U.S. DEPARTMENT OF ENERGY

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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Results of the Excreta Bioassay Quality Control Program for April 1, 2011 through March 31, 2012

CL Antonio
JA MacLellan

October 2012

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Contract 112512

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RESULTS OF THE EXCRETA BIOASSAY QUALITY CONTROL PROGRAM FOR APRIL 1, 2011 THROUGH MARCH 31, 2012 CONTRACT 112512

Cheryl L. Antonio

October 2012

Reviewed by _____ 10/31/12
Jay Maclellan Date

SUMMARY

A total of 94 urine samples and 15 fecal samples were submitted during the report period (April 1, 2011 through March 31, 2012) to GEL Laboratories, LLC in South Carolina by the Hanford Internal Dosimetry Program (IDP) to check the accuracy, precision, and detection levels of their analyses. Urine analyses for Sr, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{243}Am, ^{242}Cm, ^{244}Cm, ^{235}U, ^{238}U, ^{238}U-mass and fecal analyses for ^{241}Am, ^{238}Pu and ^{239}Pu were tested this year. The number of QC urine samples submitted during the report period represented 1.3% of the total samples submitted.

In addition to the samples provided by IDP, GEL was also required to conduct their own QC program, and submit the results of analyses to IDP. About 32% of the analyses processed by GEL during the second year of contract 112512 were quality control samples. GEL tested the performance of 17 radioisotopes for urine analyses and 3 radioisotopes for fecal analyses, all of which met or exceeded the specifications in the Statement of Work within statistical uncertainty except the minimal detectable activities for the isotopic uranium urinalysis (Table 4).

IDP concluded that GEL was performing well for all analyses tested, and concerns identified earlier were satisfactorily resolved (see section on Follow-up on Concerns During the First Contract Year).

Beginning in May 2006, it was decided to evaluate the MDA capability of the Lab based on detections of samples spiked at the CL level rather than on blanks, with the exception of ^{238}Pu and ^{243}Am. The decision not to submit blank samples, other than for ^{238}Pu and ^{243}Am, was made in order to increase the number of samples spiked at the CL and therefore improve the statistics for evaluating MDA, bias and precision. The MDA criteria would be met if less than 20 percent of the reported results for samples spiked at the Contractual Detection Level are less than the decision level (for n between 5 and 25) or less than 10 percent of the reported results are less than the decision level (for n > 25).

The isotopic uranium analysis reports on three uranium isotopes: ^{234}U, ^{235}U, and ^{238}U. The isotopes are differentiated only during counting by alpha spectrometry. All performance criteria were met within statistical variation. Of the 81 samples that GEL spiked at the CDL, all showed

detection, and the 18 samples spiked by IDP at the environmental screening level likewise all showed detection.

Because IDP used a depleted uranium source material for the isotopic uranium urinalyses, ^{233,234}U was not evaluated. However, the performance statistics for ^{235}U and ^{238}U were reviewed and the MDA for ^{235}U and the bias and precision for ^{238}U were acceptable.

No concerns were identified with the ^{238}U mass urinalysis program using inductively-coupled plasma mass spectrometry (ICPMS) and it was considered acceptable. Because IDP uses a 0.2 µg screening level for ^{238}U mass, samples spiked at 0.06 µg were discontinued. The MDA at the contractual level of 0.06 µg was evaluated through GEL's program and was found to be acceptable. The relative bias and precision were likewise acceptable. The bias and precision as tested by IDP met the acceptance criteria. The bias and precision was tested by IDP at 0.2 µg and by GEL at 1 µg/sample and at 0.05 µg/sample.

There were no samples analyzed during the second contract year for ^{236}U, therefore, the procedure was not evaluated.

The total strontium procedure is used to screen samples to determine whether analysis for ^{90}Sr is warranted. Samples with total strontium results less than 15 dpm do not undergo further analysis. Samples with results greater than or equal to 15 dpm may undergo ^{90}Y in growth to specifically determine ^{90}Sr levels. The calculated MDA, reported by GEL and tested by IDP, for the total strontium part of the analysis was less than 35% of the CL. The MDA, relative bias and precision, tested by IDP and GEL for the ^{90}Sr and total Sr procedures were all within limits. The 19 samples spiked at the contractual level by IDP were all detected. The strontium urinalysis procedure was concluded to be acceptable.

Samples spiked with ^{238}Pu and ^{239}Pu were analyzed using the same procedures and same reagents. The two isotopes are differentiated only at the end of the procedure by alpha spectrometry. Therefore, laboratory performance is expected to be similar for both isotopes using any of the seven procedures that incorporate plutonium analysis (IPU, IPA, IPS, IPSA, IPSR, IUPU, and ITPAC).

The MDAs and performance statistics for ^{239}Pu and ^{238}Pu in urine were acceptable. The MDA tested by GEL and based on 597 samples was 15% less than the criteria. The 23 samples spiked at the CL for ^{239}Pu all showed detection and the relative bias and precision met the

acceptance criteria. Out of 602 samples spiked by GEL at the CDL, 22 samples did not show detection, giving a false-negative (beta error) of 4%, which was acceptable. There were 31 blank samples submitted by IDP and analyzed for ^{238}Pu activity, none of the 31 samples detected activity in excess of the decision level. Overall the plutonium urinalyses were considered acceptable.

The MDA and performance statistics for ^{239}Pu and ^{238}Pu in feces were likewise acceptable. More than 15% of the fecal samples analyzed were duplicated to test the consistency of the aliquoting procedure. A review of the duplicate samples determined that the aliquoting procedure produced results within 3 sigma of the initial result. The fecal aliquoting procedure was acceptable. This year IDP submitted 15 actual fecal samples, 10 samples were blanks and 5 samples were spiked with very insoluble ^{239}Pu and slightly soluble ^{238}Pu. The MDA, precision and bias for ^{239}Pu and ^{238}Pu met the performance criteria. The performance statistics reported by GEL for ^{239}Pu and ^{238}Pu also met the acceptance criterion. There were no reported failed analyses but 3% of fecal analyses were flagged for low yield (less than 50%) or high yield (greater than 110%), which is within the contractual level of 10%. Overall the plutonium fecal analyses were considered acceptable.

The ^{241}Am fecal and urine analyses met the acceptance criteria for MDA, relative bias and precision. The MDA as reported by GEL was less than 5% of the contractual level. All 23 of the ^{241}Am samples spiked at the contractual detection level (CDL) were detected. Out of 367 samples spiked by GEL at the CDL, 10 samples did not show detection, giving a false-negative (beta error) of 3%, which was acceptable. The relative bias and precision as reported by GEL and tested by IDP met the performance criteria. The current AM241 urinalysis procedure was considered acceptable.

