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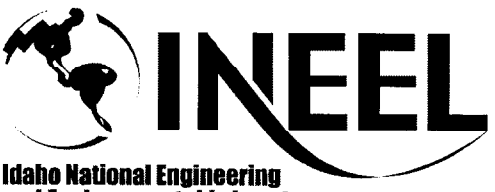
Quality Assurance Project Plan for the Analysis of Amchitka Island Samples



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ABSTRACT

This Quality Assurance Project Plan specifies quality assurance/quality control procedures employed in the analysis of Amchitka Island samples carried out by the Idaho National Engineering and Environmental Laboratory (INEEL) Analytical Laboratories under a "Work For Others" agreement. It provides project-specific implementation of Company quality program requirements, as specified in PRD-5071, "Quality Assurance Program." This Quality Assurance Project Plan supplements PLN-153, "Quality Assurance Project Plan for Analytical Laboratories Department Radioanalytical Activities."

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TABLES

ACRONYMS

ACMM	Analytical Chemistry Methods Manual
ALD	Analytical Laboratories Department
Am	americium
ASTM	American Society for Testing and Materials
CCB	continuing calibration blank
CCV	continuing calibration verification
Co	cobalt
COC	chain of custody
Cs	cesium
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
Eu	europium
GL	Group Lead
GS	gamma spectroscopy
GSTL	Gamma Spectroscopy technical leader
^{3}H	tritium
I	iodine
ICB	initial calibration blank
ICP-MS	inductively coupled plasma mass spectrometry
ICPTL	ICP-MS technical leader
ICS	interference check sample
ICSA	interference check sample, part A
ICSAB	interference check sample, part A+B
ICV	initial calibration verification
INEEL	Idaho National Engineering and Environmental Laboratory
LCS	laboratory control samples
M&TE	measurement and test equipment
MAPEP	Mixed Analyte Performance Evaluation Program
MCP	management control procedure
MDA	minimum detectable activity
MS	matrix spike
MSD	matrix spike duplicate
PLN	Plan
PRD	Program Requirements Document
PE	performance evaluation
Pu	plutonium
QA	quality assurance

QAO	quality assurance officer
QAPjP	quality assurance project plan
QA/QC	quality assurance/quality control
QC	quality control
RA	radioanalytical
RC	radiochemistry
RESL	Radiological and Environmental Sciences Laboratory
RML	Radiation Measurement Laboratory
RPD	relative percent difference
RTL	radiochemistry technical leader
Sr	strontium
Tc	technetium
TL	technical leader
TRA	Test Reactor Area
U	uranium
WFO	Work For Others (agreement)

1. PROJECT DESCRIPTION

The analysis of Amchitka Island samples is carried out by the Idaho National Engineering and Environmental Laboratory (INEEL) to establish and document different radioisotope activities in the vicinity of Amchitka Island, Alaska, which was the scene of three underground nuclear test shots during 1965-1971. At present, the U. S. Department of Energy (DOE) is moving to closure and long-term stewardship of the contaminated site. Therefore, it is necessary to reassess the marine environment with respect to possible current or future transfer of radionuclides and other contaminants to the sea, marine ecosystems (particularly sensitive or endangered species), foods harvested by fishermen in the area, and to seafood of commercial interest. The samples (soft tissue/organ tissue, skeletal material [i.e., bone or exoskeleton], and plant matter) are analyzed for ^{241}Am, $^{238,239,240}Pu$, $^{234,235,236,238}U$, ^{137}Cs, ^{152}Eu, ^{60}Co, ^{90}Sr, ^{99}Tc, and ^{129}I using alpha spectrometry, gamma spectrometry, beta counting, and inductively coupled plasma mass spectrometry (ICP-MS). The analytical results are reported to the Consortium for Risk Evaluation with Stakeholder Participation (CRESP) who has a contract with DOE to study these issues. Figure 1-1 identifies the current CRESP technical bases for the subject analyses.

This quality assurance plan supplements INEEL PLN-153, "Quality Assurance Project Plan for Analytical Laboratories Department Radioanalytical Activities," to describe the measures taken to assure the accuracy of the analyses performed by the INEEL analytical laboratories involved in this project. Both this plan and PLN-153 are written to conform with the requirements and guidelines specified in MCP-561, "Quality Program Plan/Quality Assurance Project Plan Development." This plan follows the established format of PLN-153 in lieu of the format suggested by MCP-561. Collectively, these plans include descriptions of the related measurement program, organization of the project participants, quality assurance objectives, sample receiving procedures, quality controls, performance audits, preventive maintenance, data evaluation and quality assurance reports. The subject samples will be received and analyzed at the INEEL's Test Reactor Area (TRA) Radioanalytical Laboratories.

The Analytical Laboratories Department (ALD) Quality Assurance Officer (QAO) maintains and approves this quality assurance plan and monitors compliance with its provisions. The manager of the Chemistry Department is responsible for the administration of all portions of the project performed by INEEL personnel.

