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PREPARATION AND CHARACTERIZATION OF A PERFORMANCE EVALUATION SOIL SAMPLE FOR QA/QC OF RADIOCHEMICAL ANALYSES

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INTRODUCTION

Historically, many QA/QC programs for radiochemical analyses of soil samples, as well as other matrices, have been attempted using duplicate analyses of samples. There are essentially two methods for performing duplicate sample analyses. The first method is inter-laboratory comparison which involves the analysis of samples among two or more laboratories. The second method is intra-laboratory comparison which involves the multiple analysis of samples within a single laboratory.

In cases where an inter-laboratory comparison is used, if the results from two or more laboratories compare favorably, then there is some assurance that the reported results are both precise and accurate. However, If two laboratories report significantly different results on any given sample, it is difficult to determine which laboratory has reported correctly, and a costly search for both precision and accuracy typically results.

In cases where intra-laboratory comparison is used, if the results on a single sample compare favorably, the only assurance is of precision, i.e., reproducibility, with no assurance of accuracy.

Therefore, it can be seen that the use of inter-laboratory or intra-laboratory comparisons are, by themselves, inadequate to effectively evaluate the quality of laboratory results. However, by combining aspects of both methods, a hybrid QA/QC procedure for assessing laboratory results was developed around the concepts of the Standard Reference Sample (SRS) and the Performance Evaluation Sample (PES). This paper reviews a case study of such a hybrid QA/QC program which was developed and is currently being implemented at two uranium mill sites which are in the process of reclamation.

The principal strategy of this QA/QC plan can be stated as follows: if a laboratory can initially demonstrate acceptable analytic precision and accuracy for preset data quality objectives, then, an acceptance criterion based on analytic precision alone can be established for analytical results on subsequent samples.

STANDARD REFERENCE AND PERFORMANCE EVALUATION SAMPLES

A SRS is a prepared sample for which the constituent concentrations have been determined and certified as accurate by a recognized authority such as the National Institute of Standards and Technology (NIST). The use of a SRS is essentially an inter-laboratory comparison between a laboratory of interest and the certifying authority. As stated previously, the typical problem with inter-laboratory comparisons is that if multiple laboratories return results that deviate significantly from each other, there is no easy way to determine which set of data is accurate. This problem is eliminated by using a SRS since the actual analyte concentrations are known and certified as accurate.

A PES is a prepared sample for which the constituent concentrations are not certified as accurate. However, the concentrations are known to a high degree of confidence within statistical limits based on preliminary characterization of the sample by a laboratory that has demonstrated an ability to produce

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both precise and accurate results on a SRS. The use of the PES is analogous to the utilization of a spike sample in QA/QC programs for water quality analysis. The PES is used on an ongoing basis and submitted to the laboratory as a double blind sample with groups of 10 to 20 other samples for analysis. If the reported results on a given PES aliquot are within the statistical limits of the characterization, the analyses of the accompanying samples is accepted as accurate. However, if the analyses on the PES aliquot are not within the statistical limits, alternative procedures are followed to determine whether the aliquot was outside of the limits due to laboratory error, or the aliquot was simply outside of the established confidence limits as could be expected statistically.

The question may be asked: why use a PES if a SRS is available. The answer lies in two parts. First a SRS is typically expensive and therefore cost prohibitive to use on an ongoing basis for continual QC monitoring on projects where several thousand samples are processed. Second a SRS is typically a highly processed substance which has been prepared to a very fine size fraction for purposes of homogeneity. For blind QC this is not practical because, other than silts, no soil will be visually similar to a SRS.

PLAN OVERVIEW

The plan described in this paper was a phased program that ultimately resulted in the ability to evaluate and defend both the precision and accuracy of laboratory results of radiochemical analyses of soil samples.

The first phase of the plan was the prequalification of laboratory methods and results. This was accomplished by a review of laboratory procedures followed by the submission of a SRS sample. Results of the SRS sample were reviewed to determine if the reported concentrations were consistent with the certified concentrations.