The ^{241}Am fecal duplicate samples were evaluated and it was concluded that the aliquoting procedure produced results within the control limits. This year IDP submitted five actual fecal samples spiked with very insoluble ^{241}Am and the relative bias and precision were acceptable. Overall the ^{241}Am fecal analyses were considered acceptable.

In addition to the blind audit program IDP also submitted 8 urine samples to evaluate the laboratory's capability to analyze for ^{239}Pu and ^{241}Am in media containing diethylenetriaminepentaacetate (DTPA). The purpose of the test samples was to determine whether DTPA would interfere with the radiochemistry and if so, was a separate analytical procedure for urine samples containing DTPA required to meet the performance and yield requirements. The

Hanford bioassay program recommends administering DTPA to workers if their committed effective dose levels likely to be equal to or greater than 20 mSv. The urine samples were spiked with 1 dpm of ^{239}Pu and ^{241}Am and 0.5 g of either Zn-DTPA or Ca-DTPA to simulate urine collection in the first 24-hrs following DTPA medical therapy.

The first 4 samples were analyzed using the current procedure of pre-concentrating the actinides by precipitation prior to the destruction of organics. All the samples showed detection for ^{239}Pu and ^{241}Am. The plutonium yields with this procedure averaged 86%, however, the yields for the americium analysis were only 40%, with a range of 31% - 54%. The remaining 4 samples were analyzed under a revised procedure where destruction of the organic material was performed prior to the pre-concentration of the actinides. Using the revised procedure the yield recovery for the plutonium analysis continued to be acceptable at 86% but there was a significant improvement in the americium analysis with an average yield of 97.5%.

To ensure that tracer yields meet the criteria, the standard procedure was revised to state that if a sample contains DTPA that the destruction of the organic material is to be performed prior to the pre-concentration of the actinides.

The AM243 procedure was identical to the AM241 procedure, except a different tracer is used (^{244}Cm instead of ^{243}Am). Only one of the seven blank ^{243}Am QC samples submitted showed detection resulting in a false-positive (alpha error) of 14%, which met acceptance criteria, assuming the normal statistical variation in the measurement process. The calculated MDA slightly exceeded the contractual detection level as tested by IDP and GEL each quarter as well as in the annual. The trend towards a slightly elevated MDA for the AM243 procedure was not addressed in GEL's annual report. The performance statistics for ^{243}Am, as tested by GEL, met the acceptance criteria for relative bias and precision. Because the MDA was only slightly elevated the ^{243}Am procedure was concluded to be acceptable but it will be re-evaluated during the 2012 annual audit of GEL.

IDP submitted 5 blank samples for isotopic curium analysis. All 5 samples were reported with ^{242}Cm and ^{244}Cm results less than decision levels with a resulting MDA for both isotopes meeting the acceptance criteria. IDP did not submit spiked samples; therefore performance statistics for relative bias and precision were based on the GEL QC results. GEL tested the MDA for ^{242}Cm and ^{244}Cm and the relative bias and precision for ^{244}Cm. Of the 67 samples spiked with ^{244}Cm, only 1 sample did not show detection with a false-negative (beta error) of 1.5%, which was acceptable.

The average relative bias of ^{244}Cm was slightly elevated but it was not considered a concern (see Table 4). Overall the results met the acceptance criteria and the isotopic curium urinalysis program was considered acceptable.

IDP also did not submit QC samples to test the isotopic thorium program, therefore performance statistics were based on the GEL QC results. GEL tested the MDA for ^{228}Th, ^{229}Th, ^{230}Th and ^{232}Th and the relative bias and precision for ^{232}Th. Of the 5 samples spiked with ^{232}Th, all showed detection. Overall the results met the acceptance criteria and the isotopic thorium urinalysis program was considered acceptable.

Neptunium-237 was likewise not tested by IDP and the performance statistics were supplied by GEL's QC program. Because only 4 routine samples were submitted for analysis there were less than 9 total QC samples analyzed by GEL. The average relative bias met the acceptance criteria; however, the MDA and relative precision did not. Because there were only 9 QC samples analyzed by GEL (3 blank samples, 3 at the CL to evaluate relative bias and precision) the uncertainty inherent in the measurement process precluded accurate evaluation of the performance criteria. The NP237 analysis will be reviewed during the 2012 annual audit of GEL and it will continue to be monitored.

CONTENTS

TABLES

INTRODUCTION

This report summarizes the results of the excreta bioassay quality control program's monitoring of the performance of GEL Laboratories, LLC (GEL) for samples submitted from April 1, 2011 through March 31, 2012 under contract 112512. During the reporting period GEL analyzed, under the contract with Battelle, 7958 urine and 124 fecal samples for various radionuclides. The number of samples analyzed was much greater than in previous years due to an increased work force due in part to the number of terminations resulting from the end of the American Recovery Act.

The results of the analyses are part of a system of legal records concerning internal deposition of radionuclides for workers at the Hanford Site. GEL is required to have a rigorous quality control (QC) program to ensure the accuracy of its results. In addition, the Pacific Northwest National Laboratory's (PNNL) Hanford Internal Dosimetry Program (IDP) has a QC program in place to independently check the accuracy of the results from GEL. The objective of the PNNL excreta bioassay QC program is to provide quantitative data to support the assessment of performance criteria for excreta bioassay analyses, as specified in the Statement of Work (Battelle 2010).

The reliability of the excreta bioassay program depends, to a significant extent, on the adoption and implementation of performance criteria for laboratory accuracy, precision, and detection levels. Such performance criteria are established in the Statement of Work (Battelle 2010) and include the following:

- Actual minimum detectable activities (MDAs) determined from QC samples for the year shall be equal to or less than the contractual detection level (CL) in the Statement of Work, as calculated from blank QC samples.
- The mean relative bias, B_r, shall fall within ± 20% when calculated from 15 to 50 samples spiked at greater than three times the CL, and within ± 10% when calculated from greater than 50 samples.

- The relative precision statistic, S_B, shall be less than or equal to 0.4 for samples spiked at greater than three times the CL, and less than or equal to 0.5 for samples spiked between one and three times the CL.

Formulas for MDA, B_r, and S_B, presented in the next section of this report, are based on recommendations in the Health Physics Society (HPS) Standard N13.30 (1996) and are listed in the Statement of Work. In addition to the Statement of Work (SOW) performance criteria, it is expected that the MDA shall also be such that fewer than 10% of the QC samples spiked at the CL shall be reported with values less than the decision level (i.e., twice the total propagated uncertainty of the result).

