples and heat in a water bath to enhance dissolving of the precipitate.

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If the precipitate does not readily dissolve, add 10N NaOH solution dropwise. Do not add more than 7 drops total of the 10N NaOH.

12.9.1 If there is still undissolved material, centrifuge the sample and transfer the solution to a clean disposable centrifuge tube. Submit the supernate solution for gamma spectroscopy counting for Ba-133 determination. If the resulting yield is within acceptable limits, continue with the analysis. If it is not within the expected limits, combine the supernate and the solid material and reheat.

12.10 Ensure that the sample solution volume is 25mL (+/- 1 mL) using the graduated markings on the centrifuge tube as a guide. If the sample volume is less than 25 mL, dilute the sample to 25 mL(+/- 1 mL) with 0.25M EDTA solution using the graduated markings on the centrifuge tube as a guide.

12.10.1 Optionally: Proceed to Section 12.21 to determine the radiotracer yield prior to transferring the solution to the bubbler. If this option is used, extreme care must be exercised when transferring the solution from the centrifuge tube to the bubbler in order to ensure that it is performed quantitatively.

12.11 Centrifuge and transfer the supernate to a labeled radon bubbler. Discard the centrifuge tube into an appropriate waste stream.

12.12 Connect the bubbler to the helium (nitrogen) source then open both the upper and the lower stopcocks of the radon bubbler and de-emanate the solution by slowly passing helium (nitrogen) gas through the bubbler for about 20 minutes.

12.12.1 Add 2 drops of antifoaming agent to the bubbler if excessive foaming occurs while passing the helium (nitrogen) through the solution.

12.13 Close the two stopcocks and record the time. Store the solution to allow for ingrowth of Rn-222.

12.13.1 A minimum of 4 days of ingrowth is required.

12.14 At the end of the storage period, fill the upper third of an absorption tube with magnesium perchlorate and the lower two-thirds with ascarite. Attach the drying tube to the vacuum monitoring manifold with a rubber o-ring and clamp. Ensure the end with the white magnesium perchlorate is at the top, and the ascarite end is at the bottom.

12.14.1 Note: Forminimizing corrections that would be required in subsequent calculations, the voids above the bubbler must be kept very small. Capillary tubing should be used whenever possible, and the drying tube volume with the ascarite and magnesium chlorite must be kept to a minimum. A typical system consists of a drying tube 10 cm x 1.0 cm (I.D.), with each of the drying agents occupying 4 cm and being separated by small glass wool plugs. The column can be reused several

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times before the chemicals need to be replaced as long as the ascarite appears dry and not hardened.

12.15 Attach the sample bubbler to the drying tube so the liquid containing portion of the bubbler is directly below the drying tube, and attach the helium (nitrogen) supply hose to the bubbler inlet (the thin capillary tube side).

12.16 Evacuate the desired Lucas cell using a vacuum pump and close the stopcock. Ensure a background count has been performed for the cell and detector combination prior to each use. Using the appropriate clip, firmly attach the Lucas cell to the top of the vacuum monitoring manifold connected to the correct bubbler.

12.17 Open the stopcock on the scintillation cell and check the vacuum gauge to ensure that vacuum is maintained. The gauge should indicate a vacuum of approximately -20 to -25 psi relative to atmospheric. Gradually open the outlet stopcock on the bubbler. When the stopcock is fully open and no further significant bubbling takes place, close the stopcock. The pressure gauge should still indicate a vacuum, but less vacuum relative to atmospheric, approximately -15 to -20 psi

12.18 Adjust the helium (nitrogen) gas pressure so that the gas flows at slightly above atmospheric pressure.

12.19 Reopen the outlet stopcock on the bubbler. Gradually open the inlet stopcock on the bubbler using the bubbling as a guide. Continue bubbling with the helium (nitrogen) gas until the vacuum gauge indicates neutral (atmospheric) pressure. The de-emanation process should take approximately 15-20 minutes to complete. Toward the end of the de-emanation, when the vacuum is no longer effective, it will be necessary to gradually increase the helium (nitrogen) gas pressure. When the system is at atmospheric pressure, close the inlet and outlet stopcocks of the cell and bubbler, shut off the gas, and disconnect the tubing from the bubbler inlet. Record this time as the beginning of the Rn-222 decay and ingrowth of Rn-222 daughters.

12.20 Store the scintillation cell for approximately 4 hours (minimum of 3 hours) to ensure equilibrium between radon and radon daughters. Proceed to Section 12.22 to “count” the Lucas cells.

12.21 If not already determined in Step 12.10, transfer the sample bubbler contents to a labeled 50mL centrifuge tube. Rinse the bubbler with a few mL of ASTM Type II DI water and transfer the rinses to the centrifuge tube.

12.21.1 If gamma counting is to be performed to determine yield by Ba-133 counting, dilute the tube contents to a final volume of 30mL with ASTM Type II DI water, cap the tubes, shake vigorously, and submit them to the analyst responsible for gamma counting.

12.21.2 Barium yield by gravimetric assessment (used if Ba-133 is unavailable or not suitable to sample matrix).

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12.21.2.1 If yield assessment is to be made by gravimetric measurement of barium sulfate, proceed as follows:

12.21.2.2 Add 1mL of ammonium sulfate solution (200 mg/mL) and stir thoroughly. Add 2mL conc. acetic acid until barium sulfate precipitates. Digest in a hot water bath for 10 minutes. Cool, centrifuge, and discard the supernate.

12.21.2.3 Slurry the precipitate with 10ml of ASTM Type II DI water, centrifuge and discard the supernate.

12.21.2.4 Slurry the precipitate with 7mL of ASTM Type II DI water and transfer to a tared, 2-inch stainless steel planchet. Dry the precipitate under a heat lamp, cool and re-weigh for yield determination. Refer to Section 13 of this SOP for barium recovery calculation.

12.22 Lucas Cell Counting

12.22.1 Perform the required daily source check prior to counting cells for daily background. Daily source check counting and routine maintenance for the Ludlum Counters is specified in the associated instrument operations SOP, PGH-R-064, current revision.

12.22.2 Remove the top cover from the photomultiplier tube (PMT) unit or counter, and remove the rubber protector from the base of the Lucas cell. Center the Lucas cell on the glass platform on the top of the base of the counter and carefully replace the top cover.

12.22.3 Press the top cover down firmly to ensure the counting rod makes contact with the counter base. There should be an audible click when the counting rod is properly engaged. Tighten the screws on both sides of the top cover to ensure the counting rod remains engaged through sample counting.

12.22.4 Set the count time on the front of the Model 2000 Scaler unit to the count time necessary to meet the desired reporting limit. Count times should not be less than 10 minutes, and should not routinely exceed 20 minutes.

12.9.4.1 Count times longer than 20 minutes should only be used for drinking water samples where it is necessary to achieve the Ra-226 reporting limit of 1.0 pCi/L.

12.22.5 Press the COUNT button on the front of the scaler unit. Record this time as the count start time in the appropriate section of the analysis logbook.

12.9.4.2 A red light above the COUNT button will light to indicate the unit is active. Observe counts on the LED display to ensure the counting rod is correctly engaged on the counter.

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12.9.4.3 Do not remove the top cover while the unit is counting as this may damage the photomultiplier tube.

12.22.6 Once the red light has turned off, record the counts from the LED display into the appropriate section of the analysis logbook.

12.22.7 Unscrew the screws on the sides of the top cover of the counter and carefully lift the top cover off of the counter ensuring the cell is not knocked over. Return the rubber protector to the base of the Lucas cell, and set the Lucas cell aside for evacuation.

12.22.8 Repeat steps 12.22.2 through 12.22.7 until all Lucas cells have been counted.

12.22.9 Following counting and after data have been processed, flush the Lucas cell by alternating vacuum and room air to remove Rn-222 from the cell. Store the cells with vacuum applied for a minimum of 3 hours prior to using for another sample. A new background must be counted on the cell prior to use.

13 Calculations

13.1 Refer to Attachment I of this SOP for Ra-226 associated calculations.

13.1 Any verified result for drinking water that exceeds the maximum contaminant level (MCL) established for Radium-226 must be reported to the appropriate personnel and agencies according to the specific requirements of the state where the water was sampled. The directions for reporting any results that exceed the MCL limits are documented in the State Drinking Water Emergency Reporting Requirements Binder and in Pace SOP PGH-C-025, current revision.

13.2.1 The Ra-226 MCL for drinking water is defined as >5.0 pCi/L Ra-226 individually or when summed with Ra-228.

14 Quality Control

14.1 General guidelines for drinking water samples with results that exceed the Maximum Contaminant Level are specified in Pace SOP PGH-C-025, current revision, and include the following: (All steps are to be conducted as soon as the exceedence has been identified.)

14.1.1 Verify the result(s) to ensure that there were no transcription or calculation errors and that all QC results are within the acceptable limits. Correct any problems and determine the new result. If there were no errors or the result still exceeds the MCL continue with the reporting process.

14.1.2 Immediately notify the Department Manager/Supervisor, and QA department that a reportable result has been identified. Use telephone notifications to inform the contact people if the variance is identified after hours along with an e-mail follow up to document the event.

14.1.3 Refer to the State Drinking Water Emergency Reporting Requirements Binder for the state specific information regarding the

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proper course of action to take. Time is of the essence during this process with some of the state reporting requirements as short as 1 hour from the verification of an exceedence.

14.2 Each analyst who performs this test must satisfactorily complete a Demonstration of Capability Study as documented in Section 3.4 of the most recent revision of the Quality Assurance Manual.

14.2.1 The DOC study results are evaluated against the LCS acceptance limits.

14.2.2 IDOC and DOCs for drinking water methods must be performed at a spiking level between the sensitivity level and MCL.

14.2.3 Continuing DOCs must be performed annually by each analyst who may be expected to perform the analysis during the course of the year. A Continuing DOC may be compiled from 4 successive LCS analyses from multiple batches, and are evaluated against the LCS acceptance limits.

14.3 Daily instrument Quality Control checks must be completed following the instructions detailed in the SOP for alpha scintillation counters, current revision.

14.4 See Appendix II for performance indicator evaluation calculations and criteria. Numerical performance indicators may be used to assess QC for non-drinking water samples when the default assessment indicates a QC failure. The numerical performance indicator must be within +/- 3 for all other matrices. The z-score for precision assessment may be used for drinking waters with the approval of the Department Manager/Supervisor using the +/- 2 specification.

14.5 Method Blank (MB)

14.5.1 One MB must be prepared for each analytical batch. The purpose of the MB is to monitor for cross contamination during the analytical process. When available, the MB should be prepared from a similar matrix as samples contained in the analytical batch. If appropriate blank matrix material is not available, ASTM Type II DI water (Reagent Blank) must be carried through the procedure. A reagent blank may be used for sample correction purposes following approval of a Department Manager/Supervisor or a specified designee and affected clients.

14.5.2 The results of the method blank must be <RL. The reporting limit for Ra-226 is 1.0 pCi/L.

14.5.2.1 If the method blank is out of control, individual sample results may still be reportable if results are less than the CRDL (contract required detection limit) or > 10 times the blank result. Relative sizes of the sample and blank aliquots must be factored when making this determination (raw counts).

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14.6 Laboratory Control Sample (LCS)

14.6.1 One LCS must be prepared for each analytical batch.

14.6.2 A typical detection limit is 1.0 pCi/L for Ra-226.

14.6.3 The Ra-226 spike activity must be > 2 times the detection limit.

14.6.4 A standard reference material (SRM) containing a known concentration of radium-226 radioactivity in the same matrix as the batch is analyzed with the batch.

14.6.4.1 If this material is not available, a well-characterized material (WCM) may be used.

14.6.4.2 If neither of these are available, ASTM Type II DI water may be spiked with the appropriate radium-226 standard.

14.6.5 Percent Recovery Calculation

$$\%REC = \frac{(LCSConc)}{TrueValue} * 100$$

Where:

LCSConc = Analytical result of the LCS
TrueValue= Known concentration of the LCS

14.6.6 LCS %REC acceptance limits are 73 - 135%.

14.7 Laboratory Control Sample Duplicate (LCSD)

14.7.1 A LCSD is not required for radium-226 analysis; however analysis of an LCSD must be utilized to measure batch precision whenever adequate sample volume is not available for sample DUP analysis. The LCSD must be prepared in an identical fashion as the LCS and processed identically as for other samples.

14.7.2 The LCSD must pass the acceptance criteria for the LCS and the criteria established for duplicate precision (RPD 32% or less).

14.7.3 If the LCS and LCSD both pass %REC criteria, but fail RPD criteria, the batch results may be qualified and reported at the discretion of the analyst with guidance from the Department Manager/Supervisor.

14.8 One Duplicate Sample (DUP) must be randomly assigned within each batch. The purpose of the sample DUP is to measure precision of the analytical process. Laboratory duplicates are not intended to assess precision related to the sample collection process. Sample collection precision can only be assessed through collection of duplicate samples at the time of sample collection. The sample DUP is a duplicate volume of sample processed identically as other samples in the analytical batch.