RADIONUCLIDE ANALYSIS OF MARINE SAMPLES
Four major questions the data user seeks to address: 1. Are the foods safe to eat with respect to radionuclides? 2. Within the context of available data from eco-receptors, is there any indication that biota are at risk from radionuclides? 3. Can the data from the study be used to determine which species are the best bioindicators to be used to design future monitoring, and 4. If the full range of physical and biological data obtained from the expedition indicates radionuclides above background, can we attribute increased levels of radionuclides to a particular source? Our results represent only one point in time.
The effort will involve the processing of samples primarily at Rutgers University and Vanderbilt University, with the primary analytic efforts taking place at INEEL and then subject to confirmatory processes to assure the accuracy of those analytic efforts at Vanderbilt University and another confirmatory lab still to be determined.
Initially, one composite sample (reflecting multiple individual organisms of the same species from the same general location) from each Amchitka and Kiska sampling location will be analyzed for specific radionuclide isotopes as a screening survey. This screening survey will be limited to a maximum of 25 species for analysis. The results of this screening survey will then be used to select one species from each trophic level for more extensive analysis of multiple composite samples. More than one species may be selected from a single trophic level for species that serve as primary food sources. Considerations in the selection of the species for more extensive analysis will include identification of the species that is estimated to present the greatest human health risk (considering measured radionuclide levels, isotope-specific risk factors and consumption rates) and the ability to measure isotopes indicative of the source of the radionuclides present. Although a greater number of biological samples are being obtained during the field expedition, the current program is limited in total to the analysis of approximately 600 samples for ^{137}Cs, ^{152}Eu, ^{60}Co (gamma emitters), ^{90}Sr, and 200 samples for other isotopes. Samples not analyzed are being retained for future analysis if such analysis is warranted based on findings under the current program and sufficient resources are available.
Isotopes of interest for analysis in this study are ^{137}Cs, ^{152}Eu, ^{60}Co (gamma emitters), $^{238, 239, 240, 241}Pu$, $^{234, 235, 236, 238}U$, ^{241}Am (alpha emitters), and ^{90}Sr, ^{3}H, ^{99}Tc, ^{129}I (beta emitters). ^{137}Cs and ^{90}Sr are considered the isotopes most likely to accumulate in muscle (soft tissue) and cause human health risks through consumption. Other isotopes accumulate preferentially in either skeletal material (bones or exoskeletons) or specific organs, with a lesser distribution in muscle. Thus, for programmatic efficiency, analysis for specific isotopes will focus on sample types (soft tissue or skeletal material) most likely to contain the greatest amounts of the specific isotopes and to cause human health risk. Detection limits for analyses will be below levels necessary to detect human health risks based on conservative estimates of lifetime consumption and risk thresholds. More limited analysis will be used to ascertain the distribution of specific isotopes amongst the sample types for a given biota. Ratios of isotopes of Pu (indicative of nuclear detonations) and U (indicative of nuclear reactor releases and enrichment processes) will be used to the extent possible to identify whether Amchitka test shots are the likely source of measured radionuclides in samples. Analysis procedures appropriate for each isotope in each specific analytical matrix will be validated prior to actual sample analysis.
CRESP will conduct a limited collection of both water and sediment samples. Determination about whether and if so these samples should be analyzed has not been made – and will probably be delayed until an evaluation of the total sample and data collection achieved by the expedition has been made and the final analytic methods definition and prioritization is achieved in August, 2004.

Source: IRM-CRESP, 2004

Figure 1-1. Technical Bases for the Analytical Laboratories' Amchitka Island Project

2. PROJECT ORGANIZATION AND RESPONSIBILITY

The Analytical Laboratories (Chemistry and ALD) departments are part of the INEEL's Physical Sciences organization. The relationship of the Physical Sciences organization to other INEEL organizations is depicted in company organization charts maintained by the Human Resources Department and published on the INEEL intranet.

The functional organization of the Analytical Laboratories supporting the project is shown in Figure 2-1. Primary project roles and responsibilities within these laboratories are defined in the following subsections.

2.1 Chemistry Department Manager

The Chemistry Department Manager is responsible for project administration and management oversight of laboratory operations and product quality for all project activities. The Chemistry Department Manager's responsibilities include, but are not limited to, department policy development, quality assurance program implementation, resource allocation, work status and cost control monitoring, procurement approval, oversight of preventive and corrective action implementation, and negotiation of project requirements with customers. The Chemistry Department Manager is responsible for ensuring that the laboratories within the department operate in compliance with company environmental, safety and health requirements. The Chemistry Department Manager directs self-assessments of related Chemistry Department activities.

The Chemistry Department Manager is responsible for the administration of all portions of the program performed by INEEL personnel. These responsibilities are assigned as shown in the chart on the next page.

2.2 Amchitka Island Project Manager

The Analytical Laboratories' Amchitka Island Project Manager (PM) reports directly to the Chemistry Department Manager. The PM has overall responsibility for successfully accomplishing project quality-affecting activities in accordance with this QAPjP. The PM is responsible for managing the overall implementation of project responsibilities, associated project controls, for providing final approval and transmittal of sample results to CRESP, and for ensuring the appropriate retention of project sample analysis records.

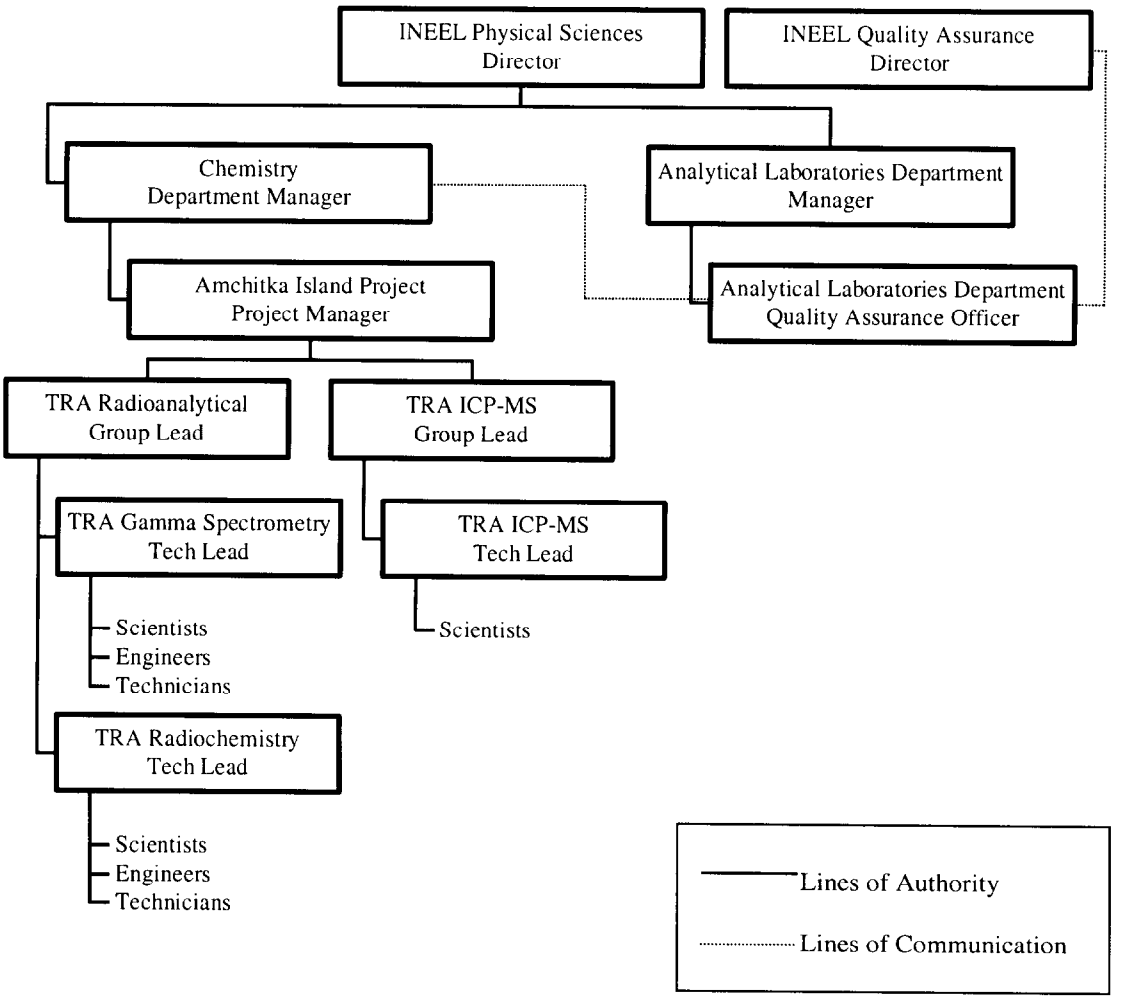

Figure 2-1. Functional organization of the Analytical Laboratories' Amchitka Island Project