The second phase of the plan was the preparation and characterization of the PES. During this phase a soil sample, consisting of approximately 1.1 tons of material, was collected and aliquots of the material were tested to provide sufficient data to determine the concentration distribution of the radionuclides of interest within a given statistical confidence.

The third phase of the plan was the periodic submission of PES aliquots with the normal project work load for periodic QC of analytic results.

PHASE I : LABORATORY PREQUALIFICATION

The first phase of the QA/QC program was the prequalification of laboratory methods and results. Yankee Atomic Environmental Laboratory (YAEL) was selected as the preferred laboratory to characterize the PES, and a review of the laboratories methods was conducted to determine the appropriateness of the analyses. Following the method review, a SRS sample was submitted to YAEL to determine if the laboratory employed the methods reliably and was capable of producing both precise and accurate results. The SRS was approximately a 500 gram sample of NIST standard reference material 4353 also known as Rocky Flats Soil Number 1 which was submitted blindly to the laboratory under the sample identification "silts". When the analyses on the SRS were reviewed, it was determined that the 2σ uncertainty of the analyses overlapped with the 2σ uncertainty of the sample certification for all analytes. Therefore, YAEL was confirmed as the selected laboratory and characterization of the PES commenced.

PHASE II: SAMPLE PREPARATION AND CHARACTERIZATION

Material Selection

The regulatory limits for soil cleanup at the sites where the PES would be used are specified in 10 CFR 40 Appendix A criterion 6(c) which states that on a 100 square meter basis concentrations of ^{226}Ra may not exceed 5 pCi/g above background in the top 15 cm of soil, or 15 pCi/g above background in 15 cm thick layers below the top 15 cm layer. As such, it was determined that the PES should have ^{226}Ra concentrations around 6 pCi/g which corresponds roughly to 5 pCi/g above background.

In addition to ^{226}Ra, the cleanup and verification plans for these sites included ^{230}Th and total uranium as well. Therefore, it was determined that the PES should contain elevated levels of these constituents. The most reasonable location for obtaining a sample having the desired ^{226}Ra concentration and elevated ^{230}Th and uranium was in the vicinity of the former ore stockpiles. As such, a sample of soil/ore mixture could be obtained, based on gamma readings, which would have the appropriate ^{226}Ra concentrations and, because the elevated ^{226}Ra was due to ore, it could be expected that the ^{230}Th and uranium would be in equilibrium thus resulting in a sample which was elevated in regard to all three analyses of interest.

Sample Preparation

The PES program was designed to produce 1024 aliquots of approximately 500 to 1000 grams. As such, approximately 1024 kg or 1.1 tons of soil was required.

The exact location to be excavated for the PES was determined based on gamma surveys using the procedures described in Fiske et al. (1994). Based on these gamma surveys, a 10 x 10 meter grid was staked and approximately 1.1 tons of soil was sampled from the top 6 inches of the grid using soil sampling augers.

Possibly the most unique aspect of the PES preparation relative to similar QC type samples was that the sample was never ground or pulverized to a fine size fraction. The primary purpose for sample milling is to achieve a relatively high degree of homogeneity throughout the sample. However, under the provisions of this plan, it was deemed that the blind quality of an unpulverized sample outweighed the risk of excessive variability. Given that no data was available regarding the uniformity of an unpulverized sample, a calculated risk was taken and preparation of the PES proceeded with homogenization by mixing alone.

The PES was initially homogenized for 4 hours using a concrete mixing truck. After the first mix, the PES was split, using a riffel type splitter, into 2 halves, each weighing approximately 512 kg. Each half was then mixed again for 2 hours, and split in half resulting in 4 samples each weighing approximately 256 kg. Mixing and splitting continued from this point using conventional portable cement mixers until the sample had been split 2^{10} times resulting in 1,024 samples each with a weight of approximately 1000 g. Each sample was bagged in a 1 gallon ziplock freezer bag and labeled with an identification number.