14.8.1 Relative Percent Difference Calculation

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$$RPD = \frac{(|R1 - R2|)}{(R1 + R2)/2} * 100$$

Where:

R1 = Result Sample 1
R2 = Result Sample 2

14.8.2 Duplicate sample RPD acceptance limits are <32% for radium-226.

14.8.3 Sample duplicate criteria cannot be applied if results are below their associated MDC.

14.8.4 Drinking water samples from the state of Arizona must be batched at a frequency of 1 duplicate for every 10 samples or fewer.

14.9 Sample Matrix Spikes (MS)

14.9.1 Because this analytical method requires the use of carriers or radiotracers for yield determination, PASI's default QC policy is that a sample matrix spike (MS) is not required for radium-226 analysis with the exception of drinking water analysis.

14.9.2 Typical detection limits for Ra-226 are 1 pCi/L. The spike amount must be > 10 times the detection limit.

14.9.3 The MS is prepared by spiking a portion of radium-226 radioactivity solution into a portion of one sample in the batch and processing identically as for other samples.

14.9.4 The purpose of the MS is to assess the affect of sample components on the analytical process. The volume of sample used for the MS must be equivalent to the volume used for sample analysis.

14.9.5 Percent Recovery Calculation

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue} * 100$$

NOTE: The SampleConc is zero (0) for the LCS and Surrogate Calculations

14.9.6 MS acceptance limits are 71 - 136% for radium-226.

14.10 Sample Matrix Spike Duplicates (MSD)

14.10.1 A sample Matrix Spike Duplicate (MSD) is not required for this analysis. When required by the customer/contract, a MSD must be prepared for each analytical batch. The MSD must be prepared as a duplicate of the MS.

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14.10.2 The MSD must pass the acceptance criteria established for the MS recovery and the criteria established for duplicate precision.

14.10.3 An MS/MSD sample analysis may be performed instead of a sample duplicate analysis. If MS/MSD are prepared instead of a sample duplicate, and the batch includes drinking water samples from the state of Arizona, the duplicate analysis criteria for frequency in Section 14.8.4 of this SOP must be met.

14.11 PASI's default criteria for carrier and/or tracer yield are 30-110% of the expected value.

14.11.1 Barium-133 is routinely used as the tracer for Ra-226 analysis. Since Ba-133 has no potential for interference during sample counting, the amount utilized as a tracer has been optimized to ensure a minimum of 400 tracer counts is achieved in five minutes during yield analysis utilizing a sodium iodide gamma detector. This amount is approximately 6500 dpm Ba-133.

14.11.2 The amount added to each sample is consistent and added with a verified pipette, but may be changed with each new Ba-133 standard. Typical Ba-133 standards are prepared at a level between 12000 and 16000 dpm/ml depending on the concentration of the Ba-133 source purchased from a NIST traceable vendor.

14.12 Summary of QC related Activities:

Method Blank	One per Batch
Reagent Blank	One per Batch (as required by client)
Duplicate Sample	One per Batch or a frequency of 10% for batches containing samples from Arizona
Matrix Spike	One per Batch (for drinking waters or as required by client)
Matrix Spike Duplicate	One per Batch or a frequency of 10% for batches containing samples from Arizona (as required by client)
Laboratory Control Sample	One per Batch
Laboratory Control Sample Dup	One per Batch in the absence of Duplicate sample

14.13 Corrective Actions for Out-Of-Control Data

14.13.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.13.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

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14.13.3 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and noted in the final report.

14.13.3.1 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.13.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.13.5 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.13.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.13.6 Laboratory Control Sample Duplicate (LCSD) – If an LCSD does not meet the recovery acceptance criteria, the entire analytical batch must be reanalyzed.

14.13.6.1 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their the reporting limit, and duplicate precision meets the acceptance criteria.

14.13.7 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report. Chemical/Tracer recoveries: If the chemical and/or tracer recovery is outside of the acceptance criteria, the sample must be reanalyzed. If a matrix interference is suspected to be the cause, sample reanalysis should be performed with a lower volume to minimize interferences.

14.13.7.1 Acceptance criteria for gravimetric carriers are 30-110% and for radioactive tracers the criteria are 10-110%. Yields as high as 130% may be reported with the approval of the Department Manager/Supervisor.

15 Method Performance

15.1 Laboratory control samples are analyzed with each batch, the results are charted to monitor control limits and trending. Each analyst must read and

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understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.2 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.3 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16 Pollution Prevention and Waste Management

16.1 Place radioactive waste into appropriate receptacles.

16.2 Discard acidified samples and unusable standards into proper waste drains.

16.3 Dispose of waste materials in accordance to type: Non-hazardous, hazardous, non-radioactive, radioactive or mixed.

17 References

17.1 ASTM E181-93, Standard Test Methods for Detector Calibration and Analysis of Radionuclides, ASTM Standards, Vol. 12.02.

17.2 Blanchard, R.L. Uranium Decay Series Disequilibrium in Age Determination of Marine Calcium Carbonates. Doctoral Thesis, Washington University, St. Louis, MO. (June 1963).

17.3 Currie, L., Limits for Quantitative Detection and Quantitative Determination, Analytical Chemistry, Vol. 40. No. 3, Pg 586-593, 1968.

17.4 Currie, L., Lower Limit of Detection: Definition and Elaboration of a Proposed Position for Radiological Effluent and Environmental Measurements, NUREG/CR - 4007, USNRC, 1984.

17.5 Ferri, E., P. J. Magno, and L. R. Setter. Radionuclide Analysis of Large Numbers of Food and Water Samples. U.S. Department of Health, Education, and Welfare, Public Health Services Publication No. 999-RH-17 (1965).

17.6 Krieger, H. L. and Whittaker, E. L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, "Radium-226 – Radon Emanation Technique," Method 903.1, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, August, 1980.

17.7 Krieger, H. L. and Whittaker, E. L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, "Radium-228 in Drinking Water," Method 904.0, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, August, 1980.

17.8 Eaton, A. D., et. al., editors, Standard Methods for the Examination of Water and Wastewater, 19th Edition, "Radium – Sequential Precipitation Method," Method 7500-Ra C., American Public Health Association, Baltimore, MD, 1995.

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17.9 Eaton, A. D., et. al., editors, Standard Methods for the Examination of Water and Wastewater, 20th Edition, "Radium – Sequential Precipitation Method," Method 7500-Ra C., American Public Health Association, Baltimore, MD, 1998.

17.10 "Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)", Final Version, July 2004.

17.11 Rushing, D. E. The Analysis of Effluents and Environmental Samples from Uranium Mills and of Biological Samples for Uranium, Radium, and Polonium. SM/41-44, Symposium on Radiological Health and Safety, Vienna, Austria (August 1963).

17.12 Steiner, E. H. "Planning and Analysis of Results of Collaborative Tests." Statistical Manual of the AOAC, Association of Official Analytical Chemists, Washington, D. C. 1975.

17.13 Table of Radioactive Isotopes, Brown and Firestone, Shirley editor, John Wiley & Sons, 1986.

17.14 Youden, W. J. "Statistical Techniques for Collaborative Tests." Statistical Manual of the AOAC Association of Official Analytical Chemists, Washington, D. C. 1975.

17.15 "American National Standard Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories", ANSI N42.23-1996.

17.16 Department of Defense Quality System Manual for Environmental Laboratories (DoD QSM), current version.

17.17 "Manual for the Certification of Laboratories Analyzing Drinking Water" Fifth Edition, January 2005, EPA 815-R-05-004.

17.18 National Primary Interim Drinking Water Regulations (NIPDWR), Part 141.15.

17.19 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.20 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.21 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.22 Pace SOP PGH-R-003, current revision (Analysis of Water Samples for Ra-228).

17.23 Pace SOP PGH-R-064, current revision (Alpha Scintillation Counter Operations).

17.24 Pace SOP PGH-C-025, current revision (MCL Violation Reporting).

17.25 Pace SOP PGH-C-027, current revision (Deionized Water Quality and Suitability).

18 Tables, Diagrams, Flowcharts, Appendices, etc.

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18.1 Attachment I: Calculations

18.2 Attachment II: Numerical Performance Indicators

19 Method Modifications

19.1 The strict co-precipitation technique specified in EPA 903.1, "Radium-226 in Drinking Water" generates a sulfate precipitate that is not easily dissolved when following the detailed methodology. The precipitation technique detailed in this SOP generates a soluble precipitate that is easily dissolved in EDTA solution. This minimizes the potential for reporting erroneous carrier yields and limits the spread of insoluble contamination in the bubbler system.

19.2 The barium/radium sulfate co-precipitation technique utilized in this SOP has been enhanced to allow for quality improvements in analysis and production efficiency. The co-precipitation technique utilized in steps 12.1 through 12.7 of this SOP mirrors the precipitation technique employed in Pace SOP PGH-R-003, current revision, Analysis of Water Samples for Ra-228. Deviations between Pace SOP PGH-R-003, current revision, and EPA 904.0, "Radium-228 in Drinking Water" are documented in Section 19 of Pace SOP PGH-R-003, current revision.

19.3 EPA Method 903.1 specifies the dissolution of the barium/radium co-precipitate generated in this procedure using 20 mL of 0.25 M EDTA solution. For some samples, it is necessary to use additional EDTA solution to dissolve the barium sulfate precipitate. EPA method 904.0 for Ra-228 analysis requires an initial addition of 25 mL of EDTA solution to dissolve the barium/radium co-precipitate. In order to maintain consistency on a sample-level basis, Pace uses 25 mL of EDTA for precipitate dissolution. Adhering to the strict solution volume prior to sample analysis ensures consistency between sample analysis volumes and calibration solution volumes, thereby ensuring consistent exchange of radon and nitrogen gas when emanating radon gas from the sample bubblers.

19.4 When using bubblers of the exact dimension specifications described in EPA 903.1, there is a high probability of loss of sample solution contained in the bubblers when emanating radon from the bubbler. This can lead to contamination of the manifold system, including the Lucas cell used for analysis. Pace utilizes a bubbler design of larger dimensions so as to limit the negative impact of sample overflow. Pace ensures the appropriate ratio of radon to nitrogen gas exchange by using equivalent bubbler solution volumes between samples and calibration sources.

19.5 The preparation of the yttrium carrier solution documented in step 10.20 of this SOP does not explicitly follow the specifications of EPA Method 904.0. Additional concentrated nitric acid and ASTM Type II DI water are added at the onset of yttrium oxide dissolution so as to enhance the dissolution. The final ratio of yttrium to nitric acid solution for the yttrium carrier prepared within this SOP matches the ratios specified in EPA 904.0.

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19.6 Counting the samples (and calibration cells) after only 3 hours from de-emanation instead of 4 hours as specified in EPA 903.1 allows for increased productivity and results in an error of < 0.47% for high activity sample and is negligible for low activity samples.

19.7 Concentration of radium by co-precipitation with barium is quantitative, however, collection of the precipitate is highly variable and is relative to individual analyst technique. Since there is inherent room for losses, any assumption that 100% of the sample makes it from initial precipitation, dissolution, and into the bubbler for analysis, biases the sample results low. Although the use of a tracer (Ba-133) is not specified in EPA 903.1, Pace's barium recovery measurement technique was determined by accrediting authorities to improve method precision and accuracy and was thereby allowed.

19.8 The use of anti-foaming agent in the bubbler to prevent samples from foaming and resulting in sample loss is not specified in EPA 903.1. The use and addition does not adversely impact the Ra-226 results.

19.9 Due to a world-wide shortage of helium gas, nitrogen gas is used as an alternate gas for the specified emanation process.

19.10 EPA Method 903.1 specifies to use 1,000 mL of sample for analysis. Pace analyzes approximately 500 mL of sample for analysis. All samples are measured by mass as specified within this SOP. Pace further restricts the analysis volume for samples known to contain matrix components that would limit analyte recovery. Pace restricts the analysis volume so as to limit the quantity of waste generated and to enhance productivity. The required detection limit of 1 pCi/L is achieved using a 500 gram analysis quantity.