2.3 Analytical Laboratories Department Quality Assurance Officer

The ALD Quality Assurance Officer (QAO) is responsible for the oversight of all QA activities within the project. The QAO reports directly to the ALD manager and is organizationally and functionally independent of project analytical activities. The QAO assists the Analytical Laboratories department managers in developing Analytical Laboratories QA policy and provides independent oversight of QA policy implementation and practice. The QAO provides QA training for project personnel. The QAO is responsible for assisting analytical laboratories' staff with developing, documenting, and evaluating quality assurance/quality control (QA/QC) procedures and practices. The QAO works with the PM to resolve disputes related to project QA requirements. If not resolved, the QAO elevates the issue progressively to successively higher levels of management, as necessary for resolution. The QAO coordinates corrective action tracking and implementation for the project and performs independent assessments of project operations. The QAO reviews and approves this QAPjP and all project implementing procedures. The QAO maintains this QAPjP and monitors compliance with its provisions.

2.4 Group Leads

The Group Leads (GL)s are responsible for overall coordination of the analytical laboratories' activities. The GLs report directly to the Chemistry Department Manager and are responsible for ensuring that analytical data are generated in accordance with this QAPjP and written and approved analytical procedures. The GLs appoint their respective staff members and ensure that they receive appropriate training. The GLs manage resource allocation within their respective laboratories and approve procurement actions per company policy. The GLs are responsible for drafting analytical implementing procedures or for assigning those tasks to appropriate project personnel. The GLs review and approve all analytical implementing procedures under their cognizance.

2.5 Technical Leaders

Technical Leaders (TLs) report to the GLs and are immediately responsible for direction of project activities at the work level. The TLs are responsible for ensuring generation of technically valid data, coordinating and scheduling work, and training personnel. The TLs are responsible for ensuring that QA practices meet the requirements of this QAPjP and that quality control (QC) practices are implemented at required frequencies. The TLs are responsible for informing the QAO, PM, and the respective GL of any concerns pertaining to data quality and for implementing corrective actions when required. The TLs provide technical direction for improving existing laboratory procedures and developing new ones. The TLs coordinate the data reporting processes and ensure that all project data receive proper technical review prior to release.

2.5.1 TRA Radiochemistry Technical Leader

The TRA Radiochemistry Technical Leader (RTL) is responsible for directing the project RC functions. These functions include sample preparations, sample separations, and radiochemical determinations using alpha and beta spectrometry techniques. The RTL coordinates with the Gamma Spectrometry TL (see section 2.5.3) to identify gamma spectrometry support requirements and needs for RC.

2.5.2 TRA ICP-MS Technical Leader

The TRA ICP-MS Technical Leader (ICPTL) is responsible for directing the project ICP-MS functions. These functions include sample preparations, sample separations, and specialized spectrochemistry techniques. The ICPTL reviews and approves all ICP-MS data packages and reports.

2.5.3 TRA Gamma Spectrometry Technical Leader

The TRA Gamma Spectrometry Technical Leader (GSTL) is responsible for directing the project GS functions. The TRA GSTL is responsible for daily operation of the Radiation Measurement Laboratory (RML). The GSTL coordinates with the RTL to ensure that all gamma spectroscopy measurements and analyses are performed within the guidelines of this QAPjP. The GSTL provides technical guidance and direction to the GS personnel.

2.6 Scientists, Engineers, and Technicians

Laboratory scientists, engineers, and technicians are responsible for performing sample analysis, data reduction, and reporting in accordance with this QAPjP and project requirements. Scientists, engineers, and technicians are responsible for following analysis and QC procedures specified in analytical methods and documenting any deviation from methods or QAPjP specifications. Scientists, engineers, and technicians are responsible for critically observing and evaluating all analytical procedures and bringing any practices and occurrences that might affect the reliability of analytical data to the attention of the appropriate TL or GL, and the QAO. They conduct the analyses, make computations, perform independent technical reviews, and transmit data to the appropriate TLs for review. Scientists, engineers, and technicians may be responsible for writing analytical methods at the direction of the TLs. Nuclear instrumentation systems support personnel are responsible for installing and servicing the nuclear instrumentation used by RC, and GS laboratories for counting samples.

2.7 Sample Custodians

Sample custodians at the TRA Radioanalytical Laboratories are responsible for the Amchitka sample receipt, and sample tracking. Sample custodians ensure that chain of custody (COC) is maintained for all project samples. After sample analysis and reporting is complete, sample custodians coordinate disposal of samples in accordance with project and company requirements.

2.8 Computer System Administrators

Computer system administrators are the analytical laboratories' personnel responsible for controlling and maintaining multi-user computer systems used at the TRA laboratories. The computer system administrators control configuration of the multi-user computer systems and ensure that procedures are in place to prevent unauthorized changes to computer software and that all changes to the system are justified and documented. MCP-550, "Software Management," and MCP-2009, "Analytical Software Control", as applicable, define specific responsibilities for computer "system administrators."

3. QUALITY ASSURANCE OBJECTIVES

Accuracy: Accuracy is a measure of how close a measured value is to a known true value. Accuracy is also referred to as relative bias because it measures the bias of an analytical system. Accuracy is normally measured through the analysis of known standards (i.e., control samples) or use of radiotracers during analysis, and is expressed in terms of percent or fraction recovery or relative bias. Accuracy quality assurance objectives for Amchitka biota samples have been defined in conjunction with the methods selection and validation process described in Figure 1-1 and Section 7. Project-specific accuracy objectives are defined in Figure 3-1.

Precision: Precision is a measure of the ability to reproduce an analytical result, and it expresses the degree of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. Precision is generally determined through the analysis of *replicate samples* (see def.) or by replicate analysis of a sample or a spiked sample. Precision quality assurance objectives for Amchitka biota samples have been defined in conjunction with the methods selection and validation process described in Figure 1-1 and Section 7. Project-specific precision objectives are defined in Figure 3-1.