METHODS

GENERAL METHODS

Urine collected from PNNL employees who are not occupationally exposed to radioactive material was prepared in the 325 Building as blank and spiked samples by PNNL Radiochemical Processing Group (RPG), according to the directions given by the PNNL Internal Dosimetry Program (IDP), following Procedure PNL-MA-565-800-20, Rev. 2. Most samples were submitted as double-blind samples, with the exception of isotopic uranium urinalyses and the spiked fecal samples. Double blind samples are scheduled with and collected by GEL as if they were personnel samples. The isotopic uranium urinalyses were scheduled as single-blind intercomparisons, which meant that GEL was aware they were intercomparison samples but unaware of the activity. The samples were scheduled as single-blinds because they were spiked with a depleted uranium source. Since depleted uranium exposures at Hanford are rare, the intercomparison samples would stand out and the QC alias names used could become known and compromise the double-blind intercomparison program. The spiked fecal samples were artificial fecal samples consisting of a soil matrix. Blank fecal samples were scheduled as double-blind samples and were actual fecal samples.

GEL analyzed urine samples for tritium, ^{90}Sr, ^{14}C, ^{237}Np,^{242}Cm, ^{244}Cm, ^{238}Pu, $^{239,240}Pu$, ^{241}Pu ^{241}Am,^{243}Am, ^{228}Th, ^{229}Th, ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{238}U (alpha spectrometry and mass analysis) and fecal samples for ^{238}Pu, $^{239,240}Pu$, ^{241}Am. To reduce costs in the intercomparison program, plutonium, americium, and strontium analyses were tested using routine sequential procedures when possible (i.e., where one urine sample is analyzed for several radionuclides). The analysis categories specified in the contract with GEL are shown in Table 1. All urinalysis samples contained approximately 1000 ml of urine, except for the samples analyzed for tritium, which contained approximately 100 ml. GEL's QC sample total is dependent on the number of analytical batches run during the year, and they were well over the 15% criteria specified in the contract.

TABLE B-3

Analytical And Reporting Requirements For Routine Processing Of Samples

Analysis (Code)	Constituents Reported	Contractual Detection Level [a] (dpm/sample) Urine	Fecal	Determination Time (business days following sample receipt)	Reporting Time[a] Email	Electronic	Written	Email Reporting Limit; (dpm/sample) [b] Urine	Fecal
Pu(∝) Isotopic (IPU)	Pu-238, Pu-239, 240	0.02	0.2	20	By close of business on day of determination	Within five business days of determination	Within 10 business days of determination	Eq. 1	Eq. 1
Pu(∝) Isotopic (IPUL)	Pu-238, Pu-239, 240	0.005		30				Eq. 1	
Am-241 (AM241)	Am-241	0.02	0.2	20				Eq. 1	Eq. 1
Am-243 (AM243)	Am-243	0.02	0.2	20				Eq. 1	Eq. 1
Cm(∝) Isotopic (ICM)	Cm-242, Cm-244[c]	0.02		20				Eq. 1	
U(∝) Isotopic (IU)	U-234, U-235, U-238	0.02		20				(d)	
Th(∝) Isotopic (ITH)	Th-228, Th-229, Th-230, Th-232	0.1	1	20				Eq. 1	Eq. 1
Np-237 (NP237)	Np-237	0.02	0.1	20				Eq. 1	Eq. 1
Tritium (H3)	H-3	10 dpm/ml		5				10 dpm/ml	
Sr-total (SR)	Sr (sum Sr-89 + Sr-90)	10		20				5	
Sr-90 (SR90)[e]	Sr-90	10		30				5	
Gamma Spectroscopy (ISPEC)	K-40, Cs-137 + Others[f]	See Table B-5		20				Eq. 1	
Gamma Spectroscopy (LEPD)	Am-241	5		20				Eq. 1	
U-236 Mass (U 236)	U-236	0.000140 µg/sample[g]		20				70 pg/sample	
U-238 Mass (U 238)	U-238	0.06 µg/sample	0.3	20				0.2 µg/sample	
Pm-147 (PM147)	Pm-147	50	200	20				Eq. 1	
Sequential Analyses:									
Pu(∝) Iso and Sr-total (IPS)	As for individual analyses			25	As for individual analyses				
Pu(∝) Iso, Am-241 (IPA)				25					
Pu(∝) Iso, Am-241, Sr-total (IPSA)				25					
Pu(∝) Iso, U-238 (IUPU)				25					
Actinide(∝) Isotopic (ITPAC)[h]				25					
Cm(∝) Iso, Am-241 (ICA)	Cm-242, Cm-244, Am-241[c]			20					
Pu(∝) Iso and U ISO (IPIU)				25					

(a) Time allowed following determination of results to receipt of results by Battelle.

(b) Email report required only when analytical results exceed level specified.

(c) Report measured activity for Cm-246, and Cm-248 upon request of the Battelle Technical Administrator.

(d) 0.15 dpm for U-234, 0.15 dpm for U-238, and the greater of 0.007dpm and Equation 5 for U-235.

(e) If total Strontium is less than 15 dpm, Y ingrowth is not required.

(f) Report all isotopes present at levels exceeding Equation 1. If ordered by the Battelle Technical Administrator, report results for radionuclides in Table B-5 specified in the processing instruction, regardless of the activity measured.

(g) CL is for U-236 in the presence of 0.2 microgram U-238 and 0.0014 microgram U-235.

(h) Pu (∝) Isotopic, Am-241, and Cm (∝) Isotopic.

TABLE 2. Number and Category of Bioassay Samples Analyzed

Procedure	FIRST CONTRACT (112512) YEAR – GEL 4/1/10 through 3/31/11				SECOND CONTRACT (112512) YEAR - GEL 4/1/11 through 3/31/12			
Code[a]	Total	IDP QC	%	GEL QC[b]	Total	IDP QC	%	GEL QC[b]
Urine								
H3	234	0	--	148	248	0	--	144
SR90, SR	293	2	1	653	1562	0	--	693
C14	12	12	100%	--	--	0	--	--
AM241	317	0	--	842	247	0	--	1101
AM243	23	4	17%	42	27	7	26%	42
U235	--	0	--	--	--	0	--	--
ICM/ICA	67	0	--	208	51	5	10	
IPU	1423	0	--	1669	1230	0	--	1806
IPUL	--	0	--	--	--	0	--	--
IPA	1232	0	--	N/A	1761	10	1	N/A
IPS	996	0	--	N/A	934	0	--	N/A
IPSA	239	17	7%	N/A	357	21	6%	N/A
IPSR	--	0	--	--	--	0	--	--
ISPEC	2	0	--	--	13	0	--	--
ITPAC	180	0	--	N/A	142	0	--	N/A
ITH	15	0	--	36	7	0	--	15
IUPU	178	0	--	N/A	103	0	--	N/A
IPIU	26	0	--	N/A	6	0	--	N/A
IU	410	12	3%	267	447	18	4%	297
NP237	7	0	--	15	4	0	--	9
U236	9	0	--	24	--	0	--	
U238 mass	1792	29	2%	28	819	33	4%	405
LEPD	--	0	--	--	--	0	--	--
PU241	--	0	--	--	--	0	--	--
Total	*7455*	*76*	*1%*	*3932*	*7958*	*94*	*1%*	*4512*
Fecal [c]								
ICM	4	0	--	6	--	0	--	
AM241	2	0	--	133	--	0	--	200
IPU	1	0	--	126	--	0	--	200
IPA	89	10	11%	N/A	124	15	12%	
Total	*96*	*10*	*10%*	*265*	*124*	*15*	*12%*	*400*

[a] Procedures not specifically tested are evaluated with isotopic results from other procedures.