20 Revisions

Document Number	Reason for Change	Date

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Document Number	Reason for Change	Date
PGH-R-007-11	1. Table of contents added. 2. Modified Section 11.6.1 to require minimum ingrowth time for calibration cells. 3. Modified Section 12.10 to require minimum ingrowth time for samples. 4. Clarified step 12.17 to document when gravimetric recovery for barium yield is allowed. 5. Section 15 modified to "Method Performance." "Pollution Prevention and Waste Management" Section moved to Section 16. 6. "References" Section moved to Section 17. 7. "Tables, Diagrams, Flowcharts, Appendices, etc." Section moved to Section 18. 8. "Deviations from Promulgated Methods" changed to Method Modifications Section moved to Section 19. 9. Revised Equation 7 to document the recovery calculation for Ba yield assessment. 10. Section 14: Added 14.7.2.1 to discuss yield criteria. Also modified Section to discuss non-conformance tracking with LabTracks and evaluating usefulness of data and qualifying or narrating to allow for when clients do not want a final report. 11. Section 17: Added references, ANSI N42, 23, TNI Standard, and DoD QSM. 12. Defined variables into Calculations Section for Ba recovery calculation. 13. Definition of UE4 in the Calculations Uncertainty Section was changed to require approval of the Department Supervisor for UE4. 14. Inserted Calculation number 15, the critical level calculation.	4/19/2012
PGH-R-007-12	1. Updated Table of Contents to include Attachments I and II. 2. Section 3.1, 10.12 – added nitrogen gas as optional to helium, and also included in parenthesis wherever helium is mentioned. 3. Section 6.5 and 12.1 – Included comment about recording observed masses and not targeting sample aliquots. 4. Section 10.2 – Added Type II DI SOP reference. 5. Section 11– defined calibration constant acceptance criteria and optimal cell constant range, process for recalibrating, assigning Ids, and repair. 6. Section 12.2 – added comment about how to proceed if methyl orange pH indicator is not red in sample. 7. Section 12 – clarified where each piece is attached when performing the radon emanation into the Lucas cell. 8. Section 12.20 – added instructions on counting cells and reference instrument operation SOP.	26June2013

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Document Number	Reason for Change	Date
	9. Section 13.2 and 14.1 – added to provide instruction for recognizing and reporting DW MCL exceedances. Pace SOP PGH-C-025 referenced. 10. Section 14.4 – added comment regarding using numerical indicators to assess QC and applicability. 11. Section 14.8.4 and 14.10.3 – added to include duplicate sample analysis requirement of 10% for Arizona, and 5% for all else. 12. Entire document – changed all references of DI water to ASTM Type II DI water to conform to method verbiage.	
PGH-R-007-13	1. Annual SOP review. 2. Section 4.2 and 4.3 – Added comments regarding preventing sources of cross contamination during emanation and in bubblers due to solids, 3. Section 6.6 – Added comment regarding documenting the use of pipette, graduated cylinders, or balances for sample measuring. 4. Section 8.2 – Inserted requirements for pH verification and documentation. 5. Section 11 – Clarified calibration acceptance criteria. 6. Section 12.1 to 12.3 – Inserted instructions for diluting samples, preparing QC samples, and ensuring QC are spiked prior to the addition of all other chemicals. 7. Section 14 – Added DOC and CDOC requirements. 8. Section 14 – Added MSD frequency for AZ DW samples. 9. Section 14.13.2 – Updated to discuss failed LCS/LCSD RPD actions and qualification. 10. Section 17 – Added DW Manual reference and NIPDWR reference. 11. Section 19.2 – Updated to point to the concurrent steps in the Ra-228 SOP PGH-R-003, instead of the EPA 904.0 method. 12. Section 19 – Added use of anti-foam agent and nitrogen gas into deviation from methods. 13. Edited for spelling and grammatical errors. 14. Reformatted document.	13Jul2014
PGH-R-007-14	1. Removed from section 5.1: Analysts must be trained as radiation workers and personal dosimeter worn. 2. Section 12.17 - Clarified the observed changes in vacuum indicated on the gauge during sample emanation. 3. Section 14.11 – Added typical Ba-133 tracer concentrations and the determination of the tracer levels.	20Feb2015
PGH-R-007-15	1. Section 10.20-Updated the preparation of yttrium carrier (18 mg/mL) in order to match the analytical process and to more closely match the method process. 2. Sections 12.9 and 12.10-Modified the volume of 0.25M EDTA solution used in the process to match the volume used for process calibration. This standardization of the volume of EDTA used, ensures consistency between samples and the calibration process.	15July2015

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Document Number	Reason for Change	Date
	3. Updated section 19, Method Modifications to address changes to this SOP revision. Added a modification specifying differences between the bubbler used and the bubbler specifications in the method, EPA 903.1.	
PGH-R-007-16	1. Section 12.20 corrected to specify the correct reference section for Lucas Cell Counting. 2. Section 19 updated to include the analysis volume difference between this SOP and the method, EPA 903.1.	14Dec2015

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Attachment I
Calculations

The **radium-226 concentration** of a sample is calculated according to the following equations:

Eq. 1 $$Act = \frac{(S_A - B_A)}{(Denom)}$$

Eq. 2 $$Denom = E * V * .22 * I_S * D_1 * D_2 * R$$

Eq. 3 $$E = \frac{(S_C - B_C)}{(A_C * I_C * D_{1C} * D_{2C})}$$

Eq. 4 $$I_S = 1 - e^{-\lambda t1}$$

Eq. 5 $$D_1 = e^{-\lambda t2}$$

Eq. 6 $$D_2 = (1-e^{-\lambda t3})/(\lambda t_3)$$

Eq. 7 $$R = \frac{M_B}{T_B} \text{ OR } R = \frac{M_{Ba133}}{T_{Ba133}}$$

Eq. 8 $$I_C = 1 - e^{-\lambda t4}$$

Eq. 9 $$D_{1C} = e^{-\lambda t5}$$

Eq. 10 $$D_{2C} = e^{-\lambda t6}$$

Where:

Act	=	Radium-226 sample concentration in pCi/unit (L, g, F, etc.)
S_A	=	gross count rate for the sample (in cpm)
B_A	=	cell background (in cpm)
S_C	=	gross count rate for the calibration source (in cpm)
B_C	=	calibration source cell background (in cpm)
A_C	=	activity of the calibration source in dpm
2.22	=	conversion factor from dpm to pCi
E	=	cell efficiency in cpm/dpm of radon-222
V	=	sample volume, mass, or fraction (in L, g, or %filter, etc)
R	=	fractional recovery of barium sulfate or Ba-133 tracer
M_B	=	mass of barium sulfate recovered (in mg)
M_{Ba133}	=	Measured sample Ba-133 Net Cts from the sodium iodide counter yield measurement
T_B	=	standardized barium carrier conc. (in mg barium sulfate per mL of barium carrier used)
T_{Ba133}	=	Measured Net Cts of the reference source for the specific sodium iodide detector used for the sample recovery determination
I_S	=	Radon-222 ingrowth factor for the sample

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D_1	=	Radon-222 decay between second de-emanantion and counting for the sample
D_2	=	Radon-222 decay during counting for the sample
I_C	=	Radon-222 ingrowth factor for the calibration source
D_{1C}	=	Radon-222 decay between second de-emanantion and counting for the calibration sample
D_{2C}	=	Radon-222 decay during counting for the calibration source
□	=	Decay constant of radon-222, (0.000125883 min^{-1})
t_1	=	the elapsed time in minutes between the first and second de-emanations for the sample
t_2	=	the elapsed time in minutes between the second de-emanation and sample counting for the sample
t_3	=	the sample counting time in minutes
t_4	=	the elapsed time in minutes between the first and second de-emanations for the calibration source in hours
t_5	=	the elapsed time in minutes between the second de-emanation and calibration source counting in hours
t_6	=	the calibration source counting time in minutes
Measured	=	either barium sulfate mass recovered in mg or Ba-133 measured by gamma spec
Expected	=	standardized barium sulfate target (in mg) or Ba-133 reference value (in pCi/L)

The sample specific **counting uncertainty** is calculated as follows.

Eq. 11 *Counting Uncertainty* $\square \frac{.96 * \sqrt{(S_A/t_3) \square (B_A/t_7)}}{\text{Denom}}$

Where:

t_7 = background count time in minutes

As summed background and analyte count rates approach zero, assumptions underlying the uncertainty calculation are violated and it will return an unrealistic value of zero (0) uncertainty when zero summed counts are observed. The following equation provides a more accurate estimate of count uncertainty at zero and near-zero count rates.

Eq. 12 ZeroUnc□ZeroActFact/SmplTime

Note 1: Depending on sample type and contract requirements the zero activity factor may be either 3.0 or 2.71. PASI's default is 2.71 consistent with the current version of ANSI N42.23. Bioassay samples must be calculated using 3.0 to be consistent with ANSI N13.30

Note 2: The Zero Count Uncertainty is compared to the count uncertainty above. The larger of the two is used as the counting uncertainty in subsequent total error calculations.

The error term is further evaluated to provide an estimate of total error hereafter referred to as the *Combined Standard Uncertainty* (CSU a.k.a. TPU).

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Eq.13

$$\text{CSU (pCi/unit)} = \sqrt{(\text{CountingUncertainty})^2 + (UE1 * Act)^2 + (UE2 * Act)^2 + (UE3 * Act)^2 + (UE4 * Act)^2}$$

UE1, UE2, UE3, and UE4 represent partial derivatives estimating the relative uncertainty at the ***95% confidence interval*** for various factors in the activity calculation as follows:

UE1 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with preparation (e.g., sample aliquot or transfers and splits prior to addition and equilibration of tracer).

UE2 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with analysis (e.g., peak integration, peak overlap, tracer contaminants).

UE3 represents combined factors estimating relative uncertainty (fractional) associated with yield correction (e.g., count uncertainty for tracer peak, SRM known value, tracer volume or mass aliquot, tracer equilibration efficiency).

UE4 represents the factor estimating additional uncertainty (activity) associated with an individual sample -- to be used in exceptional circumstances with approval of The Department Supervisor and appropriate documentation and narration only.

The Minimum Detectable Concentration (MDC) is calculated per guidance of ANSI N42.23 and N13.30 as:

Eq. 14 $$\text{MDC} = \frac{4.65 * \sqrt{B_A * t_3} + ZeroActFact}{t_3 * \text{Denom}}$$

Where B_A, t_3, *ZeroActFact*, and Denom have previously been identified.

The critical level (Lc) is calculated per guidance of ANSI N42.23 as:

Eq. 15 $$Lc = \frac{4.65 * \sqrt{(B)(1/Ts + 1/Tb)}}{Denom}$$

Where:

B, T_s, T_b, *ZeroActFact*, and Denom are as previously defined.

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Attachment II
(Numerical Performance Indicators)

1. **Method Blank (MB)**

1.1 The numerical performance indicator for the method blank is calculated by:

$$Z_{Blank} = \frac{x}{u(x)}$$

Where:
x = measured blank activity
u(x) = standard uncertainty (1 sigma) in the blank measurement

1.2 MB performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. MB performance indicator values should be recorded on a control chart.

2. **Laboratory Control Sample (LCS)**

2.1 The numerical performance indicator for a laboratory control sample is calculated by:

$$Z_{LCS} = \frac{x - c}{\sqrt{u^2(x) + u^2(c)}}$$

Where:

x = Analytical result of the LCS
c = Known concentration of the LCS
$u^2(x)$ = combined standard uncertainty (1 sigma) of the result squared.
$u^2(c)$ = combined standard uncertainty (1 sigma) of the LCS value squared.

2.2 LCS performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. Performance indicator values should be recorded on a control chart.

3. Duplicates (DUP)

3.1 These criteria are applicable for the evaluation of the Duplicate, Matrix Spike Duplicate and Laboratory Control Sample Duplicates.

3.2 The numerical performance indicator for laboratory duplicates is calculated by:

$$Z_{Dup} = \frac{x_1 - x_2}{\sqrt{u^2(x_1) + u^2(x_2)}}$$

Where:
x_1, x_2 = two measured activity concentrations

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$u^2(x_1)$, $u^2(x_2)$ = the combined standard uncertainty (1 sigma) of each measurement squared.

3.3 Duplicate sample performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. DUP performance indicator values should be recorded on a control chart for each QC sample type (Dup, MSD, LCSD)

4. **Matrix Spike/Matrix Spike Duplicate (MS/MSD)**

4.1 The numerical performance indicator for a matrix spike sample is calculated by:

$$Z_{MS} = \frac{x - x_0 - c}{\sqrt{u^2(x) + u^2(x_0) + u^2(c)}}$$

Where:
x = measured concentration of the spiked sample
x_0 = measured concentration of the unspiked sample
c = spike concentration added
$u^2(x)$, $u^2(x_0)$, $u^2(c)$ = the squares of the respective combined standard uncertainties (1 sigma) of these values.

4.2 MS performance for all matrices is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. MS performance indicator values should be recorded on a control chart.

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STANDARD OPERATING PROCEDURE

Analysis of Water Samples for Ra-228

Methods: EPA 904.0 and 9320/SM7500-RaD (Ra-228)

SOP NUMBER:	PGH-R-003-17
REVIEW:	R. Kinney
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-R-003-16
REVIEW DATE:	Upon Procedural Change

APPROVALS

General Manager	12/17/15 Date
Senior Quality Manager	12/17/15 Date
Department Manager/Supervisor	12/17/15 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

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1. Purpose

1.1 This SOP documents the analytical procedure to be used for the analysis of drinking water and other aqueous samples for Ra-228 content. This SOP is based on EPA 904.0, 9320, and SM7500-RaD.

2. Scope and Application

2.1 This procedure is applicable for the analysis of radium-228 in drinking water, wastewater, and other aqueous matrices. Without qualification, this procedure, as written, is compliant with Method 904.0 of "*Prescribed Procedures for Measurement of Radioactivity in Drinking Water,* EPA-600/4-80-032", Method 9320 of "*Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW846), Volume 1C, Third Edition", and Standard Method 7500-Ra D of "*Standard Methods for the Examination of Water and Wastewater*".

2.2 Radium-228 in an aqueous sample is determined by the isolation and direct measurement of Ac-228, the beta-emitting daughter of Ra-228, utilizing a gas flow proportional counter.