Representativeness: The representativeness objective expresses the degree to which data accurately and precisely represent a characteristic of a population. Representativeness of sample analyses is achieved by use of standardized sample handling protocols to maintain sample integrity and analysis of laboratory blanks to monitor laboratory contamination..

Completeness: Completeness is a measure of the amount of valid analytical data obtained from a measurement system compared to the amount expected under current normal conditions. Valid analytical data are those generated when analytical systems were in control, i.e., all *calibration* (see def.) verification checks and other non-matrix checks (e.g., *blank samples* (see def.) and control samples) met project-specified acceptance criteria. The data user (CRESP) will evaluate and determine analytical completeness.

Comparability: Comparability expresses the confidence with which one data set can be compared to another. The TRA Radioanalytical group participates in the Mixed Analyte Performance Evaluation Program (MAPEP) sponsored by DOE-RESL. In addition to this evaluation program, the CRESP project plans to provide simulated samples like Amchitka samples to use as blind samples in the project, and Vanderbilt University is performing analyses of duplicate Amchitka samples for comparison evaluation by the CRESP project.

Minimum Detectable Activities: Minimum detectable activity (MDA) is an *a priori* estimate of the detection capabilities of a given measurement system and method for radionuclide analyses. This estimate is based on the premise that from knowledge of the background count and other measurement system parameters, an *a priori* limit can be estimated for a particular measurement. The MDAs (also known as detection limits) for Amchitka biota samples have been defined in conjunction with the methods selection and validation process described in Figure 1-1 and Section 7. Project required detection limits are defined in Figure 3-1.

Instrument Detection Limits: Instrument detection limits (IDLs) are determined for all target isotopes determined by quantitative analysis for each ICP-MS method and instrument used by the analytical laboratories for analyses of Amchitka biota samples. These provisions only apply

to ICP-MS, and not to radioanalytical methods. The IDL represents the minimum amount of target isotope that can be measured and reported for a given instrument and method with 99% confidence that the isotope amount is greater than zero. IDLs are calculated using the equation in Section 12, based on the average of the standard deviations of three sets of at least seven replicate standard analyses (three readings per analysis) run on three non-consecutive days. The standard used has analyte concentrations approximately 2 to 5 times the anticipated IDL. IDLs are determined quarterly, or whenever a change in instrument operating parameters affect detection capability, whichever is more frequent. IDLs are not required for qualitative analyses (e.g. isotopic ratio determinations).

IDLs are determined using standards with noninterfering matrices and therefore represent optimum obtainable analytical performance. Actual instrument detection limits in complex sample matrices will be higher than those IDLs determined using clean matrices, owing to matrix effects or interfering contaminants.

3.1 Customer Performance Evaluation Program

The CRESP Amchitka Project customer plans to conduct a performance evaluation study, as defined in PLN-153, to verify the accuracy of their program data. Blind samples will be submitted to the laboratories along with actual Project samples.

Table 3-1. Quality assurance objectives for Amchitka Island sample analysis.

Radionuclide / Technique	Sample Matrix	Minimum Detection (Bq/g)	Precision (RPD)	Accuracy (% R)
^{129}I / LEPS[1]	Soft tissue	7.4E-03	40 (for >20 Bq/g)	75-150 (for >20 Bq/g)
	Plant	7.4E-03	40 (for >20 Bq/g)	75-150 (for >20 Bq/g)
^{137}Cs, other gamma emitters / Gamma Spectrometry	Soft tissue	3.7E-02	20 (for >20 Bq/g)	80-120 (for >20 Bq/g)
	Skeletal	3.7E-02	20 (for >20 Bq/g)	80-120 (for >20 Bq/g)
	Plant	3.7E-02	20 (for >20 Bq/g)	80-120 (for >20 Bq/g)
^{99}Tc / ICP-MS[2]	Soft tissue	3E-01	15	75-105
	Plant	3E-01	15	75-105
Pu/U Isotopic Ratios/ ICP-MS[3]	Skeletal	N/A	N/A	N/A
	Plant	N/A	N/A	N/A
^{241}Am, ^{238,239,240}Pu, ^{234,235,236,238}U /Alpha Spectrometry	Skeletal (based on 2 g. wet)	6E-04	20 (for >2E-02 Bq/g)	80-120 (for >2E-02 Bq/g)
	Plant (based on 10 g. wet)	1.1E-04	20 (for >4E-03 Bq/g)	80-120 (for >4E-03 Bq/g)

Table 3-1 continued. Quality assurance objectives for Amchitka Island sample analysis.

Radionuclide / Technique	Sample Matrix	Minimum Detection (Bq/g)	Precision (RPD)	Accuracy (% R)
^{90}Sr / Gas Proportional Counting	Soft tissue (based on 100 g. wet)	4E-04	20 (for > 0.004 Bq/g)	80-120 (for >0.004 Bq/g)
	Skeletal (based on 2 g. wet)	2E-02	20 (for > 0.2 Bq/g)	80-120 (for >0.2 Bq/g)
	Plant (based on 10 g. wet)	4E-03	20 (for > 0.04 Bq/g)	80-120 (for >0.04 Bq/g)

[1] These accuracy and precision objectives are conditional on the presence of iodine and no interference from other gamma emitters such as europium, cesium, etc.

[2]Assumptions are a 15 g sample (wet), 0.5 pg/mL detection limit in a 10 mL solution, and a 90% "yield" of Re. Detection limit is also somewhat variable because it is dependant upon the Ru content in the sample and the actual Re recovery. Generally, the cleanup procedure minimizes the Ru interference correction effects on the detection limit as Ru is <1-2 pg/mL. Precision is an estimate based upon the propagated errors for the analyte (1-3%), the Re correction (1-3%), long-term precision during an analysis period (2-5%), variability in laboratory spiked samples (96±3.5%) and an arbitrary factor for "ash content" (lower ash content seems to give lower recoveries). The PE samples had a lower ash content than the laboratory spike samples and the recovery tended to be somewhat lower (88±4%) than the laboratory spiked samples. Range for the PE and laboratory spiked samples is from 80.4% to 102%. If sample availablity precludes duplicate sample preparations, precision will be estimated as the percent relative standard deviation of the spiked blank data set.