[b] N/A = not available. QC samples are tracked as isotopic analyses not as multiple analyses.

[c] Analyses not analyzed (IPUBA, IRA, ITPAC, IUPU, UNAT, IU, AM243)

Table 2 presents a breakdown of the numbers and categories for all bioassay samples analyzed, including personnel and QC samples. From 94 urine and 15 fecal QC samples submitted by IDP to GEL during the reporting period, GEL reported 7958 analytical urine results for 20 different analytes and 124 fecal results for 3 different analytes. The 94 QC samples represent 1.3% of the total analyses performed by GEL. In addition to these samples, GEL analyzed 4912 internal QC samples. The QC samples analyzed equaled 32% of the samples analyzed by GEL under their contract with Battelle.

GEL's performance was checked by determining detection level, bias, and precision based on the results of blank and spiked samples. Spiked samples fell into two categories: those spiked near the CL and those spiked at equal to or greater than three times the CL. These two categories were necessary to check compliance with the criteria for relative precision (S_B) specified by the Statement of Work. Satisfying these two categories also verified that GEL could detect sample activities near the CL.

DETECTION LEVELS

Various mathematical expressions and terminology can be used to describe a detection level. The statistical approach specified in the Statement of Work basically follows that of Currie (1968) and HPS N13.30 (HPS 1996). However, the HPS N13.30 formulas were modified to account for the difference between a priori estimates of detection levels based on counts (Currie 1968) and a posteriori estimates based on total activity, where chemical yield is determined specifically for each sample.

Two test criteria were used: the decision level (L_c) and the MDA (also called the detection level). The decision level was defined in the Statement of Work as the quantity of radioactivity or mass above which there is at least 95% confidence that the sample is not a blank (Type I error). If the measured value was greater than the L_c, the sample was considered likely to contain the radionuclide of interest. If the measured value was less than L_c, then the result was considered indistinguishable from a blank. The L_c was determined solely by measuring blank samples. Before the L_c was calculated, results that were significant outliers were eliminated from the data set. Outliers were identified by the use of the criteria of ASTM E178-94 (ASTM 1994).

Mathematically, L_c is defined by the following equation:

$$L_c = 2s_A$$

where, s_A equals the combined standard uncertainty of the net analyte reported.

The MDA was based on a 95% probability of detecting activity when the actual activity is equal to the MDA, and conversely a 5% probability of the results falling below the L_c and being judged to contain no activity (Type II error). The MDA, expressed in units of disintegrations per minute, is calculated from the same set of blanks as the L_c (outliers excluded), using the following equation:

$$MDA = \overline{X_o} + 2(t_{n-1})\, s_o + \frac{(t_{n-1})^2}{ERT}$$

Where

$\overline{X_o}$ = mean net result for the replicate blank samples, in disintegrations per minute

n = number of replicate blank measurements

(t_{n-1}) = the 95th quantile of the "student-t" distribution with (n-1) degrees of freedom

s_o = standard deviation of the net blank, in units of disintegrations per minute

E = the typical counter detection efficiency in counts per disintegration

R = the average fractional chemical recovery or yield

T = the typical counting time.

The above equation is considered appropriate for use with replicate blank results and for comparison with the equation in the contract statement of work, which is calculated with mean count data. In keeping with the philosophy of HPS N13.30, if t^2 is less than 3, then 3 is used instead. For uranium mass analyses, the analytical method does not produce count data; the unit for the analysis result and MDA is micrograms. Thus, the "3" term is not an appropriate part of the equation for the uranium mass analysis.

The present contract 112512 with GEL, implemented on February 24, 2010, specifies an operational year that ends March 31st, each year. This QC report covers the first operational year of that contract, and includes samples analyzed by GEL during period of April 1, 2011 through March 31, 2012.

The MDA values GEL calculates for their QC reports are based on mean values for parameters of equation 2 of the contract statement of work, and not replicate measurements. GEL also uses synthetic samples, whereas IDP uses real fecal and urine samples.

The IDP QC samples were evaluated by first calculating the L_c from blank samples, excluding outliers. This L_c was compared with the L_c calculated from GEL's own QC samples. Then, the MDA was calculated and compared with the CL and the MDA calculated from GEL's own QC samples. Values used for E, R, and T in the MDA equation were obtained from the laboratory; they are listed in Table 3. Finally, the percentage of QC samples spiked at the CL that were measured by the laboratory as having less than the decision level (i.e., no activity was detected) was determined; this percentage was then compared with the 5% allowed in the Statement of Work. Outliers were included in this test.

BIAS

Relative bias is defined as the mean fractional deviation of the reported results from the true values of spikes added to the samples. The formulas in the Statement of Work used to measure bias in sample results are the same as those in HPS N13.30 (1996). The mean relative bias, Br, is determined using:

$$B_r = \sum_{i=1}^{m} \sum_{j=1}^{n} \frac{B_{rij}}{N}$$

where n = number of spike samples in each level
m = number of spike levels
N = total number of spiked samples
B_{rij} = bias of a single measurement, defined as:

$$B_{rij} = \frac{(A_{ij} - A_{ai})}{A_{ai}}$$

where A_{ij} = the jth measured value of the ith spike level,
A_{ai} = the true value of the ith spike level

TABLE 3. Typical Chemical Yield (R), Typical Detector Efficiencies (E), and Counting Time (T) Values from GEL Quality Control Report