2.3 The efficiency of the Gas flow proportional counting (GFPC) system used for radioactivity measurement fluctuates relative to the energy of radioactivity emissions. Actinium-228 has a half life of 6.3 hours, so it is not practical to perform system calibrations directly with Ac-228, therefore, a beta isotope of similar energy is utilized for calibration purposes. This SOP requires that Sr-89 be utilized for calibration purposes.

2.4 Pace Analytical services, Inc. (PASI) applies isotope decay correction only in instances where the total impact in the analysis result is 2% or greater. Assuming a maximum hold time of 180 days, a 2% isotope decay would occur only for radioisotopes with a half-life of 17.14 years or less. The parameters reported using this SOP are affected by this policy and results for Ra-228 are decay corrected to the collection date and time supplied by the client.

3. Summary of Method

3.1 Radium in aqueous samples is pre-concentrated by co-precipitation with barium and lead as a sulfate. Barium and radium are isolated from lead by repeated precipitation as a sulfate from EDTA solution. The final purified barium/radium sulfate precipitate is dissolved in EDTA solution and stored to allow ingrowth of Ac-228, the beta-emitting daughter of Ra-228.

3.2 Following the ingrowth of Ac-228, potentially interfering radioisotopes of lead that may be present are removed by precipitation as lead sulfide. Actinium-228 in the sample is separated by co-precipitation with yttrium as hydroxide, then converted to yttrium oxalate and mounted for beta counting by GFPC. Radium recovery is determined by gravimetric measurement of barium sulfate precipitate recovered during analysis, or by use of Ba-133 as a radiotracer. Actinium recovery is determined by gravimetric measurement of yttrium oxalate precipitate recovered during analysis.

4. Interferences

4.1 The presence of high levels of Sr-90 in a water sample will produce a positive bias to the Ra-228 activity measured.

4.2 Elemental barium contained in the water sample will result in a falsely high gravimetrically measured barium yield and will result in an underestimation of Ra-228 content. This interference will not affect the yttrium or Ba-133 results. Ba-

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133 radiotracer is utilized to eliminate possible chemical recovery biases which would occur if stable barium was present in the sample and yield determination was performed gravimetrically.

4.3 In some samples, unidentified sample interferences can cause Ba-133 to carryover to the final source planchet, elevating the sample beta count rate, and biasing the sample result high. Additional instructions for determining if Ba-133 carryover has occurred are outlined in Section 12.5 of this SOP.

4.4 Samples containing excessive sodium and calcium will cause excess sulfate precipitate to form during the initial sulfate precipitation steps. Excessive sulfate precipitates can cause low chemical yields, because the additional precipitate may not completely dissolve in EDTA during the initial ingrowthing steps. Additional steps in Section 12.7 are designed to minimize the interference of sodium and calcium sulfate precipitates.

5. Safety

5.1 Procedures must be carried out in a manner that protects the health and safety of all personnel. Since this analysis is for a radioactive constituent, the sample must be treated as radioactive. Analysts must be trained as radiation workers and personal dosimeter worn.

5.2 At a minimum, eye protection, a laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves will be cleaned immediately.

5.3 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye-protection, gloves, and lab coat must be worn.

5.4 Exposure to radioactivity and chemicals must be maintained as low as reasonably achievable. Samples known to be hazardous and/or radioactive, must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 In order to minimize the potential for cross contamination of high and low levels of radioactive samples, good housekeeping and good laboratory practices are essential and must be strictly adhered to.

5.6 Organic samples of unknown content must be handled with extreme caution and under the direct instruction of a department manager or manager-specified designee. Direct treatment of organic matrices with strong oxidizing chemicals such as nitric acid and/or hydrogen peroxide is strictly prohibited.

5.7 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the SDS files maintained in the laboratory and in the PASI-PGH Chemical Hygiene Plan.

6. Definitions

6.1 See the Glossary Section of the most recent version of the Pace Analytical Services, Inc. Quality Assurance Manual for commonly used laboratory terms.

6.2 Batch: For all matrices, an analytical batch contains 20 or fewer samples of a similar matrix, prepared at the same time, by the same analyst, using the same reagents.

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6.3 Throughout this procedure, approximate weights and measures will be designated by the use of whole numbers when referring to masses exceeding 1gor volumes in excess of1mL. Measurements of masses and volumes so designated can be made with top loading balances, graduated cylinders, etc. For approximate measures below 1gor1mL, the word "approximately" must be used prior to the described mass or volume.

6.4 Throughout this procedure, exact or critical mass and volumes will be designated by the use of one or more decimal places. Measurements of mass and volumes so designated should be made with accurate analytical instruments such as analytical balances, calibrated pipettes, etc.

6.5 Any reference to a “hot water bath” indicates a container filled with water, which has been heated to a temperature just below the boiling point of the water.

6.6 When aliquotting samples on a balance, the observed mass on the balance must be recorded in preparation logbooks to the lowest mass indicated on the balance. Sample aliquot masses must not be targeted. Once sample is removed from the sample container and transferred to a beaker, it must not be removed from the beaker.

6.7 The method utilized for obtaining the sample aliquot, whether on a balance, in a graduated cylinder, or by pipette, must be clearly annotated in the preparation logbook.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

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7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Aqueous samples

8.1.1 Containers used for sample collection must never be re-used. Either plastic or glass containers may be used for sample collection.

8.1.2 Aqueous samples must be preserved at the time of collection by adding enough concentrated (16N) HNO_3 to the sample to make the sample pH <2. Typically, two mL of 16N HNO_3 per liter of sample is sufficient to obtain the desired pH. Samples must be preserved within five days of collection. If samples are collected without preservation, they must be received by the laboratory and preserved within five days of collection. Following preservation with acid, samples must be held in the original container for a minimum of 16 hours, and the pH must be rechecked by laboratory personnel prior to removing sample for analysis. The pH recheck date and time, the initials of the analyst verifying the pH, as well as any adjustments or notes regarding the preservation must be recorded in the pH Verification Logbook.

8.1.2.1 For dissolved analysis, samples must be filtered through a 0.45□m membrane filter and preserved to a pH <2.

8.1.2.2 For total analysis, the sample is not filtered, but is preserved.

8.1.3 Refrigeration is not required for aqueous samples.

8.1.4 The maximum hold time for samples analyzed by this procedure is 180 days between sample collection and sample analysis.

9. Equipment and Supplies

9.1 Gas Flow Proportional Counting System. (Low background beta <3 cpm). Refer to SOP PGH-R-002, current revision “Gas Flow Proportional Counter Operation” for instructions on GFPC system operation.

9.2 Software supplied with the instrument to control instrument operation. Refer to SOP PGH-R-002, current revision “Gas Flow Proportional Counter Operation” for applicable software details.

9.3 Computer capable of running the Gas Flow Proportional Counter System software, monitor, mouse, keyboard, and printer. Refer to SOP PGH-R-002, current revision “Gas Flow Proportional Counter Operation” for computer hardware specifications.

9.4 Electric hot plate.

9.5 Centrifuge, capable of greater than 2500 rpm.

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9.6 Centrifuge tubes, 50 mL high density polyethylene, or equivalent.

9.7 Filter paper, Fisherbrand Q2, 11.0cm diameter, or equivalent.

9.8 Membrane filter, 0.45□m, 47mm, Metricel®, or equivalent.

9.9 Drying lamp.

9.10 Glassware, various sizes.

9.11 Stirring Rods, glass.

9.12 Stainless steel counting planchets. 2 inch diameter, 1/8 inch deep.

9.13 Analytical balance (capable of measuring to 0.0001g).

9.14 Top Loading balance (capable of measuring to 0.01g).

9.15 Vortex mixer.

10. Reagents and Standards

10.1 Reagents should be prepared from reagent grade chemicals, unless otherwise specified below. Reagent water must be at least ASTM Type II quality or better. NOTE: Consult the Safety Data Sheets for the properties of these reagents, and how to work with them.

10.2 Distilled or deionized (DI)water. ASTM Type II generated as specified in Pace SOP PGH-C-027, current revision.

10.3 Acetic acid, 17.4N: glacial CH_3COOH (conc.), sp. Gr. 1.05, 99.8%.

10.4 Ammonium hydroxide, 15N: NH_4OH (conc.), sp. Gr. 0.90, 56.6%.

10.5 Ammonium oxalate, 5%: Dissolve 50.0g $(NH_4)_2C_2O_4$ H_2O in boiling ASTM Type II DI water, cool, and dilute to 1.0 L with ASTM Type II DI water.

10.6 Ammonium sulfate, 200g/mL: Dissolve 200g $(NH_4)_2SO_4$ in water and dilute to 1.0L with ASTM Type II DI water.

10.7 Ammonium sulfide, 2%: Dilute 2.0mL $(NH_4)_2S$, (20-24%), to 20mL with ASTM Type II DI water.

10.8 Barium carrier, 16mg/mL, standardized. Dissolve 28.46 g $BaCl_2$ $2H_2O$ in water, add 5.0mL 16N HNO_3, and dilute to 1.0L with ASTM Type II DI water.

10.9 Barium-133 standard solution, NIST traceable for use as a radiotracer for yield monitoring.

10.10 Citric acid, 1M: Dissolve 192.0g $C_6H_8O_7$ H_2O in water and dilute to 1.0L with ASTM Type II DI water.

10.11 EDTA reagent, basic (0.25M): Dissolve 20 g NaOH in 750mL ASTM Type II DI water, heat and slowly add 93 g disodium ethylenedinitriloacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2$ $2H_2O$) while stirring. Dilute to 1.0L with ASTM Type II DI water.

10.12 Lead carrier, 150mg/mL: Dissolve 239.7 g $Pb(NO_3)_2$ in ASTM Type II DI water, add 5.0mL 16N HNO_3 and dilute to 1.0 L with ASTM Type II DI water.

10.13 Lead carrier, 1.5 mg/mL: Dilute 10mL lead carrier (150 mg/mL) to 1.0L with ASTM Type II DI water.

10.14 Methyl Orange Indicator, 0.1%: Dissolve 1.0g methyl orange indicator in 1.0L ASTM Type II DI water.

10.15 Nitric acid, 16N: HNO_3 (conc.), sp. gr. 1.42, 70.4%.

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10.16 Nitric acid, 6N: Add 375mL of 16N HNO_3 to 500mL of deionized water, cool and dilute to 1Liter with ASTM Type II DI water.

10.17 Nitric acid, 1N: Dilute 62.5mL 16N HNO_3 to 1Liter with deionized water.

10.18 Radium-228 standard solution, NIST traceable for use as a Laboratory Control Sample spiking material.

10.19 Sodium carbonate, 2N: dissolve 124 g Na_2CO_3 H_2O (or 106 g Na_2CO_3) in ASTM Type II DI water and dilute to 1Liter with ASTM Type II DI water.

10.20 Sodium hydroxide, 18M: Dissolve 720g NaOH in ASTM Type II DI water and dilute to 1.0L with ASTM Type II DI water.

10.21 Sodium hydroxide, 10M: Dissolve 400g NaOH in ASTM Type II DI water and dilute to 1.0L with ASTM Type II DI water.

10.22 Strontium carrier, 10mg/mL: Dissolve 24.16 g $Sr(NO_3)_2$ in ASTM Type II DI water and dilute to 1.0L with ASTM Type II DI water.

10.23 Strontium-89 standard solution, NIST traceable for use in instrument calibration.

10.24 Sulfuric acid, 18N: Cautiously mix 1 volume 36N H_2SO_4 (conc.) with 1 volume of ASTM Type II DI water in a tub of ice or cool water. As water evaporates replace with ASTM Type II DI water to desired final volume.

10.25 Sulfuric acid, 0.1N: Dilute 5.56 mL of 18N sulfuric acid to 1.0L using ASTM Type II DI water.

10.26 Yttrium carrier, 18 mg/mL: Add 22.85 g Y_2O_3 to an Erlenmeyer flask Add 50mL of ASTM Type II DI water. Carefully add 40mL of concentrated nitric acid. Heat the mixture to boiling while stirring on a magnetic stirring hotplate. The solution must heat to boiling. Additional water and nitric acid may be added as necessary to aid in dissolution. Scrape the bottom of the Erlenmeyer flask with a Teflon scraper if the yttrium oxide is caked onto the glass. Do not add more than 100mL of nitric acid total. Upon complete dissolution, remove the beaker from the hotplate and cool completely. Dilute to 1Liter with ASTM Type II DI water.

10.27 Yttrium carrier, 9 mg/mL: Dilute 500mL yttrium carrier (18 mg/mL) to 1.0L with ASTM Type II DI water. Standardize this carrier in accordance with the steps outlined in section 11.

10.28 Strontium-yttrium mixed carrier, 0.9 mg/mL Sr^{+2} – 0.9 mg/mL Y^{+3}:

10.28.1 Solution A: Dilute 100mL yttrium carrier (18 mg/mL) to 1.0L with ASTM Type II DI water.

10.28.2 Solution B: Dissolve 4.348 g $Sr(NO_3)_2$ in ASTM Type II DI water and dilute to 1.0L with ASTM Type II DI water.