[3] Parameters as listed are not applicable since the result is a ratio. In general, the concentration in the final 1 mL sample must be greater than at least 1 pg/mL for both isotopes in the ratio even to be able to determine a reasonable ratio. For example, using some average actual DL estimates, ^{239}Pu must be >0.02 pCi total in the sample and ^{240}Pu must be >0.06 pCi total in the sample to determine a ratio. Precision will be progressively worse as the concentrations approach this level. The ^{238}U/^{235}U ratio in tap water for n=4 is 137.5±2.4 (expected 137.88) and the ^{238}U/^{234}U is 4060±240 (^{234}U is elevated in all groundwaters). Total U in ground waters is the range of ~1000 pg/mL or so ^{238}U is ~992.7 pg/mL, ^{235}U is ~7.2 pg/mL and ^{234}U would only be ~0.055 pg/mL or slightly greater due to the enrichment in groundwater. As for Pu, so far all of the samples we have seen have either been spiked with ^{239}Pu or ^{240}Pu but not both.

4. SAMPLING PROCEDURES

Sample collection procedures are not applicable to RA laboratory activities. Sample collection is the responsibility of organizations sending samples to RA laboratories (i.e. the CRESP Amchitka Project).

5. SAMPLE CUSTODY

The TRA Radioanalytical Laboratories receive samples from the CRESP Amchitka Project and maintain sample custody in accordance with the provisions summarized in PLN-153.

Tissue or skeletal samples (original matrix) are stored in a freezer at less than, or equal to, - (minus) 10^{o} C.

The analytical holding time for all samples is six months from sample collection. Project personnel will make every effort within their control to satisfy these holding times. Any failure to meet these holding times will be discussed in the associated data report.

6. CALIBRATION PROCEDURES

Calibration procedures summarized in PLN-153 apply to the Amchitka Island Project. The following provisions apply for ICP-MS systems used in quantitative analysis with external standardization. Applicable ACMM methods will define the calibration requirements for qualitative analyses (e.g. isotopic ratio determinations), and the basis for response factor estimates, where applicable, for any isotope dilution procedures.

The ICP-MS systems undergo daily mass calibration and resolution checks in the mass regions of interest, using tune standards, as specified in the respective analysis method. The ICP-MS systems are also calibrated daily with use for all target analytes. The ICP-MS calibration method provides nonmathematical methods, such as matrix matching standards, to compensate for such interfering elements. *Calibration standards* (see def.) contain the same acid matrix as the samples to be analyzed. Calibration curves are established based on the analyte response and are determined by the relationship between standard concentration and analyte response.

The accuracy of the calibration standards and the resulting calibration plots are verified initially (before analysis of samples) using a mid-range standard from an independent (second) source, when available. This standard is referred to as the initial calibration verification (ICV) standard. It must be in the same acid matrix as the calibration standards. When unavailable, the lack of second source standards will be discussed in associated data reports.

The calibrations are verified during the daily analytical *run* (see def.) by analysis of a continuing calibration verification (CCV) standard. The CCV is a midrange standard that contains the same acid matrix as the samples but does not have to be prepared from an *independent standard* (see def.) source. The CCV is used to determine calibration drift over the duration of the analytical run and is analyzed at a specified frequency throughout the analytical run and at the end of the run.

Initial *calibration blank* (see def.) (ICB) and continuing calibration blank (CCB) verifications, consisting of blank acid matrix, are also analyzed at the beginning, during, and at the end of the analytical run. The ICB is used to verify the accuracy of the calibration curve. The CCBs are used to determine baseline drift over the duration of the analytical run.

If any of the calibration verification QC samples (i.e., ICV, CCV, ICB, or CCB) do not meet acceptance criteria, the analysis is stopped, the problem corrected, and any samples analyzed under the noncompliant conditions are reanalyzed.

Calibration procedures must, as a minimum, specify the measurement standards or equipment used, the required parameter, range, the required accuracy of the measurement, and the acceptable tolerance of each measurement parameter.

Calibration frequency, procedures, requirements and acceptance criteria are defined in applicable ACMM methods.

7. ANALYTICAL PROCEDURES

Analytical procedures and requirements summarized in PLN-153 apply to the Amchitka Island Project. Table 7-1 identifies the specific methods procedures supporting the project, and their application. Analysis procedures appropriate for each isotope in each specific analytical matrix have been validated, in support of the latest CRESP objectives, prior to actual sample analysis.

Isotopes	**Technique**	**INEEL Method(s)**	**Matrix**
^{129}I	Gamma-Ray Spectrometry (LEPS)	ACMM-3606	soft tissue/plant
^{137}Cs, other gamma emitters	Gamma-Ray Spectrometry	ACMM-3606	soft tissue/skeletal/plant
^{99}Tc	Prep/Analysis (ICP-MS)	ACMM-3705	soft tissue/plant
Pu/U Isotopic Ratios	Analysis (ICP-MS)	ACMM-3710	skeletal/plant
^{241}Am, $^{238,239,240}Pu$, $^{234,235,236,238}U$	Separations *(including initial Sr separation)* /Alpha Spectrometry	ACMM-3804	large samples; soft tissue/skeletal/plant
^{241}Am, $^{238,239,240}Pu$, $^{234,235,236,238}U$	Separations *(including initial Sr separation)* /Alpha Spectrometry	ACMM-3816	small samples; soft tissue/skeletal/plant
^{90}Sr	Final Separations /Gas Proportional Counting	ACMM-3815	soft tissue/skeletal/plant

Table 7-1. Amchitka Island Project Analysis Methods

7.1 Modification of ACMM Methods for Special Sample Matrices

Approved routine analysis methods must occasionally be modified for unusual sample matrices or conditions encountered during analysis. Method modifications must be documented, justified and approved by the appropriate technical leader (or designated alternate) before data are reported to the customer. Customers are notified of significant method modifications. MCP-2001, "Control of Analytical Methods and Procedures" and MCP-2008, "Analytical Data Recording, Review, and Reporting, " provide further detail for documenting method modifications.

7.2 Method Performance Demonstrations

New methods may be selected and adapted from published EPA, ASTM, or other standard method protocols, or developed in the laboratory. When standard method protocols are implemented as written, the requirements and QC criteria of the source protocol are followed to demonstrate successful method performance. For use with routine samples, the method must be incorporated into the ACMM per procedures in MCP-2001.

For ACMM methods based on or modified from EPA protocols, the laboratory performs and maintains all method performance demonstrations required by SW-846 and water/wastewater methods. If analytical procedures other than those based on EPA protocol are used for environmental/regulatory analyses, the laboratory demonstrates and documents that the procedure is capable of providing appropriate performance for its intended application. Such demonstration includes consideration of precision, accuracy, recovery, representativeness, comparability, and sensitivity relative to the intended use of the method, as applicable.