Matrix	Nuclide/ Method	Count Minutes	*Contract Limit*[(a)]	Counter Efficiency 2010-2011	Counter Efficiency 2011-2012	Chemical Yield 2010-2011	Chemical Yield 2011-2012
Urine	^{3}H	20	*20*	0.243	0.243	N/A	N/A
	Total Sr	45	*10*	0.379	0.379	0.707	0.722
	^{241}Am	2520	*0.02*	0.391	0.391	0.869	0.840
	^{243}Am	2520	*0.02*	0.391	0.391	0.862	0.391
	^{242}Cm/^{244}Cm	2520	*0.02*	0.391	0.391	0.869	0.840
	^{237}Np	2520	*0.02*	0.391	0.391	0.648	0.712
	^{239}Pu/^{238}Pu	2520	*0.02*	0.391	0.391	0.740	0.795
	IPUL	10000	*0.005*	---	---	---	---
	^{228}Th/^{230}Th/^{232}Th	2520	*0.1*	0.386	0.386	0.765	0.897
	^{234}U/^{235}U/^{238}U	2520	*0.02*	0.386	0.386	0.870	0.792
	^{238}U mass	--	*0.06*	N/A	N/A	N/A	N/A
Fecal	^{241}Am	960	*0.8*	0.391	0.391	0.864	0.866
	^{238}Pu/^{239}Pu	960	*0.2*	0.391	0.391	0.827	0.866

(a) Units dpm/sample except dpm/mL for ^{3}H, and µg/sample for U.
(b) Only one sample analyzed
(c) NA = Not available. No samples completed.

Outliers were excluded from the test, but not ignored for the procedure evaluation. As stipulated in the Statement of Work, the mean relative bias shall fall within ± 20% when calculated from 15 to 50 spiked samples, and within ± 10% when calculated from over 50 samples.

PRECISION

The precision statistic used for this contract was S_B from HPS N13.30 (1996), but the limits differ from that standard. S_B is given by:

$$S_B = \sqrt{\sum_{i=1}^{m}\sum_{j=1}^{n}\frac{(B_{rij} - B_r)^2}{(N-1)}}$$

where the symbols are the same as for relative bias (B_r).

The above equation is valid for samples spiked at one or more levels, subject to the limits for the relative precision, which depend on the activity of the spikes relative to the CL. Specifically, the relative precision statistics shall be less than or equal to 0.4 for samples spiked greater than three times the CL and less than or equal to 0.5 for samples spiked between one and three times the CL. Outliers were not included in the determination of precision.

FINDINGS

Results from three types of QC samples were available: 1) those prepared by GEL and analyzed as single-blinds (spike amount unknown to the analyst), 2) those submitted by IDP and analyzed as single-blinds (spike amount unknown to the analyst), and 3) those submitted by IDP and analyzed as double-blinds (spike amount and sample origin unknown to the analyst).

Single-blind samples this year included 31 urine samples prepared by RPG. There were 8 samples submitted to test the procedure for analyzing samples containing DTPA, 5 samples to test the ICA analysis and 18 samples to test the IU analysis. Because a depleted uranium source is used to spike the samples, isotopic uranium analyses are run as single-blinds. The remaining 78 audit samples submitted by IDP were double-blind samples and included 15 actual fecal samples. The results of the statistical tests (see Table 4 and Appendix A) are discussed below. Statistical results from the present and previous years are compared in Table 5.

OUTLIERS

Analytical results that are biased by "blunders" during the analysis should not be included in the data set used for the statistical evaluation of the analytical procedure, but too many outliers would indicate poor laboratory performance (see Table 6). GEL (see Appendix B) identified some outliers associated with their laboratory control samples (blanks and spiked). In future QC reports GEL has been asked not to classify QC data points as outliers and remove them from the database if the result was a statistical anomaly. However, if there was a laboratory error resulting in an erroneous result, then the associated data can be excluded from the performance statistics. Any outliers removed from the data tables need to be addressed in the observation section.

TABLE 4. Summary of Statistical Values by Nuclide

	Sample	Blank (dpm)				Spike level at CL (dpm)			Spike Level > 2CL (dpm)		
Isotope[a]	Source	n	L_c	MDA	**CL**	n	B_r	S_B	n	B_r	S_B
^{3}H(dpm/mL)	**IDP**	0	…	…	**20**	0	…	…	0	…	…
	GEL	72	0.4	5.0	**20**	72	-0.102[e]	0.08	0	…	…
^{14}C (dpm/ml)	**IDP**	0	…	…	**10**	0	…	…	0	…	…
Total Sr/^{90}Sr	**IDP**	0	…	…	**10**	19	-0.04	0.10	0	…	…
	GEL	229	0.7	6.5	**10**	231	0.02	0.17	231	0.05	0.09
^{237}Np	GEL	3	0.02	0.03[c]	**0.02**	3	-0.25 [f]	0.59[f]	3	-0.15	0.22
^{228}Th	GEL	5	0.01	0.02	**0.1**	0	…	…	0	…	…
^{229}Th	GEL	5	0.01	0.02	**0.1**	0	…	…	0	…	…
^{232}Th	GEL	5	0.01	0.02	**0.1**	5	-0.04	0.13	5	-0.08	0.10
^{230}Th	GEL	5	0.02	0.03	**0.1**	0	…	…	0	…	…
^{242}Cm	**IDP**	5		0.01	**0.02**	0	…	…	0	…	…
	GEL	66	0.00	0.01	**0.02**						
^{243,244}Cm	**IDP**	5	0.00	0.01	**0.02**	0	…	…	0	…	…
	GEL	66	0.01	0.01	**0.02**	67	0.202[e]	0.33	67	0.04	0.16
^{238}Pu-urine	**IDP**	31	0.00	0.01	**0.02**	0	…	…	0	…	…
	GEL	597	0.01	0.01	**0.02**	0	…	…	0	…	…
feces	**IDP**	10	0.02	0.04	**0.2**	0	…	…	5	-0.06	0.14
	GEL	51	0.03	0.08	**0.2**	0	…	…	0	…	…
^{239,240}Pu-urine	**IDP**	0	…	…	**0.02**	23	-0.12	0.25	8	-0.07	0.04
	GEL	597	0.01	0.02	**0.02**	602	0.03	0.29	602	0.03	0.09
feces	**IDP**	10	0.02	0.04	**0.2**	0	…	…	0	-0.17	0.16
	GEL	51	0.05	0.12	**0.2**	51	-0.02	0.26	51	0.02	0.08
^{241}Am-urine	**IDP**	5	0.00	0.01	**0.02**	23	0.05	0.24	8	-0.12	0.03
	GEL	364	0.01	0.02	**0.02**	367	0.05	0.29	367	-0.05	0.09
feces	**IDP**	10	0.02	0.05	**0.2**	0	…	…	5	-0.13	0.09
	GEL	51	0.04	0.10	**0.2**	51	0.04	0.20	51	-0.04	0.09
^{243}Am-urine	**IDP**	7	0.01	0.023 [c]	**0.02**	0	…	…	0	…	…
	GEL	14	0.01	0.024 [c]	**0.02**	14	0.00	0.29	14	-0.01	0.10
^{233,234}U	**IDP**	0			**0.02**	0	…	…	0	…	…
	GEL	99	0.02	0.039[d]	**0.02**	0	…	…	0	…	…
^{235,236}U	**IDP**	18	0.01	0.02	**0.02**	0	…	…	0	…	…
	GEL	99	0.01	0.02	**0.02**	0	…	…	0	…	…
^{238}U	**IDP**	0	…	…	**0.02**	0	…	…	18	0.00	0.16
	GEL	99	0.02	0.034[d]	**0.02**	99	0.02	0.32	99	0.01	0.10
^{236}U (ICPMS)[b]	**IDP**	0	…	…	**140 pg**	0	…	…	0	…	…
	GEL	0	…	…	**140 pg**						
^{238}U (ICPMS)[b]	**IDP**	0	…	…	**0.06 µg**	0	…	…	33	-0.03	0.28
	GEL	81	0.01	0.02	**0.06 µg**	81	0.10	0.19	81	-0.01	0.06