10.28.3 Combine Solutions A and B and label.

11. Calibration

Beta radioactivity emissions are inhibited by the medium through which they must travel. For this reason, when counting radioactivity emissions by gas flow proportional counting, system efficiency decreases as sample residue thickness increases. Over the applicable mass range for this method, this “self-attenuation” effect may be insignificant with certain gas flow counting systems. If it can be demonstrated that counting efficiency fluctuates by less than 2% over the applicable mass range, for a particular instrument, then calibrations need not take mass-attenuation into account. Otherwise, an appropriate system calibration that corrects for this “self-absorption” characteristic must be

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performed. Detector calibrations are performed universally independent of sample analysis matrix type. The calibration values determined by application of this process are applied universally for all matrices for which the analytical process is defined in this SOP.

11.1 Beta self-absorption calibration using Sr-89:

11.1.1 The applicable counting mass range for this method is between approximately 10 mg and approximately 30 mg. If it has been demonstrated that the instrument efficiency varies less than 2% over this mass range for the analyte of interest (Sr-89), then correction for self-attenuation is not required for this method. If self-attenuation is not applicable, then instrument calibration should be performed using a minimum of four calibration sources prepared at the optimum sample analysis mass (approximately 20 mg).

11.1.2 For a mass attenuation calibration using Sr-89, to labeled, disposable centrifuge tubes, add varying amounts of strontium carrier solution (10 mg/mL) which will generates a final theoretical strontium carbonate mass range that covers the practical mass range. This expected residue mass range is based on the routine gravimetric target mass for analysis andPASI's minimum and maximum allowable gravimetric recovery limits for this test. An example calibration source setup may be as follows:

Cal. Source Number	Volume of Sr carrier (10 mg/mL)
1	0.5 mL
2	1.0 mL
3	1.5 mL
4	2.0 mL
5	2.5 mL

11.1.3 For a calibration where the average of four efficiencies will be used, add 2.0mL of standardized strontium carrier to each of four labeled centrifuge tubes.

11.1.4 Add between 500 and 1500 dpm (by mass) of a NIST traceable Sr-89 standard to each calibration tube and record the standard mass on the bench sheet. Equivalent amounts of Sr-89 solution should be used for each source. Dilute each calibration solution to approximately 20 mL with ASTM Type II DI water.

Note: The specified calibration source activities have been optimized to allow manageable count times for individual sources. Maximum calibration source activities have been set to minimize the potential impact of any cross contamination within the detector system.

11.1.5 Add 5 mL of conc. NH_4OH solution to each calibration tube.

11.1.6 Add 5 mL of 2N Na_2CO_3 solution to each tube, then heat them in a hot water bath for 15 minutes. Remove each calibration tube from the hot water bath and allow it to cool.

11.1.7 Centrifuge each calibration source for 10 minutes and discard the supernate.

11.1.8 Wash the carbonate precipitate with 20mL of ASTM Type II DI water. Centrifuge and discard the supernate.

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11.1.9 Slurry the carbonate precipitate with a few mL of ASTM Type II DI water and quantitatively transfer it to a tared, 2-inch stainless steel planchet.

11.1.10 Dry the calibration sources under a heat lamp, and proceed with Step 11.1.11.

11.1.11 Re-weigh each source to determine the mass of strontium carbonate recovered.

11.1.12 Count calibration sources in a low-background gas flow proportional counting system as detailed in the instrument SOP, PGH-R-002, "Gas Flow Proportional Counter Operation" current revision. Count each calibration source in each detector requiring calibration long enough to acquire 10,000 net beta counts. Perform efficiency calculations as detailed in Attachment 1 of this SOP.

11.2 Calibration curve acceptance criteria

Calibration curves generated by the process detailed in this SOP must meet the following minimum criteria to be used for sample analysis.

11.2.1 Instrument mass-attenuation calibration must include a minimum of five calibration points for each detector being calibrated. Non-mass-attenuation calibrations must include a minimum of four calibration points with final source mass near the optimum method mass of 20 mg.

11.2.2 If the RSD between all calibration efficiency points is less than 5%, the average efficiency of the calibration points should be calculated and used in all sample calculations.

11.2.3 If the RSD of the efficiencies of the calibration points is greater than 5%, plot the system efficiency (as cpm/dpm) versus source mass (in mg) for each calibration source. Utilize a least squares curve-fitting, exponential or polynomial whichever yields the best fit against the measured data.

11.2.4 Following regression analysis, measured pCi values for each calibration source must be calculated using the calibration curve. Each measured source should be within 10% of known. If the value is not within 10%, assess the point using a z-score. If the z-score for the point is greater than 2.56, the point must be removed from use for calculation purposes. Calibration points may not be removed from the calibration curve without approval of the Department Manager/Supervisor.

11.2.5 Following the removal of individual points, the efficiency must be recalculated using the data for the remaining calibration sources and the calculation process must be repeated until the criteria established in this SOP have been met. A narrative discussing technical justification for modifications or exclusions of any calibration point must be created and kept with the calibration data.

11.3 Calibration Frequency

11.3.1 Calibrations or calibration re-verification for tests associated with drinking water analyses must be performed on an annual basis.

11.3.2 As allowed by specifications within the Manual for the Certification of Laboratories Analyzing Drinking Water, calibration sources may be retained for calibration re-verification purposes. Since Sr-89 is the isotope used for determining efficiency for Ra-228 calculations, and the half-life is less than 2 months, it is not practical to save Sr-89 calibration

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sources and reuse them to verify a calibration. New sources must be prepared for verification or calibrations and analyzed annually.

11.3.3 New sources used for verification purposes must be prepared at a similar mass and activity as those used in the initial calibration. Depending on the type of initial calibration used, a minimum of three sources of varying mass must be used to verify a mass attenuation curve, or a minimum of two sources of similar mass must be used to verify an average efficiency.

11.3.4 For the mass attenuation verification, the calculated activity of each of the three verification sources must be within 10% of their target source activity. Any detector not meeting this criteria requires a full calibration as outlined beginning in Section 11.1.2 of this SOP.

11.3.5 For an average efficiency verification, the calculated average efficiency of the two verification sources must be within 10% of the average efficiency determined in the initial calibration. Any detector not meeting these criteria requires a full calibration as outlined beginning in Section 11.1.3 of this SOP.

11.4 Yttrium carrier standardization

11.4.1 Yttrium carrier standardization must be performed prior to analyzing samples in which the yttrium carrier was used.

11.4.2 Add 1.0mL of yttrium carrier (9mg/mL) to each of 5 labeled centrifuge tubes.

11.4.3 Add 20mL 0.25M EDTA solution to each centrifuge tube.

11.4.4 Add 5mL 18M NaOH, stir well, and digest in a hot water bath until yttrium hydroxide coagulates. Centrifuge samples and discard the supernatant.

11.4.5 Dissolve the samples in 2.0 mL of 6N HNO_3, add 5.0 mL of ASTM Type II DI water, and re-precipitate yttrium as a hydroxide by adding 3.0 mL of 10N NaOH.

11.4.6 Heat the samples in a hot water bath for 12 minutes. Centrifuge the samples and discard the supernate.

11.4.7 Dissolve the precipitate in 1.0 mL of 1.0 N HNO_3. Cap the samples and vortex to mix. If cloudy, add 1.0 N HNO_3 dropwise until the solution is clear, up to 6 drops.

11.4.8 Heat the samples in a hot water bath for 3 minutes.

11.4.9 Remove the samples and add 3 mL ASTM Type II DI water and 2.0 mL of 5% ammonium oxalate solution to precipitate yttrium oxalate.

11.4.10 Cap and vortex the samples and return them to the hot water bath for an additional 3 minutes.

11.4.11 Remove the samples form the hot water bath, centrifuge, and discard the supernate.

11.4.12 Add 10.0mL of ASTM Type II DI water to each sample, and 6 drops each of the 1.0 N HNO_3 and 5% ammonium oxalate solution.

11.4.13 Cap and vortex the samples to break up the precipitate.

11.4.14 Return the samples to the hot water bath for 3 minutes. Remove and centrifuge the samples, discard the supernate.

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11.4.15 Slurry the precipitate in 6.6 mL of ASTM Type II DI water and quantitatively transfer the contents to a tared planchet placed under a heatlamp. Evaporate the samples to dryness and allow them to cool completely before reweighing.

11.4.16 Enter the tare and gross masses into the yttrium standardization calculation spreadsheet. Calculate the average mass of the five standards and the corresponding percent RSD and standard deviation among them.

11.4.17 The five standard masses must agree within 5% RSD and within ± 3 standard deviations to use the average mass.

11.4.18 Enter the average concentration into the Ra-228 activity calculations spreadsheet as the yttrium target mass for chemical recovery purposes.

11.5 Barium Carrier standardization

11.5.1 Pace employs Ba-133 tracer as the default yield monitor in this procedure. The following steps are included in this SOP in the event the Ba-133 yield assessment cannot be made. Barium carrier standardization is only necessary to perform when required.

11.5.2 Pipette 2.0mL barium carrier to each of 5 labeled centrifuge tubes.

11.5.3 Add 20mL 0.25M EDTA solution and 5mL 18N NaOH to each centrifuge tube.

11.5.4 Add 4mL 16N HNO_3 and swirl to mix.

11.5.5 Add 2.0mL ammonium sulfate (200 mg/mL) .

11.5.6 Add 3mL acetic acid. Cap the samples and vortex to mix.

11.5.7 Heat in a hot water bath for 15 minutes until the precipitate settles.

11.5.8 Centrifuge and discard the supernatant. Rinse the precipitate with 15mL of ASTM Type II DI water. Vortex vigorously.

11.5.9 Centrifuge and discard the supernatant.

11.5.10 Slurry the precipitate in 7mL of ASTM Type II DI water and transfer quantitatively to a tared 2 inch stainless steel planchet. Heat to dryness under an infrared lamp.

11.5.11 Calculate the average of the five standards masses and the corresponding percent RSD and standard deviation among them. The five standard masses must agree within 5% RSD and within ± 3 standard deviations to use the average mass.

11.5.12 Enter the average concentration into the Ra-228 activity calculations spreadsheet as the barium target mass for chemical recovery purposes.

12. Procedure

Unless specified otherwise, the documented analysis process must be followed, as written, including the order of analytical process and the addition of chemicals.

12.1 Weigh 800g of aqueous sample into an appropriately sized beaker. Record the observed measured mass of sample to the lowest decimal on the balance. Do not remove sample from the beaker once it has been added. The actual quantity

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of sample used may be less than 800 grams if matrix interferences are expected or there is limited sample quantity available to the laboratory. If less than 800g of sample is used, dilute the sample with ASTM Type II DI water to the 800mL mark on the beaker. Fortify the pH of diluted samples by adding 2mL of HNO_3.

12.2 Prepare a Method Blank (MB), Laboratory Control Sample (LCS), and Laboratory Control Sample Duplicate (LCSD) by weighing 800g of ASTM Type II DI water into an appropriately sized beaker. Add 2.0mL of concentrated nitric acid to the MB, LCS, and LCSD. Add the appropriate amount of Ra-228 spike solution to the LCS and LCSD based on the requirements listed in section 14.6.3.

12.3 If a Matrix Spike (MS) is prepared, add the appropriate amount of Ra-228 spike solution to the MS sample based on the requirements listed in section 14.9.2.

12.4 To all samples and QC, add 5mL of 1M citric acid ($C_6H_8O_7$ H_2O) and a few drops methyl orange indicator and stir. The solution should be red.

12.4.1 If the solution does not turn red, verify the pH of the original sample. If the pH is correct (acidic <2.0), proceed with the analysis. If the pH is not correct, go to Section 8.1.2.

12.5 Add 1mL lead carrier (150 mg/mL), 2mL strontium carrier (10 mg/mL), 2.0mL barium carrier (16 mg/mL), and 1mL yttrium carrier (18 mg/mL). PASI's default procedure for yield determination is made using Ba-133 radiotracer. Add an appropriate quantity of Ba-133 to each sample according to the guidelines in section 12.33.1 of this SOP. Stir well. Heat to incipient boiling and maintain at this temperature for 30 minutes.

12.5.1 Note: The default yield determination method is the use of Ba-133 tracer with tracer recovery determined by sodium iodide counting. For some samples, the Ba-133 tracer carries over to the sample planchet used for measurement of Ac-228 by GFPC counting. The sample components or interferences that are the cause of this phenomenon have not been identified. Discoloration of the final source prepared for Ac-228 counting may be an indication that interference exists, especially for samples yielding a dark oxalate precipitate for the count source.

12.5.2 The presence of Ba-133 on the Ac-228 (Y) oxalate planchet can be confirmed by direct qualitative counting on a gamma spectrometer or recounting the sample planchet on a GFPC detector the following day. Contributions to the beta count rate which are caused by Ba-133 carryover will be consistent from one day to the next due to the relatively long half life of Ba-133 versus the short half life of the Ac-228.

12.5.3 Unless samples have historically indicated the pattern of interference indicated in 12.5.1, all samples should be analyzed using the Ba-133 tracing approach. For all cases, the quantity of barium carrier added is the same.

12.5.4 Samples exhibiting Ba-133 carryover may be re-ingrowthed and reanalyzed providing the Ba-133 tracer yield is significant enough to be able to meet the required MDL upon reanalysis (greater than 50%). Otherwise, the sample should be reprepped using a lower aliquot, and possibly using stable barium carrier in lieu of Ba-133 tracer to determine chemical yield.