8. DATA REDUCTION, VALIDATION, AND REPORTING

Data reduction, validation, and reporting procedures summarized in PLN-153 apply to the Amchitka Island Project.

The frequency of QA review for the Project may be as frequent as 100%, but should not be less frequent than 5 %.

Project data reports will include measured results (including associated uncertainty for Radioanalytical methods) and associated QC sample results.

Quantitative results will be reported in S.I. units. Typical reporting units for solid samples include: Bq/g, and Bq/kg. Typical reporting units for liquid samples include: Bq/mL, and Bq/L.

9. INTERNAL QUALITY CONTROL CHECKS AND FREQUENCY

Internal quality control provisions summarized in PLN-153 apply to the Amchitka Island Project. Additionally, the following provisions (throughout Section 9, below) apply to ICP-MS analyses:

QC samples are routinely analyzed with samples to evaluate, establish, and monitor analytical method, instrument, and analyst performance. These QC samples may originate during sample collection and during sample analysis. Those QC samples originating during sample collection are referred to as field QC samples, and their introduction into the analytical process is the responsibility of the sampling organization or sample requestor. Preparation and analysis of laboratory QC samples is the responsibility of the TRA Laboratories. QC samples and elements discussed in this section are those typical to EPA SW-846 and other similar standard protocol requirements.

9.1 Field QC Samples

Field QC samples are designed to determine and monitor the effect of sample collection, handling, and transportation on sample data quality. Collection of these samples is the responsibility of the sample requestor or sampling organization. The TRA laboratories handle, analyze, and report results for field QC samples in the same manner as actual *field samples* (see def.). The sample requestors are responsible for evaluating and interpreting field QC results. Results of these QC samples do not provide information on laboratory performance and must not be used for that purpose. The following subsections describe field QC samples typically submitted to the analytical laboratories for analysis.

9.1.1 Field Blanks

Field blanks are designed to identify and monitor contaminants introduced during various stages of the sample collection, handling, and transportation processes. Types of field blanks include the following:

- Equipment rinsates, also called equipment blanks, which monitor the adequacy of decontamination processes used to clean sample collection equipment between samples
- Preservative blanks, which monitor for analyte contamination in chemical preservatives (e.g., nitric acid) added to the sample

Field blanks must be identified to the laboratory so that they are not used by the laboratory to prepare matrix-dependent laboratory QC samples (see Section 9.2).

9.1.2 Field Replicates

Field replicate QC samples are designed to determine and monitor the precision of the sample collection process. Field replicates, also known as field duplicates, or co-located samples, are independent samples that are collected as close as possible to the same point in space and time, i.e., two separate samples taken from the same source.

9.1.3 Field Control Standards

Field control standards are standard materials of known analyte concentration designed to monitor the effect of sample storage and transportation on analyte concentrations. Field control standards must not be confused with performance evaluation samples submitted to the laboratory with the intent to monitor laboratory performance (see Section 3). The sample requestor is responsible for ensuring that analyte concentrations in field control standards are appropriately chosen so as not to cause instrument/equipment contamination problems at the laboratory. If field control standard analyte concentrations must be so high that laboratory contamination is a potential problem, the sample requestor must notify the laboratory of the expected concentration or concentration range of the control standard.

9.2 Laboratory QC Elements

The type and number of laboratory QC elements analyzed differ for specific sample matrices and analytes. Laboratory QC elements are of three general types: those that are associated with samples in a specific *analytical batch* (see def.), those that are associated with a specific instrument or method analysis sequence, and those that are associated with the results of a particular sample. These types of laboratory QC elements are commonly referred to as batch QC, analysis QC, and sample-specific QC, respectively. Individual QC elements can also be classified as matrix-dependent QC or matrix-independent QC. Matrix dependent QC elements are those whose results are influenced by sample matrices. Results of such QC elements cannot be totally controlled by the laboratory. Matrix-independent QC elements are those whose results are not influenced by sample matrices and are completely under the control of the laboratory. Classification of laboratory QC elements is shown in Table 9-1. Only results of matrix-independent QC elements are used to judge laboratory performance and determine laboratory completeness.

Acceptance criteria for laboratory QC elements are method-dependent. ACMM methods and related EPA protocols specify the acceptance criteria for QC elements discussed in this section. Acceptance criteria for laboratory QC specified in ACMM methods and related EPA protocols are those required for trace-level analysis using external standardization. In cases where such measurements are not required or appropriate (e.g., isotope dilution analysis or qualitative determinations such as isotopic ratios of Pu and U), less stringent QC acceptance criteria may be used with customer concurrence.

Specific instructions for preparation (including frequency and concentrations) and analysis of QC elements are included in the ACMM methods identified in Section 7. QC elements are handled using the same preparation and analysis procedures as are used on actual samples. QC results are reported separately from sample results. Results of QC elements are never used by the laboratory to correct or adjust sample results (e.g., no bias correction is performed). Interference correction includes compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

Table 9-1. Classification of laboratory QC elements.

	Matrix-Dependent QC	Matrix-Independent QC
Batch QC	Matrix spike Matrix spike duplicate Laboratory duplicate	Reagent blank/preparation blanks Laboratory Control Sample
Analysis QC	Analytical spike Serial dilution	Initial calibration verification (ICV and ICB) Continuing calibration verification (CCV, CCB) ICP-MS Tune Standard Interference check sample
Sample-specific QC	Tracers	N/A

9.2.1 Batch QC samples

Samples are analyzed in analytical batches. An analytical batch consists of twenty or fewer samples of similar matrix that are either analyzed simultaneously by a specific analytical method or sequentially on a continuous basis within a working period. A working period may extend over several days when sample preparation and analysis procedures require it. *Batch QC samples* (see def.) are associated with the actual samples by an analytical batch number and cannot be shared between analytical batches.

When the analytical process includes separate sample preparation and determinative analysis steps (e.g., digestion or extraction of the sample followed by analysis of the extract), batch QC samples are normally introduced at the beginning of the sample preparation procedure. Batch QC samples typically consist of a *reagent blank* (see.def.), a *laboratory control sample* (see def.) (LCS), a matrix spike (MS) sample, and a laboratory duplicate or matrix spike duplicate sample (MSD). These QC samples are discussed below.

9.2.1.1 Reagent Blanks

Blank samples are used to determine and monitor analyte contamination resulting from the analytical process. Reagent blanks, (sometimes known as method blanks, laboratory blanks, or preparation blanks) consist of an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The reagent blank is carried through the complete sample preparation procedures and analytical procedures.