(a) Analyzed in urine matrix unless otherwise noted.
(b) Units for performance indicators are the same as the units for CL.
(c) Failed performance criterion.
(d) Possible environmental contaminant.
(e) Within statistical uncertainty
(f) No criteria when there are less than 15 samples

TABLE 5. Comparison of Quality Control Statistics Between the First and Second Contract Year with GEL Using QC Samples Submitted by IDP

	Report	Blanks			Spike Level at CL			Spike Level at > 3CL		
Nuclide	Year[(a)]	n	L_c	MDA	n	B_r	S_B	n	B_r	S_B
^{3}H	2011	0	…	…	0	…	…	0	…	…
	2010	0	…	…	0	…	…	0	…	…
Sr	2011	0	…	…	19	-0.04	0.10	0	…	…
	2010	3	1.707	4.119	16	-0.05	0.09	0	…	…
U	2011	0	…	…	0	…	…	33	-0.03	0.28
(ICPMS)	2010	2	0.005	0.051	0	…	…	27	-0.05	0.24
^{235}U	2011	18	0.007	0.018	0	…	…	0	…	…
	2010	12	0.003	0.011	0	…	…	0	…	…
^{238}U	2011	0	…	…	0	…	…	18	-0.004	0.16
	2010	0	…	…	0	…	…	12	0.04	0.11
^{238}Pu	2011	31	0.003	0.010	0	…	…	0	…	…
(urine)	2010	17	0.003	0.011	0	…	…	0	…	…
^{238}Pu	2011	10	0.016	0.043	0	…	…	5	-0.06	0.14
(fecal)	2010	5	0.011	0.037	0	…	…	5	-0.08	0.08
^{239}Pu	2011	0	…	…	23	-0.12	0.25	8	-0.07	0.04
(urine)	2010	3	0.006	0.023 (e)	14	0.05	0.29	0	…	…
^{239}Pu	2011	10	0.016	0.043	0	…	…	5	-0.17	0.16
(fecal)	2010	5	0.011	0.036	0	…	…	5	-0.16	0.18
^{241}Am	2011	5	0.003	0.011	23	0.05	0.24	8	-0.12	0.03
(urine)	2010	3	0.008	0.025 (e)	14	0.00	0.18	0	0.00	0.00
^{241}Am	2011	10	0.018	0.047	0	…	…	5	-0.13	0.09
(fecal)	2010	5	0.032	0.079	0	…	…	5	-0.12	0.11
^{243}Am	2011	7	0.009	0.023 (c)	0	…	…	0	…	…
	2010	4	0.006	0.019	0	…	…	0	…	…
^{242}Cm	2011	5	0.000	0.006	0	…	…	0	…	…
	2010	0	…	…	0	…	…	0	…	…
$^{243,244}Cm$	2011	5	0.002	0.010	0	…	…	0	…	…
	2010	0	…	…	0	…	…	0	…	…

(a) Report Year reflects the year of the first quarter or the start of the contract year.
Note: L_c and MDA units same as CL. B_r and S_B are unitless (fractional values).

TABLE 6. Other Indicators of Analytical Uncertainty (IDP Samples)

Nuclide	IDP QC Samples Analyses	IDP QC Samples Outliers	Performance Evaluation Samples Spikes at CDL IDP	Spikes at CDL GEL	False Negatives (%) IDP	False Negatives (%) GEL	Analytical Samples 2011-2012 Yield Flags	Analytical Samples 2011-2012 Failed Analyses
Urine								
^{3}H	0	0 (0)	0	72	0 (0)	0 (0)		
Sr	21	0 (0)	19	231	0 (0)	0 (0)	2%	
^{235}U	18	0 (0)	0	0	0 (0)	---	1%	
^{238}U	18	0 (0)	18	99	0 (0)	7% (7)	1%	
^{238}Pu	31	0 (0)	0	0	0 (0)	---	5%	1%
^{239}Pu	31	0 (0)	23	602	0 (0)	4% (22)	5%	1%
^{241}Am	31	0 (0)	23	367	0 (0)	3% (10)	1%	1%
^{243}Am	7	0 (0)	0	14	0 (0)	0 (0)	1%	
U-ICPMS [(a)]	33	0 (0)	33	81	0 (0)	0 (0)		
Total	*190*		*116*	*1466*				
Feces								
^{241}Am	15	0 (0)	5 [(a)]	51	0 (0)	0 (0)		
^{238}Pu	15	0 (0)	5 [(a)]	0	0 (0)	0 (0)	3%	
^{239}Pu	15	0 (0)	5 [(a)]	51	0 (0)	0 (0)	3%	
Total	*45*		*0*	*102*				

(a) sample spiked at >3 CL

TRITIUM

Effective June 2006, the tritium intercomparison program by IDP was discontinued; performance indicators will be evaluated through GEL's QC program. The control samples run by GEL also met all the acceptance criteria tested as part of the quality control program. The tritium analyses were considered acceptable.

STRONTIUM-90 AND TOTAL STRONTIUM

The total strontium procedure is used to screen samples to determine whether analysis for ^{90}Sr is warranted. Samples with total strontium results less than 15 dpm do not undergo further analysis. Samples with results greater than or equal to 15 dpm may undergo ^{90}Y in growth to specifically determine ^{90}Sr levels. The calculated MDA, reported by GEL and tested by IDP, for the total strontium

part of the analysis was less than 35% of the CL. The MDA, relative bias and precision, tested by IDP and GEL for the ^{90}Sr and total Sr procedures were all within limits. The 19 samples spiked at the contractual level by IDP were all detected. The strontium urinalysis procedure was concluded to be acceptable.