12.6 If necessary, add a few drops methyl orange indicator again as it is destroyed upon prolonged heating. Add 15N NH_4OH until a definite yellow color is obtained, then add a few additional drops. Precipitate lead and barium sulfates

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by adding 18N H_2SO_4 until the red color reappears, then add 0.25mL in excess. Add 5mL of $(NH_4)_2SO_4$ (200 mg/mL) and stir the sample vigorously until a precipitate forms. Allow the solution to heat for a minimum of 30 minutes and remove the samples to cool.

12.7 Allow the sample precipitate to settle overnight or for a minimum of 2 hours, and siphon off most of the supernatant liquid and discard, saving the precipitate.

12.7.1 The layer of precipitate should be relatively thin on the bottom of the beaker. If a significant amount of precipitate forms, it may be an indication of the presence of excessive sodium or calcium in the sample.

12.7.2 Sodium sulfate and calcium sulfate are soluble in cold water. Calcium sulfate, in particular, has an inverse solubility relationship with temperature, so the colder the water, the more calcium sulfate dissolves.

12.7.3 To remove most of the extra sodium and calcium sulfate precipitate, add ASTM Type II DI water to the beaker up to 800 mL mark on the beaker, stir the sample vigorously, remove the stir rod, and place the sample beaker in an ice water bath or refrigerator for a minimum of thirty minutes or until the precipitate settles completely.

12.7.4 Siphon off the supernatant liquid and discard, saving the precipitate.

12.7.5 Repeat steps 12.7.3 and 12.7.4 two additional times, and proceed to step 12.8 to transfer the reduced precipitate to a centrifuge tube.

12.8 Transfer the precipitate with the aid of 0.1 N sulfuric acid to a 50mL disposable centrifuge tube; centrifuge, and discard the supernatant liquid.

12.8.1 Sample centrifuging compacts the precipitate to the point where it should be possible to completely invert the tube during decanting to remove all of the supernatant chemical solution. When decanting, carefully tilt the tubes until it can be determined that the precipitate is compacted fully then invert the tube to fully decant. Adhere to this requirement for all subsequent decantations from centrifuge tubes.

12.9 Add 25mL EDTA solution to the sulfate precipitate. Vortex vigorously, and heat in a water bath to enhance dissolving of the precipitate. If the precipitate does not readily dissolve, add 10M NaOH solution dropwise. Do not add more than 7 drops of 10M NaOH.

12.9.1 If there is any undissolved material remaining, centrifuge the sample and transfer the solution to a clean disposable centrifuge tube. Submit the supernate solution for NaI detector counting for Ba-133 determination. If the resulting yield is within acceptable limits continue with the analysis. If it is not within the expected limits, combine the supernate and the solid material and reheat.

12.9.2 White precipitate is indicative of sulfate precipitates, and every effort must be made to dissolve as much as possible. Precipitates of any other color are more indicative of solids which may have been present in the sample prior to preparation and can be centrifuged from the sample and discarded in the appropriate waste receptacle.

12.10 To the dissolved sample in EDTA solution, add 1mL strontium-yttrium mixed carrier and stir thoroughly. Add a few drops of 10M NaOH if any precipitate forms.

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12.11 Add 1mL $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add 2 mL of acetic acid (glacial), with stirring, until the white precipitate of barium (radium) sulfate has formed. Digest in a hot water bath until the precipitate settles and the solution clears. Centrifuge the sample and discard the supernatant.

12.12 Add 20mL EDTA solution to the sample, vortex vigorously, and heat it until the precipitate dissolves. If needed, add 10M NaOH dropwise to enhance dissolution. Do not add more than 7 drops.

12.13 Repeat steps 12.11 and 12.12 one additional time. **At the conclusion of step 12.12 note the time of the last barium sulfate precipitation. (This is the beginning of the Ac-228 ingrowth).**

12.14 Add 20mL of EDTA solution.

12.15 Add 1.0mL yttrium carrier (9 mg/mL standardized) and 1mL lead carrier (1.5 mg/mL). Vortex the sample and heat in a hot water bath for 10 minutes to ensure equilibrium between the yttrium carrier and the actinium in the solution and to dissolve any precipitate.

12.15.1 If the precipitate does not readily dissolve, add 10M NaOH solution drop wise. Do not add more than 7 drops. Cap the centrifuge tube and vortex to mix then store a minimum of 36 hours to allow complete ingrowth of Ac-228. It is important to note that no precipitate is present at this point.

12.16 Following ingrowth, add 0.3mL $(NH_4)_2S$ and stir well. Add 0.5 mL of 10M NaOH. Cap the tube and vortex until lead sulfide flocks. Wait a minimum of **10 minutes** then centrifuge and decant supernatant into a clean, labeled tube.

12.17 Add 1mL lead carrier (1.5 mg/mL). Add 0.1mL $(NH_4)_2S$ and four drops of 10M NaOH to repeat the precipitation of lead sulfide as before (step 12.1.13). Cap the tube and vortex until lead sulfide flocks. Wait a minimum of **10 minutes** then centrifuge and decant supernatant into a clean tube.

12.18 Filter the supernatant through a 11.0 cm diameter Fisherbrand type Q2 or equivalent filter paper into a clean labeled tube.

12.19 NOTE: It is important to proceed without delay to the final separation and count of the Actinium 228 activity to minimize decay. Optimally, the following steps will take approximately 3 hours to complete.

12.20 Add 5mL 18M NaOH, stir well, and digest in a hot water bath for **12 minutes** until yttrium hydroxide coagulates. Centrifuge samples and decant supernatant into a clean, labeled centrifuge tube. Save the supernatant for Ba-133 yield determination, step 12.33. **(Record the time that the 18M NaOH is added [time of separation]; this is the end of the actinium-228 ingrowth time and beginning of Ac-228 decay time)**.

12.21 To remove residual Ba-133 tracer which can cause erroneously high sample results, add 5 mL of ASTM Type II DI water to each sample, vortex, and centrifuge. Discard the supernate.

12.22 Carefully dissolve the precipitate in 0.5 mL 6N HNO_3. Cap and vortex the samples to ensure dissolution. Add 5mL ASTM Type II DI water. Reprecipitate yttrium hydroxide by adding 3mL 10M NaOH. Heat and stir in a hot water bath for **12 minutes** until precipitate coagulates. Centrifuge sample and discard supernatant.

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12.23 To remove residual hydroxide and Ba-133 tracer, add 5 mL of ASTM Type II DI water to each sample, vortex and centrifuge. Discard the supernate.

12.24 Dissolve the precipitate in 0.25 mL of 1N HNO_3. Cap the tubes and vortex. The samples should be cloudy.

12.25 Remove the caps from the tubes and add 1N HNO_3 dropwise to each sample until the samples are almost clear. Do not add excess, as this will result in fractionation of the Ac-228 from the yttrium carrier, biasing results low. Include a note in the preparation logbook for any samples that do not turn clear.

12.26 Cap the samples, vortex and return them to the hot water bath for **3 minutes**.

12.27 Add 3.5mL of DI and add 2mL 5% ammonium oxalate. Cap and vortex the samples.

12.27.1 The samples should appear “milky” at this step.

12.28 Heat the samples in a hot water bath for **3 minutes**. (Prolonged heating may result in significant dissolution of yttrium oxalate back into solution and reduced yield recovery.) Centrifuge the samples and discard supernate.

12.29 Add 10mL ASTM Type II DI water to the precipitate. Add 6 drops of 1N HNO_3 and 6 drops of 5% ammonium oxalate.

12.30 Vortex vigorously and heat in a hot water bath for **3 minutes**. (Prolonged heating may result in significant dissolution of yttrium oxalate back into solution and reduced yield recovery.) Centrifuge sample and discard supernatant.

12.31 Slurry the oxalate precipitate with 6.6mL of ASTM Type II DI water and transfer quantitatively to a tared, 2-inch stainless steel planchet. Dry under an infrared lamp, cool, and reweigh to determine yttrium recovery.

12.32 To determine Ra-228 (Ac-228) content, count samples in a low-background gas flow proportional counting system as detailed in the instrument SOP, PGH-R-002, “Gas Flow Proportional Counter Operation” current revision. The specific Gas Flow Proportional detectors utilized must have been calibrated following instructions in Section 11 of this SOP.

12.32.1 Following beta counting, perform calculations as detailed in Attachment 1 of this SOP. Note: Due to the short half-life of Ac-228 (6.02 hours), it is imperative to count sources as soon as possible following yttrium hydroxide precipitation as performed in Step 12.20 of this SOP.

12.32.2 The maximum practical count time for achieving the RL of 1.0pCi/L is 600 minutes. Samples which do not meet the RL within 600 minutes may require re-ingrowth or reprep depending on the possible reasons the samples could not meet the RL.

12.33 Barium-133 Yield Assessment

12.33.1 Barium-133 is diluted from a NIST traceable solution. Approximately 2500-3000 dpm is added to each sample. The amount added is based on minimizing the required count time for yield determination while ensuring the tracer does not carryover and contribute extraneous counts during the final sample count by GFPC counting.

12.33.1.1 Dilute the barium solution from step 12.20 to 30mL with ASTM Type II DI water. Cap the tube and shake it to mix the sample thoroughly.

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12.33.1.2 Prepare a Ba-133 reference solution by adding a known quantity of barium-133 tracer to a 50mL centrifuge tube. Add 20mL of 0.25M EDTA solution and 5mL 18M NaOH. Dilute to 30mL with ASTM Type II DI water. Cap and shake to mix. (The proportion of the quantity added to the samples in 12.5 and the quantity added to the reference solution must be known in order for the yields to be determined.)

12.33.1.3 Count the reference solution and samples for Ba-133 gamma activity on a sodium iodide detector. Perform Ba-133 yield calculations as detailed in Attachment 1 of this SOP.

12.34 Barium yield by gravimetric assessment (used if Ba-133 is unavailable or for samples suspected to have interference from the use of Ba-133 tracer as indicated in Section 12.5 of this SOP.)

12.34.1 Perform Steps 11.5.4 through 11.5.10 on the solution saved from step 12.20.

12.34.2 Calculate the mass recovered on the planchet and calculate chemical recovery based on the target barium sulfate mass obtained during the barium carrier standardization.

13. Calculations

13.1 Refer to Attachment I of this SOP for Ra-228 associated calculations.

13.2 Any verified result for drinking water that exceeds the maximum contaminant level (MCL) established for (the sum of) Radium 228 and Radium 226 must be reported to the appropriate personnel and agencies according to the specific requirements of the state where the water was sampled. The directions for reporting any results that exceed the MCL limits are documented in the State Drinking Water Emergency Reporting Requirements Binder and Pace SOP PGH-C-025, current revision.

13.2.1 The MCL for radium in drinking water is Ra-226 + Ra-228 ≥5pCi/L OR either Ra-226 OR Ra-228 ≥ 5 pCi/L.

14. Quality Control

14.1 General guidelines for drinking water samples with results that exceed the Maximum Contaminant Level include the following: (All steps are to be conducted as soon as the exceedence has been identified.)

14.1.1 Verify the result(s) to ensure that there were no transcription or calculation errors and that all QC results are within the acceptable limits. Correct any problems and determine the new result. If there were no errors or the result still exceeds the MCL continue with the reporting process.

14.1.2 Immediately notify the Department Manager/Supervisor or specified designee, Department Manager/Supervisor and Quality department that a reportable result has been identified. Use telephone notifications to inform the contact people if the variance is identified after hours along with an e-mail follow up to document the event.

14.1.3 Refer to the State Drinking Water Emergency Reporting Requirements Binder for the state specific information regarding the proper course of action to take. Time is of the essence during this process with some of

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the state reporting requirements as short as 1 hour from the verification of an exceedence.

14.2 Each analyst who performs this test must satisfactorily complete a Demonstration of Capability Study as documented in Section 3.4 of the most recent revision of the Quality Assurance Manual.

14.2.1 The DOC study results are evaluated against the LCS acceptance limits.

14.2.2 IDOC and DOCs for drinking water methods must be done at a spiking level between the sensitivity level and MCL.

14.3 Daily instrument Quality Control checks for gas flow proportional counter must be completed following the instructions detailed in the SOP for Gas Flow Proportional Counter Operation, PGH-R-002 (current revision).

14.4 See Appendix II for performance indicator evaluation calculations and criteria. Numerical performance indicators may be used to assess QC for non-drinking water samples when the default assessment indicates a QC failure. The numerical performance indicator must be within +/- 3 for all other matrices. The z-score for precision assessment may be used for drinking waters with the approval of the Department Manager/Supervisor using the +/- 2 specification.

14.5 Method Blank (MB)

14.5.1 One MB must be prepared for each analytical batch. The purpose of the MB is to monitor for cross contamination during the analytical process. When available, the MB should be prepared from a similar matrix as samples contained in the analytical batch. If appropriate blank matrix material is not available, ASTM Type II DI water (Reagent Blank) must be carried through the procedure. A reagent blank may be used for sample correction purposes following approval of the Department Manager and affected clients.

14.5.2 The results of the method blank must be less than the reporting limit.

14.5.2.1 If the Method Blank is out of control, individual sample results may still be reportable if results are less than the CRDL (contract required detection limit) or greater than 10 times the blank result. Relative quantities of the sample and blank must be factored when making this determination (raw counts).