A minimum of one reagent blank is analyzed for all target analytes with every analytical batch. The acceptance criteria for analyte concentrations in reagent blanks depends on the analytical method but is normally set in relationship to one or more of the following: (a) the method or instrument detection limit for the analyte, (b) the regulatory or client-specified limit for the analyte, or (c) a percentage of the measured analyte concentration in the associated samples. When the preparation method includes a fusion process, this blank is called a fusion blank. When solid samples are prepared using both a fusion process and a separation process, then both a preparation blank and a fusion blank are required.

If analyte concentrations in reagent blanks exceed acceptance criteria, all associated samples in the analytical batch are reprepared and reanalyzed for affected analytes. In cases where insufficient sample volumes, analytical holding times, or other special circumstances preclude repreparation and reanalysis of the samples, the data for affected samples and analytes are flagged and qualified in the data report.

9.2.1.2 Laboratory Control Samples

Laboratory control samples (LCSs) are used to document the accuracy of the analytical method. LCSs, also known as fortified blanks, consist of a known matrix spiked with known concentrations of target analytes. LCSs for spectrochemistry methods contain all target analytes or parameters requested for the method. The LCS is carried through the entire sample preparation and analysis process.

A minimum of one LCS is analyzed with every analytical batch. If independent-source calibration verification standards are not specified for a particular method, the LCS must be prepared from an independent standard source from that used to prepare the calibration standards. LCS results normally are calculated as percent recovery of the analyte. If LCS results do not meet acceptance criteria, all associated samples in the analytical batch are reprepared and reanalyzed for affected target analytes. In cases where insufficient sample volumes, analytical holding times, or other special circumstances preclude repreparation and reanalysis of the samples, the data for affected samples and analytes are flagged and qualified in the data report.

9.2.1.3 Matrix Spike Samples

Matrix spike (MS) samples are used to assess and document the bias of a method in a given sample matrix. MSs, also known as fortified samples, consist of a separate *aliquot* (see def.) of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis, when feasible (available radionuclide spike sources may not be of a sufficiently concentration to provide a meaningful spike recovery after multiple sample dilutions), and the matrix spike is carried through the entire analytical process. Matrix spikes for spectrochemistry methods contain all target analytes or parameters requested for the method.

A minimum of one MS is prepared and analyzed with every analytical batch. Sample requestors may specify the sample on which the matrix spike is to be performed. MS results are calculated as percent recovery of the spiked amount of analyte(s).

The ratio of the amount of spike added to the unspiked sample concentration must be considered when assessing MS results. If the spike added is significantly less than the original sample concentration (e.g., spike added is less than 1/4 of the unspiked sample concentration), no meaningful percent recovery can be determined because the increase in analyte response resulting from the spike may be insignificant compared to the analytical uncertainty of the unspiked value. If MS results do not meet acceptance criteria, individual results for noncompliant target analytes are flagged and qualified in the data report for all samples in the analytical batch. Because the MS is a matrix-dependent QC sample, associated samples are not reprepared and reanalyzed.

9.2.1.4 Laboratory Duplicate Samples

Laboratory duplicate samples are used to monitor the precision of a method for a given sample matrix. Laboratory duplicates consist of replicate aliquots taken from the same sample and carried independently through the sample preparation and analysis process.

A minimum of one laboratory duplicate or matrix spike duplicate (see Section 9.2.1.5) is prepared and analyzed per analytical batch. Laboratory duplicates are used for those methods for which spiking is inappropriate, or when sample analyte concentrations are known to be high enough (i.e., sufficiently above method detection limits) that a meaningful determination of precision can be made. Sample requestors may specify which sample is to be used for the laboratory duplicate.

Laboratory duplicate results are calculated as relative percent difference (RPD). If laboratory duplicate results do not meet acceptance criteria, individual results for noncompliant target analytes are flagged and qualified in the data report for all associated samples in the analytical batch. Because the laboratory duplicate is a matrix-dependent QC sample, associated samples are not reprepared and reanalyzed. Results of laboratory duplicates are not, by themselves, representative of overall laboratory precision performance because sample inhomogeneity as well as method imprecision can affect the results.

9.2.1.5 Matrix Spike Duplicate Samples

MSD samples are used to document the precision and bias of an analytical method in a given sample matrix and may be used in lieu of laboratory duplicates. MSDs consist of an additional aliquot of the sample used for the MS, spiked in the same manner as the MS. The spiking occurs prior to sample preparation and analysis, and the matrix spike duplicate is carried through the entire analytical process. Matrix spike duplicates for spectrochemistry methods contain all target analytes or parameters requested for the method.

MSDs are used instead of laboratory duplicates in cases where the target analyte concentration range of the sample is unknown, or when the target analyte concentrations are too low (i.e., too close to the method detection limit) to accurately determine method precision for a given matrix. At the request of the customer, MSDs may be analyzed in addition to laboratory duplicates. When MSDs are used in lieu of laboratory duplicate, a minimum of one MSD is prepared and analyzed with every analytical batch. Sample aliquot sizes are kept as close as possible to minimize the contribution of aliquot size differences to the overall difference between MS and MSD results.

MSD results are calculated as percent recovery of the spiked amount of analyte(s) and as the RPD between the MS and MSD results. The percent recovery for the MSD is calculated and evaluated identically to that of the MS (see Section 9.2.1.3). The RPD is normally calculated between the recovery of the MS and the recovery of the MSD in order to normalize for any differences in sample aliquot size.

If MSD percent recovery or RPD results do not meet acceptance criteria, individual results for noncompliant target analytes are flagged and qualified in the data report for all samples in the

analytical batch. Because the MSD is a matrix-dependent QC sample, associated samples are not reprepared and reanalyzed.

9.2.2 Analysis QC

Analysis QC elements for spectrochemical methods (i.e. ICP-MS) are introduced during determinative analysis and are generally associated with samples by time and date of analysis. These QC elements are used to monitor the performance of the analytical system during analysis, and to identify any interference effects occurring during the analysis process. The types of analysis QC elements required vary for different analytical techniques. In most cases, those analysis QC elements that are matrix-independent can be shared between analytical batches. Matrix-dependent QC elements must be performed on an analytical batch basis and cannot be shared between analytical batches. Those *analysis QC samples* (see def.) that function as calibration verification standards (i.e., tuning standard, ICB, ICV, CCB, and CCV) are discussed in Section 6.

Preparation requirements and acceptance criteria for each QC element specific to a particular spectrochemical technique are discussed in the appropriate ACMM methods.