PLUTONIUM-238 AND –239

Samples spiked with ^{238}Pu and ^{239}Pu were analyzed using the same procedures and same reagents. The two isotopes are differentiated only at the end of the procedure by alpha spectrometry. Therefore, laboratory performance is expected to be similar for both isotopes using any of the seven procedures that incorporate plutonium analysis (IPU, IPA, IPS, IPSA, IPSR, IUPU, and ITPAC).

The MDAs and performance statistics for ^{239}Pu and ^{238}Pu in urine were acceptable. The MDA tested by GEL and based on 597 samples was 15% less than the criteria. The 23 samples spiked at the CL for ^{239}Pu all showed detection and the relative bias and precision met the acceptance criteria. Out of 602 samples spiked by GEL at the CDL, 22 samples did not show detection, giving a false-negative (beta error) of 4%, which was acceptable. There were 31 blank samples submitted by IDP and analyzed for ^{238}Pu activity, none of the 31 samples detected activity in excess of the decision level. Overall the plutonium urinalyses were considered acceptable.

The MDA and performance statistics for ^{239}Pu and ^{238}Pu in feces were likewise acceptable. More than 15% of the fecal samples analyzed were duplicated to test the consistency of the aliquoting procedure. A review of the duplicate samples determined that the aliquoting procedure produced results within 3 sigma of the initial results. The fecal aliquoting procedure was acceptable. This year IDP submitted 15 actual fecal samples, 10 samples were blanks and 5 samples were spiked with very insoluble ^{239}Pu and slightly soluble ^{238}Pu. The MDA, precision and bias for ^{239}Pu and ^{238}Pu met the performance criteria. The performance statistics reported by GEL for ^{239}Pu and ^{238}Pu also met the acceptance criterion. There were no reported failed analyses but 3% of fecal analyses were flagged for low yield (less than 50%) or high yield (greater than 110%), which is within the contractual level of 10%. Overall the plutonium fecal analyses were considered acceptable.

ISOTOPIC URANIUM

The isotopic uranium analysis reports on three uranium isotopes: ^{234}U, ^{235}U, and ^{238}U. The isotopes are differentiated only during counting by alpha spectrometry. The MDA reported by the lab for ^{234}U and ^{238}U were elevated and they did not meet the contractual detection level and the MDA

reported for ^{235}U was at the contractual level. It was assumed that there were environmental contaminants; however, the analysis will be further reviewed in the 2012 audit of the lab. All performance criteria were met within statistical variation. Of the 81 samples that GEL spiked at the CDL, all showed detection, and the 18 samples spiked by IDP at the environmental screening level likewise all showed detection.

Because IDP used a depleted uranium source material for the isotopic uranium urinalyses, $^{233,234}U$ was not evaluated. However, the performance statistics for ^{235}U and ^{238}U were reviewed and the MDA for ^{235}U and the bias and precision for ^{238}U were acceptable.

URANIUM MASS

No concerns were identified with the ^{238}U mass urinalysis program using inductively-coupled plasma mass spectrometry (ICPMS) and it was considered acceptable. Because IDP uses a 0.2 µg screening level for ^{238}U mass, samples spiked at 0.06 µg were discontinued. The MDA at the contractual level of 0.06 µg was evaluated through GEL's program and was found to be acceptable. The relative bias and precision were likewise acceptable. The bias and precision as tested by IDP met the acceptance criteria. The bias and precision was tested by IDP at 0.2 µg and by GEL at 1 µg/sample and at 0.05 µg/sample.

URANIUM-236 VIA INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICPMS)

The performance statistics for the ^{236}U analysis using ICPMS were not evaluated since no samples were submitted during the second contract year.

AMERICIUM-241

The ^{241}Am urine analyses met the acceptance criteria for MDA, relative bias and precision. The MDA as reported by GEL was less than 5% of the contractual level. All 23 of the ^{241}Am samples spiked at the contractual detection level (CDL) were detected. Out of 367 samples spiked by GEL at the CDL, 10 samples did not show detection, giving a false-negative (beta error) of 3%, which was acceptable. The relative bias and precision as reported by GEL and tested by IDP met the performance criteria. The current AM241 urinalysis procedure was considered acceptable.

The MDA and performance statistics for ^{241}Am in feces were likewise acceptable. Like the plutonium analysis program for feces, more than 15% of the fecal samples analyzed were duplicated to test the aliquoting procedure. The ^{241}Am fecal duplicate samples were evaluated and it was concluded that the

aliquoting procedure produced results within the control limits. This year IDP submitted five actual fecal samples spiked with very insoluble ^{241}Am and the relative bias and precision were acceptable. Overall the ^{241}Am fecal analyses were considered acceptable.

AMERICIUM-243

The AM243 procedure was identical to the AM241 procedure, except a different tracer is used (^{244}Cm instead of ^{243}Am). Only one of the seven blank ^{243}Am QC samples submitted showed detection resulting in a false-positive (alpha error) of 14%, which met acceptance criteria, assuming the normal statistical variation in the measurement process. The calculated MDA slightly exceeded the contractual detection level as tested by IDP and GEL each quarter as well as in the annual. The trend towards a slightly elevated MDA for the AM243 procedure was not addressed in GEL's annual report. The performance statistics for ^{243}Am, as tested by GEL, met the acceptance criteria for relative bias and precision. Because the MDA was only slightly elevated the ^{243}Am procedure was concluded to be acceptable but it will be re-evaluated during the 2012 annual audit of GEL.

ISOTOPIC CURIUM

IDP submitted 5 blank samples for isotopic curium analysis. All 5 samples were reported with ^{242}Cm and ^{244}Cm results less than decision levels with a resulting MDA for both isotopes meeting the acceptance criteria. IDP did not submit spiked samples; therefore performance statistics for relative bias and precision were based on the GEL QC results. GEL tested the MDA for ^{242}Cm and ^{244}Cm and the relative bias and precision for ^{244}Cm. Of the 67 samples spiked with ^{244}Cm, only 1 sample did not show detection with a false-negative (beta error) of 1.5%, which was acceptable. The average relative bias of ^{244}Cm was slightly elevated but it was not considered a concern (see Table 4). Overall the results met the acceptance criteria and the isotopic curium urinalysis program was considered acceptable.

ISOTOPIC THORIUM

IDP also did not submit QC samples to test the isotopic thorium program, therefore performance statistics were based on the GEL QC results. GEL tested the MDA for ^{228}Th, ^{229}Th, ^{230}Th and ^{232}Th and the relative bias and precision for ^{232}Th. Of the 5 samples spiked with ^{232}Th, all showed detection. Overall the results met the acceptance criteria and the isotopic thorium urinalysis program was considered acceptable.