14.6 Laboratory Control Sample (LCS)

14.6.1 One LCS must be prepared for each analytical batch.

14.6.2 Typical detection limits are 1 pCi/L for Ra-228.

14.6.3 The Ra-228 spike activity must be between 2 and 10 times the detection limit.

14.6.4 A reference material containing a known concentration of radium-228 radioactivity in the same matrix as the batch is analyzed with the batch.

14.6.4.1 If this material is not available, a well-characterized material (WCM) may be used.

14.6.4.2 If neither of these are available, ASTM Type II DI water may be spiked with the appropriate radium-228 standard.

14.6.5 Percent Recovery Calculation

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$$\%REC = \frac{(LCSConc)}{TrueValue} * 100$$

Where:

LCSConc = Analytical result of the LCS
TrueValue = Known concentration of the LCS

14.6.6 LCS %REC acceptance limits are 60-135%.

14.7 Laboratory Control Sample Duplicate (LCSD)

14.7.1 An LCSD is not required for radium-228 analysis; however analysis of an LCSD must be utilized to measure batch precision whenever adequate sample quantity is not available for sample DUP analysis. The LCSD must be prepared in an identical fashion as the LCS and processed identically as for other samples.

14.7.2 The LCSD must pass the acceptance criteria for the LCS and the criteria established for duplicate precision (RPD 36% or less).

14.7.3 If the LCS and LCSD both pass %REC criteria however fail RPD criteria the batch results may be qualified and reported at the discretion of the analyst with guidance from the department manager.

14.8 Sample Duplicate (DUP)

14.8.1 One Duplicate Sample (DUP) must be randomly assigned within each batch. The purpose of the sample DUP is to measure precision of the analytical process. Laboratory duplicates are not intended to assess precision related to the sample collection process. Sample collection precision can only be assessed through collection of duplicate samples at the time of sample collection. The sample DUP is a duplicate quantity of sample processed identically as other samples in the analytical batch.

14.8.2 For batches with drinking water samples originating from the state of Arizona, Duplicate Samples (DUP) must be randomly assigned within each batch at a frequency of no less than 10%. A batch of 10 samples or fewer must contain at least one duplicate sample. A batch of greater than 10 samples up to 20 samples must contain a minimum of two duplicate samples if the batch contains samples originating from Arizona.

14.8.3 Relative Percent Difference Calculation (RPD)

$$RPD = \frac{(|R1 - R2|)}{(R1 + R2)/2} * 100$$

Where

R1 = Result Sample 1
R2 = Result Sample 2

14.8.4 Duplicate sample RPD acceptance limits are <36% for radium-228.

14.8.5 Sample duplicate criteria cannot be applied if results are below their associated MDC.

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14.8.6 Due to the limits for acceptable LCS/LCSD recovery, it is possible to have an acceptable LCS and LCSD, and still not meet the duplicate samples RPD acceptance limit. In this case, if the individual LCS and LCSD recovery criteria are met, the sample data may be reported with narration.

14.9 Sample Matrix Spikes (MS)

14.9.1 Because this analytical method requires the use of carriers or radiotracers for yield determination, PASI's default QC policy is that a sample matrix spike (MS) is not required for radium-228 analysis with the exception of drinking water analysis.

14.9.2 Typical detection limits for Ra-228 are 1 pCi/L. The spike amount must be greater than 10 times the detection limit.

14.9.3 The MS is prepared by spiking a portion of radium-228 radioactivity solution into a portion of one sample in the batch and processing identically as for other samples.

14.9.4 The purpose of the MS is to assess the affect of sample components on the analytical process. The quantity of sample used for the MS must be equivalent to the quantity of sample used for sample analysis.

14.9.5 Percent Recovery Calculation

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue} * 100$$

NOTE: The SampleConc is zero (0) for the LCS

14.9.6 MS acceptance limits are 60-127% for radium-228.

14.10 Sample Matrix Spike Duplicates (MSD)

14.10.1 A sample Matrix Spike Duplicate (MSD) is not required for this analysis. When required by the customer/contract, a MSD must be prepared for each analytical batch. The MSD must be prepared as a duplicate of the MS.

14.10.2 The MSD must pass the acceptance criteria established for the MS recovery and the criteria established for duplicate precision.

14.11 PASI's default criteria for carrier and/or tracer yield are 30-110% of the expected value.

14.12 Summary of QC related Activities:

Method Blank	One per Batch
Reagent Blank	One per Batch (as required by client)
Duplicate Sample	One per Batch or a frequency of 10% for batches containing DW samples from Arizona.
Matrix Spike	One per Batch (for drinking waters or as required by client)
Matrix Spike Duplicate	One per Batch (or a frequency of 10% for batches containing DW samples from Arizona.or as required by client)

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Laboratory Control Sample	One per Batch
Laboratory Control Sample Dup	One per Batch (in absence of Duplicate sample)

14.13 Corrective Actions for Out-Of-Control Data

14.13.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis and evaluate the usefulness of the data in the final report.

14.13.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.13.3 Matrix Spike Recovery (MS) – MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS are met (matrix interference). If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and noted in the final report.

14.13.4 An acceptable LCS does not automatically indicate matrix interference for a failed MS. The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.13.5 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.13.6 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.13.7 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.13.8 Laboratory Control Sample Duplicate (LCSD) – If an LCSD does not meet the recovery acceptance criteria, the entire analytical batch must be reanalyzed.

14.13.9 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their reporting limit, and duplicate precision meets the acceptance criteria.

14.13.10 If there is no available sample volume remaining for re-analysis and evaluate the usefulness of the data in the final report. Carrier Recovery: If analysis of samples other than drinking water matrices results in a carrier recovery outside of the default acceptance range, results may be reported with appropriate qualification and approval of the client. If analytical results are reported, they are noted in the case narrative. For all other analyses (including Drinking Water analysis), samples that result in a carrier recovery outside of the default acceptance range must be reanalyzed. If reanalysis results in a carrier recovery outside of the default acceptance range, the results are reported and qualified.

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14.13.10.1 Default acceptance limits are 30-110% for gravimetric carriers. Results as high as 130% may be reported with permission of the Department Manager/Supervisor or manager-specified designee.

14.13.11 Tracer Recovery: If analysis of samples other than drinking water matrices results in a tracer recovery outside of the default acceptance range, results may be reported with appropriate qualification and approval of the client. If analytical results are reported, the results are noted in the case narrative. For all other analyses (including Drinking Water analysis), samples that result in a tracer recovery outside of the default acceptance range must be re-analyzed. If re-analysis results in a tracer recovery outside of the default acceptance range, the results are reported, and noted in the case narrative. For Ra-228 analysis using Ba-133 tracer, the uncertainty calculations for yield measurement include a maximum allowable 1 sig. uncertainty of 5% which correlates to 400 net tracer counts. If tracer yield measurement results in the acquisition of less than 400 net tracer counts, the result must be appropriately qualified.

14.13.11.1 Default acceptance limits are 10-110% for radioactive tracers. Results as high as 130% may be reported with permission of the department manager or manager-specified designee.

14.14 Contingencies for handling Out-of-Control or Unacceptable Data

14.14.1 Method Blank (Reagent Blank): If the sample is exhausted, evaluate the usefulness of the data and appropriately qualified and/or narrated.

14.14.2 Duplicates: If the sample is exhausted evaluate the usefulness of the data and appropriately qualified and/or narrated.

14.14.3 Matrix Spike Recovery: If a Matrix Spike Duplicate is analyzed and the spike recoveries are not comparable, and the sample is exhausted, evaluate the usefulness of the data and appropriately qualified and/or narrated.

14.14.4 Matrix Spike Duplicate: If a Matrix Spike Duplicate is analyzed and the spike recovery is not comparable to the Matrix Spike and the sample is exhausted, evaluate the usefulness of the data and appropriately qualified and/or narrated.

14.14.5 Carrier Recovery: If the sample is exhausted evaluate the usefulness of the data and appropriately qualified and/or narrated.

14.14.6 Tracer Recovery: If the sample is exhausted, evaluate the usefulness of the data and appropriately qualified and/or narrated.

15. Method Performance

15.1 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.2 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.3 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

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15.4 Laboratory control samples are analyzed with each batch, the results are charted to monitor control limits and trending.

16. Pollution Prevention and Waste Management

16.1 Place radioactive waste into appropriate receptacles.

16.2 Discard acidified samples and unusable standards into proper waste drains.

16.3 Dispose of waste materials in accordance to type: Non-hazardous, hazardous, non-radioactive, radioactive or mixed.

17. References

17.1 Krieger, H. L. and Whittaker, E. L., *Prescribed Procedures for* Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, "Radium-228 in Drinking Water," Method 904.0, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, August, 1980.

17.2 Eaton, A. D., et. al., editors, Standard Methods for the Examination of Water and Wastewater, 20th Edition, "Radium – Sequential Precipitation Method," Method 7500-Ra D., American Public Health Association, Baltimore, MD, 1998.

17.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW846), Volume 1C, Third Edition, "Radium-228," Method 9320, U. S. Government Printing Office, Washington, D.C., September 1986.

17.4 ASTM E181-93, Standard Test Methods for Detector Calibration and Analysis of Radionuclides, ASTM Standards, Vol. 12.02.

17.5 Table of Radioactive Isotopes, Brown and Firestone, Shirley editor, John Wiley & Sons, 1986.

17.6 Currie, L., Limits for Quantitative Detection and Quantitative Determination, Analytical Chemistry, Vol. 40. No. 3, Pg 586-593, 1968.

17.7 Currie, L., Lower Limit of Detection: Definition and Elaboration of a Proposed Position for Radiological Effluent and Environmental Measurements, NUREG/CR - 4007, USNRC, 1984.

17.8 “American National Standard Calibration and Usage of Alpha/Beta Proportional Counters”, ANSI N42.25-1997.

17.9 “Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)”, July 2004, Final.

17.10 “American National Standard Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories”, ANSI N42.23-1996.

17.11 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.12 Department of Defense Quality System Manual (DoD QSM) version 4.2 (or most recent version).

17.13 “Manual for the Certification of Laboratories Analyzing Drinking Water” Fifth Edition, January 2005, EPA 815-R-05-004.

17.14 National Primary Interim Drinking Water Regulations (NIPDWR), Part 141.15.

17.15 Pace Pittsburgh SOP, PGH-R-002, current revision, Gas Flow Proportional Instruments Operation.

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17.16 Pace SOP PGH-C-025, current revision (MCL Violation Reporting).

17.17 Pace SOP PGH-C-027, current revision (Deionized Water Quality and Suitability).

17.18 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.19 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.20 Pace Analytical Services, Inc. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Attachment I: Calculations

18.2 Attachment II: Numerical Performance Indicators

19. Method Modifications.

19.1 For routine analysis of aqueous samples, PASI's default process for measuring the quantity of sample to be analyzed is to measure the mass of sample transferred and the mass of sample used is documented in the appropriate logbook. Subsequent calculations for analysis of aqueous samples assume the density of aqueous samples to be 1.0 g/mL. For these samples, analysis results are reported in volume units without density correction.

19.2 EPA method 904.0 specifies the use of 10mL of lead carrier with a concentration of 15 mg/mL, while this procedure uses 1 mL of lead carrier with a concentration of 150 mg/mL. The amount of lead added is equivalent. PASI uses a more concentrated solution to reduce the chemical reagent footprint within the laboratory.

19.3 For Section 12.8 of this SOP, samples are siphoned and centrifuged to isolate the barium precipitate, whereas, the EPA method 904.0 specifies filtering the sample to collect the precipitate. Sample losses due to this difference are accounted for with the barium yield determination and do not adversely affect sample results.

19.4 In Section 12.21 and 12.23 of this SOP, a rinse of the yttrium hydroxide precipitate using ASTM Type II DI water has been added to enhance removal of residual Ba-133 tracer which could contribute to the beta count rate during sample analysis. Ba-133 tracer is not utilized in EPA method 904.0. Sample losses due to the rinses are accounted for with the yttrium oxalate yield determination and do not adversely affect sample results.

19.5 EPA method 904.0 specifies the addition of 2mL of 6N HNO_3 for the second yttrium hydroxide precipitation and 1mL of 1N HNO_3 for the initial yttrium oxalate precipitation. The correlating steps in this procedure have reduced the volumes to 0.5mL of 6N HNO_3 and 0.25mL of 1N HNO_3. The reduction in acid is necessary, due to the ASTM Type II DI water rinses of Sections 12.21 and 12.23. Excessive acidity causes actinium and yttrium to fractionate, creating a chemical disconnect between the analyte (actinium-228) and the carrier (yttrium), contributing to a low bias for analytical results.

19.6 EPA Method 904.0 specifies to use 1,000 mL of sample for analysis. Pace analyzes approximately 800 mL of sample for analysis. All samples are measured by mass as specified within this SOP. Pace further restricts the analysis volume for samples known to contain matrix components that would limit

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analyte recovery. Pace restricts the analysis volume so as to limit the quantity of waste generated and to enhance productivity. The required detection limit of 1 pCi/L is achieved using a 800 gram analysis quantity.