9.2.2.1 Serial Dilution Samples

Serial dilution (see def.) samples are used to detect the influence of matrix interferences that may suppress or enhance analyte response during analysis. If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (a factor of at least 100 times greater that the concentration in the reagent blank), then serial dilution samples are prepared by performing a five-fold dilution of a sample digestate and analyzing it. The sample chosen for the serial dilution analysis should have analyte concentration high enough (nominally 50 times the IDL) that the concentration of the diluted sample can be accurately determined. Serial dilutions cannot be shared between analytical batches and must be analyzed at a minimum frequency of one per analytical batch for ICP-MS analyses, when applicable.

Serial dilution results are calculated as percent difference between the original undiluted sample results and the diluted sample results. When corrected for the dilution factor, the diluted sample results must agree with the results of the original undiluted sample within specified limits. Actions taken in response to serial dilution failure depend on which analytical technique and EPA protocol is being used. Actions include flagging and qualifying data in the data report.

9.2.2.2 Interference check samples

Interference check samples (ICSs) are also required for ICP-MS analyses to demonstrate that interference and background correction factors are correctly applied when isobaric interferences are possible at the masses of interest. This QC element is comprised of two separate standards, one containing interfering analytes only (the ICSA) and one containing interfering analytes and all target analytes (the ICSAB). The ICSA and the ICSAB are analyzed at the beginning (before sample analyses but after calibration verification). In addition the ICSA and ICSAB solutions must be analyzed periodically so that no more than 12 hours elapses between analyses of ICSA

and ICSAB. If acceptance criteria are not met, the analysis run is stopped, and the problem is corrected before further analyses can take place. Any associated samples are reanalyzed for the noncompliant target analytes

9.2.3 Sample-specific QC Elements

In addition to the analysis QC elements discussed in the previous section, additional sample-specific QC elements are monitored for ICP-MS analyses.

9.2.3.1 Tracers

For most routine analyses, samples are individually spiked with radionuclide tracers (non-target analyte nuclides) to monitor analyte recovery through the analytical process.

10. PERFORMANCE AND SYSTEM AUDITS AND FREQUENCY

Performance and system audits provisions summarized in PLN-153 apply to the Amchitka Island Project; however, the self-assessments, discussed therein, are the responsibility of the Chemistry Department for this project.

11. PREVENTIVE MAINTENANCE

Preventive maintenance provisions summarized in PLN-153 apply to the Amchitka Island Project

12. SPECIFIC ROUTINE PROCEDURES FOR QUALITY ASSURANCE

Specific routine quality assurance procedures summarized in PLN-153 apply to the Amchitka Island Project. Additionally, the following provisions apply to ICP-MS analyses:

Instrument Detection Limit (IDL) Calculation

IDLs are calculated for each target analyte on all applicable instruments and analysis systems using the following equation:

$$IDL = 3 \times \left(\frac{s_1 + s_2 + s_3}{3} \right)$$

where

s_1, s_2, *and* s_3 = the standard deviations obtained on three nonconsecutive days from seven replicate analyses of a standard solution (see Section 3).

13. CORRECTIVE ACTION

Corrective action provisions summarized in PLN-153 apply to the Amchitka Island Project.

14. RECORDS MANAGEMENT

Records management provisions summarized in PLN-153 apply to the Amchitka Island Project.

15. PERSONNEL TRAINING AND QUALIFICATION

Personnel training and qualification provisions summarized in PLN-153 apply to the Amchitka Island Project.

16. PROCUREMENT

Procurement provisions summarized in PLN-153 apply to the Amchitka Island Project.

17. REFERENCES

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MCP-550, "Software Management," latest revision.

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MCP-2001, "Control of Analytical Methods and Procedures," latest revision.

MCP-2008, "Analytical Data Recording, Review, and Reporting," latest revision.

MCP-2009, "Analytical Software Control," latest revision.

PLN-153, "Quality Assurance Project Plan For Analytical Laboratories Department Radioanalytical Activities," latest revision.

PRD-5071, "Quality Assurance Program," latest revision.

Appendix A

Definitions

Aliquot—A measured portion of a field sample taken for analysis.

Analysis QC samples—Those QC samples associated with specific samples by the date and time of analysis. These QC samples may be shared between analytical batches. Examples of analysis QC samples include calibration verifications, and instrument tune standards.

Analytical Batch—A batch of samples consisting of twenty or fewer samples and associated QC of similar matrix which are either analyzed simultaneously or processed sequentially on a continuous basis within the same working period by the same analyst.

Batch QC Samples—Those QC samples associated with specific samples through the analytical batch. Batch QC samples must be unique per analytical batch, and cannot be shared between analytical batches. Examples of batch QC samples include reagent blanks, laboratory control samples and MS/MSDs.

Blank Sample—An analyte-free matrix that undergoes preparation and analysis processes identical to those used on actual samples. Reagent blank samples include only the reagents used in the procedure, while matrix blank samples include matrix material as similar to actual samples as possible. The blank sample is used to document the absence of contamination resulting from the laboratory sample preparation and analytical process or cross-contamination between samples. Matrix blank samples are analyzed whenever uncontaminated sample matrix material is available.

Calibration—The comparison of measurement and testing equipment (M&TE) or a measurement standard of unknown accuracy to a measurement standard of known accuracy to detect, correlate, report or eliminate by adjustment any variations in the accuracy of the instrument or measurement standard being compared.

Calibration blank—A volume of acidified ASTM Type II (conductivity) water used to determine the calibration zero-response for spectrometer calibration.

Calibration standards—A series of known-concentration standards used to establish instrument response during calibration.

Day—Unless otherwise specified, day shall mean calendar day.

Field sample—A portion of material received for analysis that is contained in single or multiple containers and identified by a unique customer sample number.

Independent standard—A standard composed of analytes from a different source (i.e., different manufacturer) than that used for initial calibration standards.

Laboratory control sample (LCS) —A control sample of known composition used to indicate method accuracy that is analyzed with field samples using the same analytical methods.

Reagent blank—An analyte-free matrix that undergoes preparation and analysis processes identical to those used on field samples. The reagent blank is used to document contamination resulting from the laboratory sample preparation and analytical process. Also referred to as preparation, fusion, or laboratory blanks.

Replicate Samples—Separate aliquots from the same sample that are prepared and analyzed to verify the reproducibility of the procedures.

Run—A continuous analytical sequence consisting of prepared samples and all associated quality control samples.

Serial dilution —The dilution of a sample by a factor of five for spectrochemical analysis. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferants or non-linear instrument response.