Laboratory Preparation and Analysis

Twenty eight aliquots of the PES were submitted to Yankee Atomic Environmental Laboratory for characterization of the sample. Approximately 800 g of each aliquot was uniformly blended and split into two sample aliquots; 30 grams for the isotopic uranium and thorium analyses, and 750 grams for ^{226}Ra by gamma-ray spectrometric analysis. The 30 gram sample was weighed wet, dried in a large drying oven to constant weight and re-weighed to determine the wet-to-dry weight ratio. The dried sample, including the small pebbles and stones, was then pulverized to approximately 200 mesh by a mill or a mortar and pestle.

The 750 g aliquots for ^{226}Ra gamma-ray spectrometric analysis was transferred to a tarred polystyrene container and uniformly compressed to eliminate voids, especially at the top of the container. The contained sample was then weighed to determine its net wet weight. A polypropylene screw cap was attached to the container and the container sealed using a polystyrene glue. After the sealant dried, the cap-container interface was wrapped by several layers of vinyl electric tape. The sample was set aside for a 38 day ^{222}Rn and progeny ingrowth period to permit complete secular equilibrium with ^{226}Ra. All ^{226}Ra analyses by gamma-ray spectrometry were performed on an automatic changer system consisting of a 15 sample capacity changer system and a 15% Ge(Li) detector having a 2.0 keV FWHM resolution. The system was calibrated with NIST traceable standards and verified with the NIST Rocky Flats soil standard reference material (#4353-1). Samples were analyzed for approximately 6,000 seconds to achieve a 3% relative counting uncertainty (1σ). All results were reported in pCi/g-dry after the application of the wet-to-dry weight ratio.

Approximately one gram of the dried pulverized soil from each aliquot was transferred to a pre-labeled PFA/Type HP Teflon beaker and standardized ^{229}Th and ^{232}U tracers added. The sample was then completely digested by repeated additions of concentrated HCl and HF while heating. The dried sample residue was dissolved in concentrated HNO_3 and a 2% boric acid solution, and heated to near dryness. The residual was dissolved in 9M HCl and centrifuged. Uranium and thorium in the supernatant were separated and purified through the standardized anion exchange technique using a pre-treated Bio-Rad AG-1X8 100-200 mesh resin. The eluted U and Th fractions from the column were evaporated to dryness and the U fraction treated with HCl while the Th fraction treated with $HClO_4$. After proper oxidation and reduction of the separate Th and U fractions, the thorium and uranium were co-precipitated with neodymium fluoride and mounted on 0.1 micron, 25 mm VCWP Gelman filters. Each filter paper was attached to a plastic flat mount with double adhesive tape and counted in an alpha particle spectrometry system having an Ion-Implanted Planar Silicon (PIPS) detector. For the neodymium fluoride microgram precipitate, typical resolution achieved ranged between 40 and 80 keV. Typical chemical recoveries were approximately 90% and 75% for uranium and thorium, respectively. The samples were analyzed for approximately 60,000 seconds to achieve a 4% relative counting uncertainty (1σ), All results were reported in pCi/g-dry.

Statistical Analyses

As discussed previously, the PES was prepared to visually resemble typical soil samples taken for verification of radiological compliance. A PES aliquot is submitted with every 10 to 20 verification samples. If the result of the analysis on the PES is within the statistical limits of acceptability, the analyses on the accompanying verification samples is accepted as accurate.

The acceptance control limits for the PES were established using the 5 and 95 percentile parameters of the PES characterization data. Percentile parameters were used to establish the control limits because no assumptions regarding the underlying data distribution was necessary. Such would not be the case if parametric descriptive statistics were applied which require a normal distribution. The results of the characterization are provided in Table 1. Using the 5 and 95 percentile parameters of these data the limits of acceptability given in Table 2 were established. Given that these limits were established using the 5 and 95 percentile parameters, it must be recognized that the expected success rate of passing the QC test, assuming that there have been no changes in the analytical precision and accuracy, is 90%. Therefore there is a 10% probability of failing the QC test even if the analyses on a particular aliquot are accurate. In recognition of this fact, procedures for identifying whether QC failures were due to analytic error, or PES variability were designed. It should be noted that to date, 93.5% of the PES aliquots have passed the QC test.