20. Revisions

Document Number	Reason for Change	Date
PGH-R-003-13	1. Added note at step 12.5.1 to describe process for full decantation of sample in centrifuge tubes. 2. Revised section 12.12 to wait 10 minutes rather than five for lead flocking to occur. 3. Added steps 12.18 and 12.20 to perform a 5mL DI water rinse to remove Ba-133 tracer interference from samples. 4. Revised step 12.19 to use 0.5 mL 6N HNO3 instead of 2.0 mL to prevent fractionation of yttrium due to high acid content 5. Revised step 12.21 to use 0.25 mL of 1N HNO3 and to add dropwise to just slightly cloudy, to prevent fractionation of yttrium due to high acid content. 6. Revised step 12.22 and 12.23 to place samples in the hot water bath for 3 minutes following the addition of 1N HNO3 in following with the EPA written method. 7. Revised step 12.25 and 12.27 to limit the time the yttrium oxalate precipitate is in the hot water bath to 3 minutes to prevent yield losses. 8. Added 14.8.5 to include the ability to report samples results when a LCS/LCSD RPD failure occurs. 9. Modified section 14.5.1 to require approval of the Department Manager for approval to blank correct sample results. 10. Revised section 14 to address default criteria for gravimetric carriers and radioactive tracers. 11. Change wording in section 14 to address non-conformance with LabTracks and also to evaluate data and appropriately qualify or discuss in narrative for reports that do not include a case narrative.	25Apr2012
PGH-R-003-14	1. Updated Cover page, headers/footers for this revision 2. Added Arizona Drinking water batching requirements for Duplicate to Section 14.8.2.	11July2012
PGH-R-003-15	1. Updated Cover Sheet, Headers and Footers. 2. Section 4: Added noted interferences and the step in this SOP where they are addressed. 3. Section 6: Added reference to glossary section of QAM for definitions of terms and added section regarding recording observed measurements, prohibiting weight targeting, and not removing sample from beakers once added. 4. Section 10: Added ASTM Type II DI water preparation and reference, changed all DI water to ASTM Type II DI water throughout document. 5. Section 11: Added calibration frequency requirements, documentation required for removal of calibration points.	23Sep2013

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Document Number	Reason for Change	Date
	6. Section 12: Added comment regarding performing steps and chemical additions in order specified. 7. Section 12.2: Inserted steps to ensure the Ra-228 spike is added to LCS/LCSD samples after the initial sample acidification and prior to any other chemical additions. 8. Section 12.3: Inserted to ensure Ra-228 spike additions to the MS are specified to occur prior to all chemical additions. 9. Section 12.5: Added information regarding determining if Ba-133 carryover has occurred and how to proceed. 10. Section 12.7: Added instructions on reducing excess sulfate precipitates due to calcium and sodium interferences. 11. Section 12.9.2: Clarified types of precipitates expected and which need to be dissolved. 12. Section 14: Added criteria for appropriate use of Numerical Performance Indicators. 13. Section 17: Updated references. 14. Section 19: Added comments regarding Pace's default sample measurement technique, density assumptions, and how to use the quantity measurement in the spreadsheet. 15. Attachment II: Updated combined standard uncertainties are assessed at 1 sigma.	
PGH-R-003-16	1. Annual SOP review and update. 2. Section 2.1 – Included reference to standard methods. 3. Section 2.4 – Moved the decay correction application discussion from Section 3 to be consistent with other Pace SOPs. 4. Section 8.1.2 – Added pH verification requirement and recording. 5. Section 8.4 – Added hold time requirement. 6. Section 9 – Added reference for instrument SOP and GFPC instrument components. 7. Section 9.7 and 9.9 – Changed filter paper to current brand and type being utilized by laboratory, added sample planchet dimensions. 8. Section 10 – Included preparation of Na_2CO_3 solution since it is used in calibration process. 9. Section 11.3 – Inserted to specify amount of strontium carrier added to calibration sources when preparing average efficiency calibration (not mass attenuation). 10. Section 11.3.3-11.3.5– Added source preparation requirements for verification sources and calibration verification acceptance criteria. 11. Section 11.4.1 and 11.5.1 – Inserted comment for when carrier standardization is required. 12. Section 12.1 – Inserted instructions for diluting samples. 13. Section 12.5 – Changed order of chemical addition to match EPA method 904.0, inserted strontium carrier – inadvertently omitted in prior revision.	13Jul2014

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Document Number	Reason for Change	Date
	14. Section 12.9 – changed EDTA amount from 20 mL to 25 mL to match EPA method 904.0. 15. Section 12.33.1 – Included amount of Ba-133 added to samples and comment regarding concentration. 16. Included reference to actual GFPC Pace SOP, PGH-R-002, current rev where instrumentation discussed throughout document. 17. Section 14.12 – Included AZ DW QC requirements for duplicate and MSD. 18. Section 15.3 – Included CDOC requirements. 19. Section 17 – Added GFPC Instrument SOP, PGH-R-002, current revision. 20. Section 19 – Added notable deviations from methods including concentration of lead carrier, siphoning versus filtration, use of Ba-133 and ASTM Type II DI rinses, decreased acid volumes for 6N and 1N HNO_3 additions. 21. Reformatted document.	
PGH-R-003-17	1. Updated Section 4.3 to reference the correct SOP location which addresses Ba-133 carryover and bias. 2. Updated Section 4.4 to reference the correct SOP location which specifies the treatment option for samples generating excess calcium sulfate and sodium sulfate during the initial sample pre-concentration. 3. Section 19 updated to include the analysis volume difference between this SOP and the method, EPA 904.0.	17Dec2015

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Attachment I – (Calculations)

The **radium-228 concentration** of a sample is calculated according to the following equations:

Eq. 1 $A = \frac{(S - B)}{(Denom)}$

Eq. 2 $Denom = E * V * .22 * D * I * C * X * R_A * R_B$

Eq. 3 $D = e^{-\lambda t1}$

Eq. 4 $C = \frac{1(1 - e^{-\lambda t3})}{\lambda t3}$

Eq. 5 $X = e^{-\lambda 2t4}$

Eq. 6 $I = 1 - e^{-\lambda t2}$

Eq. 7 $\lambda = \frac{\ln 2}{T_{1/2}}$

Eq. 8 $\lambda 2 = \frac{\ln 2}{T_{1/2Ra}}$

Eq. 9 $R_A = \frac{M_Y}{T_Y}$

Eq. 10 $R_B = \frac{M_B}{T_B}$ OR $R_B = \frac{M_{Ba133}}{T_{Ba133}}$

Where:

A = Ra-228 concentration in pCi/L.
S = Sample gross beta count rate (in cpm).
B = Background beta count rate (in cpm).
2.22 = Conversion factor from dpm to pCi.
E = Detector efficiency (As determined in Section 11 of this SOP)
V = Sample volume (in liters).
D = Ac-228 decay factor between initial precipitation and start of count.

I = Fractional ingrowth of Ac-228 into the purified radium sample

C = Ac-228 decay factor from beginning of count to midpoint of count.

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X = Ra-228 decay factor from sample collection date and time to count start date and time.
t1 = Decay time in hours between final yttrium hydroxide precipitation and midpoint of count time.
t2 = Ingrowth time in hours between first yttrium hydroxide precipitation and second yttrium hydroxide precipitation.
t3 = Count time in hours.
t4 = Decay time in days between the sample collection date and the sample count date.
$T_{1/2}$ = Half-life of Ac-228 in hours (6.02 hours).
$T_{1/2Ra}$ = Half-life of Ra-228 in years (5.75 years)
R_A = Fractional recovery of yttrium.
R_B = Fractional recovery of barium.
M_Y = Mass of yttrium oxalate recovered (in mg).
M_B = Mass of barium sulfate recovered (in mg).
M_{Ba133} = Measured sample Ba-133 Net Cts from the sodium iodide counter yield measurement
T_Y = Standardized yttrium carrier conc. (in mg yttrium oxalate per mL of yttrium carrier used)
T_B = Standardized barium carrier conc. (in mg barium sulfate per mL of barium carrier used)
T_{Ba133} = Measured Net Cts of the reference source for the specific sodium iodide detector used for the sample recovery determination.

The sample specific **counting uncertainty** C.U. is calculated as follows.

Eq. 11 $$C.U. = \frac{1.96 * \sqrt{(S/T_S) + (B/T_B)}}{Denom}$$

Where:

T_S = Count time for the sample (in minutes)
T_B = Count time for the background count (in minutes)
S, B, and Denom as previously defined.

As summed background and analyte count rates approach zero, assumptions underlying the uncertainty calculation are violated and it will return an unrealistic value of zero (0) uncertainty when zero summed counts are observed. The following equation provides a more accurate estimate of count uncertainty at zero and near-zero count rates.

Eq. 12 $$ZeroUnc = ZeroActFact/SmplTime$$

Note 1: Depending on sample type and contract requirements the zero activity factor may be either 3.0 or 2.71. PASI's default ZeroActFact is 2.71 consistent with the current version of ANSI N42.23. Bioassay samples must be calculated using 3.0 to be consistent with ANSI N13.30

Note 2: The Zero Count Uncertainty is compared to the count uncertainty above. The larger of the two is used as the counting uncertainty in subsequent total error calculations.

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The error term is further evaluated to provide an estimate of total error hereafter referred to as the *Combined Standard Uncertainty* (CSU a.k.a. TPU). The CSU is calculated as follows:

Eq. 13 $$CSU\,(pCi/U) = \sqrt{(C.U)^2 + (UE1 * A)^2 + (UE2 * A)^2 + (UE3 * A)^2 + (UE4 * A)^2}$$

Where:

UE1, UE2, UE3, and UE4 represent partial derivatives estimating the relative uncertainty at the ***95% confidence interval*** for various factors in the activity calculation as follows:

UE1 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with preparation (e.g., sample aliquot or transfers and splits prior to addition and equilibration of tracer).

UE2 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with analysis (e.g., peak integration, peak overlap, tracer contaminants).

UE3 represents combined factors estimating relative uncertainty (fractional) associated with yield correction (e.g., count uncertainty for tracer peak, SRM known value, tracer volume or mass aliquot, tracer equilibration efficiency).

UE4 represents the factor estimating additional uncertainty (activity) associated with an individual sample -- to be used in exceptional circumstances with approval of the Department Manager and appropriate documentation and narration only.

The Minimum Detectable Concentration (MDC) is calculated per guidance of ANSI N42.23 and N13.30 as:

Eq. 14 $$MDC = \frac{4.65 * \sqrt{B * T_S} + ZeroActFact}{T_S * Denom}$$

Where:

B, T_S, ZeroActFact, and Denom are as previously defined.

The critical level (Lc) is calculated per guidance of ANSI N42.23 as:

Eq. 15 $$Lc = \frac{4.65 * \sqrt{(1/T_s + 1/T_b)B}}{Denom}$$

Where:

B, T_s, T_b, *ZeroActFact*, and Denom are as previously defined.

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Attachment II - (Numerical Performance Indicators)

1. **Method Blank (MB)**

1.1 The numerical performance indicator for the method blank is calculated by:

$$Z_{Blank} = \frac{x}{u(x)}$$

Where:
x = measured blank activity
u(x) = combined standard uncertainty (1 sigma) in the blank measurement

1.2 MB performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. MB performance indicator values should be recorded on a control chart.

2. **Laboratory Control Sample (LCS)**

2.1 The numerical performance indicator for a laboratory control sample is calculated by:

$$Z_{LCS} = \frac{x - c}{\sqrt{u^2(x) + u^2(c)}}$$

Where:

x = Analytical result of the LCS
c = Known concentration of the LCS
$u^2(x)$ = Combined standard uncertainty (1 sigma) of the result squared.
$u^2(c)$ = Combined standard uncertainty (1 sigma) of the LCS value squared.

2.2 LCS performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. Performance indicator values should be recorded on a control chart.

3. Duplicates (DUP)

3.1 These criteria are applicable for the evaluation of the Duplicate, Matrix Spike Duplicate and Laboratory Control Sample Duplicates.

3.2 The numerical performance indicator for laboratory duplicates is calculated by:

$$Z_{Dup} = \frac{x_1 - x_2}{\sqrt{u^2(x_1) + u^2(x_2)}}$$

Where:
x_1, x_2 = two measured activity concentrations
$u^2(x_1)$, $u^2(x_2)$ = the combined standard uncertainty (1 sigma) of each measurement squared.

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3.3 Duplicate sample performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. DUP performance indicator values should be recorded on a control chart for each QC sample type (Dup, MSD, LCSD)

4. **Matrix Spike/Matrix Spike Duplicate (MS/MSD)**

4.1 The numerical performance indicator for a matrix spike sample is calculated by:

$$Z_{MS} = \frac{x - x_0 - c}{\sqrt{u^2(x) + u^2(x_0) + u^2(c)}}$$

Where:
x = Measured concentration of the spiked sample
x_0 = Measured concentration of the unspiked sample
c = Spike concentration added
$u^2(x)$, $u^2(x_0)$, $u^2(c)$ = the squares of the respective combined standard uncertainties (1 sigma) of these values.

MS performance for all matrices is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. MS performance indicator values should

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