Table 1. PES Characterization Data

Sample ID	^{234}U			^{235}U			^{238}U			^{230}Th			^{226}Ra		
1037	2.96	±	0.18	0.130	±	0.035	2.94	±	0.18	3.92	±	0.31	5.12	±	0.14
1066	2.93	±	0.18	0.142	±	0.036	2.91	±	0.18	5.22	±	0.38	4.76	±	0.14
2036	2.76	±	0.17	0.097	±	0.029	2.89	±	0.17	3.83	±	0.32	6.30	±	0.23
2090	2.67	±	0.17	0.135	±	0.035	2.56	±	0.17	4.26	±	0.27	5.66	±	0.22
2125	2.63	±	0.16	0.090	±	0.029	2.71	±	0.17	5.42	±	0.42	7.64	±	0.24
3001	2.59	±	0.17	0.110	±	0.032	2.65	±	0.17	3.64	±	0.33	4.75	±	0.19
3064	2.74	±	0.18	0.113	±	0.032	2.67	±	0.17	4.11	±	0.35	5.63	±	0.21
3105	3.54	±	0.21	0.157	±	0.038	3.37	±	0.20	5.98	±	0.42	6.24	±	0.16
4025	3.06	±	0.18	0.128	±	0.034	3.16	±	0.19	5.83	±	0.41	6.59	±	0.24
4077	2.66	±	0.17	0.114	±	0.032	2.76	±	0.17	4.08	±	0.32	5.89	±	0.21
4091	2.76	±	0.19	0.133	±	0.037	2.83	±	0.19	3.82	±	0.23	6.03	±	0.22
4099	2.73	±	0.10	0.126	±	0.020	2.72	±	0.10	4.04	±	0.18	4.85	±	0.12
4113	3.06	±	0.18	0.169	±	0.038	3.12	±	0.18	5.12	±	0.36	5.77	±	0.21
5007	2.93	±	0.11	0.124	±	0.021	2.87	±	0.10	4.02	±	0.19	10.25	±	0.15
5112	2.92	±	0.18	0.104	±	0.032	3.07	±	0.19	5.96	±	0.39	7.46	±	0.24
6030	2.54	±	0.16	0.113	±	0.032	2.66	±	0.17	6.13	±	0.43	6.63	±	0.22
7013	3.75	±	0.22	0.172	±	0.040	3.61	±	0.21	5.17	±	0.36	5.99	±	0.21
7024	2.89	±	0.10	0.123	±	0.019	2.83	±	0.10	4.98	±	0.21	5.38	±	0.13
7029	2.70	±	0.18	0.135	±	0.036	2.69	±	0.18	4.57	±	0.37	7.25	±	0.23
7037	2.58	±	0.17	0.097	±	0.030	2.60	±	0.17	5.18	±	0.42	6.60	±	0.23
7063	2.86	±	0.17	0.142	±	0.035	2.83	±	0.17	5.89	±	0.42	5.78	±	0.21
7071	2.96	±	0.19	0.139	±	0.037	2.71	±	0.18	4.54	±	0.32	7.87	±	0.25
7079	2.50	±	0.17	0.106	±	0.032	2.35	±	0.16	3.88	±	0.30	6.95	±	0.22
7094	3.05	±	0.19	0.124	±	0.035	2.77	±	0.18	4.98	±	0.33	6.26	±	0.22
7119	3.89	±	0.22	0.179	±	0.041	3.82	±	0.22	4.81	±	0.30	6.37	±	0.22
8056	3.08	±	0.19	0.167	±	0.039	3.18	±	0.19	5.05	±	0.34	6.83	±	0.23
8099	2.95	±	0.18	0.133	±	0.035	2.93	±	0.18	4.64	±	0.34	6.74	±	0.23
8117	2.69	±	0.18	0.137	±	0.036	2.63	±	0.17	5.11	±	0.36	6.47	±	0.22

Uncertainty reported at 2σ.

Table 2. Acceptance Criteria

Radionuclide	PES Acceptance Range (pCi/g)
^{234}U	2.52 < Result < 3.83
^{235}U	0.093 < Result < 0.176
^{238}U	2.44 < Result < 3.73
^{230}Th	3.5 < Result < 6.1
^{226}Ra	4.75 < Result < 9.3

REFERENCES

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