NEPTUNIUM-237

Neptunium-237 was likewise not tested by IDP and the performance statistics were supplied by GEL's QC program. Because only 4 routine samples were submitted for analysis there were less than 9 total QC samples analyzed by GEL. The average relative bias met the acceptance criteria, however, the MDA and relative precision did not. Because there were only 9 QC samples analyzed by GEL (3 blank samples, 3 at the CL, and 3 to evaluated relative bias and precision) the uncertainty inherent in the measurement process precluded accurate evaluation of the performance criteria. The NP237 analysis will be reviewed during the 2012 annual audit of GEL and it will continue to be monitored.

ANALYSIS OF URINE SAMPLES CONTAINING DTPA

In addition to the blind audit program IDP also submitted 8 urine samples to evaluate the laboratory's capability to analyze for ^{239}Pu and ^{241}Am in media containing diethylenetriaminepentaacetate (DTPA). The purpose of the test samples was to determine whether DTPA would interfere with the radiochemistry and if so, was a separate analytical procedure for urine samples containing DTPA required to meet the performance and yield requirements. The Hanford bioassay program recommends administering DTPA to workers if their committed effective dose levels likely to be equal to or greater than 20 mSv. The urine samples were spiked with 1 dpm of ^{239}Pu and ^{241}Am and 0.5 g of either Zn-DTPA or Ca-DTPA to simulated urine collection in the first 24-hrs following DTPA medical therapy.

The first 4 samples were analyzed using the current procedure of pre-concentrating the actinides by precipitation prior to the destruction of organics. All the samples showed detection for ^{239}Pu and ^{241}Am. The plutonium yields with this procedure averaged 86%, however, the yields for the americium analysis were only 40%, with a range of 31% - 54%. The remaining 4 samples were analyzed under a revised procedure where destruction of the organic material was performed prior to the pre-concentration of the actinides. Using the revised procedure the yield recovery for the plutonium analysis continued to be acceptable at 86% but there was a significant improvement in the americium analysis with an average yield of 97.5%.

To ensure that tracer yields meet the criteria, the standard procedure was revised to state that if a sample contains DTPA that the destruction of the organic material is to be performed prior to the pre-concentration of the actinides.

FOLLOW-UP ON CONCERNS DURING THE FIRST 112512 CONTRACT YEAR

There were a few concerns carried over from the first contract year, primarily an increasing low and high yield rate seen in the isotopic plutonium and americium-241 analyses for both fecal and urine, in the isotopic uranium analysis and with the strontium analysis. In the statement of work, table B-10 outlines the criteria for flagging samples for low or high tracer yields and for designating an analysis as failed due to tracer yield concerns. During the second contract year the percent of flagged yield samples declined in all categories with the exception of isotopic curium urinalyses, which increased to 2.2% from 1.1%. The yield flags and failed analysis rate will continue to be monitored but the concern from the first contract year was sufficiently addressed by the lab.

Incident reports issued during the first contract year and their follow-up are reported in Appendix B. All incidents were closed out with the exception of DOELAP certification for the carbon-14 analysis program. This was addressed in the 2010-2011 Annual Report, however, in the 2012 DOELAP testing GEL failed to meet the performance criteria for carbon-14 urinalyses again. However, since the routine carbon-14 program was removed from the statement of work, the lack of certification to GEL for carbon-14 analyses is not relevant to our routine monitoring program. The carbon-14 program will continue to be monitored because it is an option that may have to be utilized in an incident response.

SUMMARY OF THE BIOASSAY QUALITY CONTROL REPORT FROM GEL INCORPORATED, FOR THE CONTRACT 112512 SECOND YEAR 2011/2012[(a)]

GEL reported all analytical batches were analyzed with a reagent blank (Umass only), matrix blank or both. GEL considered blanks in control when the calculate MDA was less than the Contract Limit (CL) and the L_c was less than ½ CL (see Appendix B). In addition, the chemical tracer yields were evaluated against the yield requirements stated in the subject contract. Overall, GEL believed that the blank and spike data for each analytical process demonstrated that the analyses were in control.

In the review GEL indentified laboratory control samples that had yields greater than 125% as well as one excreta sample that had a tracer yield greater than 125%. GEL also indentified laboratory control samples that met the criteria for low yield, but likewise a review of excreta sample results found the low yield rate to be acceptable. The urine sampling program showed acceptable levels for tracer yields for all analyses. The isotopic plutonium urinalysis program showed the highest yield flag rate at 5%, which is below the 10% level for follow-up.

RESULTS FROM INTERCOMPARISON PROGRAMS

GEL participated in two intercomparison programs (Appendix C – Intercomparison Programs) in the first contract year. Between August and October 2011, GEL participated in the National Institute of Standards and Technology's program testing the relative bias and precision for ^{60}Co, ^{137}Cs, ^{238}Pu, ^{240,239}Pu, ^{241}Am, ^{230}Th, ^{235}U, ^{238}U, ^{234}U and ^{90}Sr in synthetic feces. GEL met the acceptance criteria for relative bias and precision for all isotopes. GEL also participated in the National Institute of Standards and Technology's program testing the relative bias and precision for ^{241}Am+^{243}Cm, ^{60}Co, ^{57}Co, ^{137}Cs, ^{226}Ra, ^{238}Pu, ^{240,239}Pu, ^{241}Am, ^{230}Th, ^{235}U, ^{238}U, ^{234}U and ^{90}Sr, in synthetic urine. GEL met the acceptance criteria for relative bias and precision on all isotopes.

In 2012 GEL participated in session 15 of DOELAP (GEL was Lab-2) and was tested for ^{60}Co, ^{137}Cs, ^{238}Pu, ^{240,239}Pu, ^{241}Am, ^{230}Th, ^{228}Th, ^{232}Th, ^{237}Np ^{235}U, ^{238}U, ^{234}U and ^{90}Sr in synthetic feces. GEL met the acceptance criteria for relative bias and precision for all isotopes in feces. For the urine program, GEL was tested in ^{14}C, ^{3}H,^{60}Co, ^{137}Cs, ^{238}Pu, ^{240,239}Pu, ^{241}Am, ^{230}Th, ^{228}Th, ^{232}Th, ^{237}Np ^{235}U, ^{238}U, ^{234}U, ^{238}U-mass and ^{90}Sr in synthetic urine. GEL passed the performance statistics for relative bias and precision for all isotopes except ^{14}C.

In 2011 GEL participated in the PROCORAD intercomparison program for carbone-14 in urine

and the average bias for the 4 samples tested was 2%, which was significantly different from their performance with the DOELAP performance samples. The cause for the discrepancy is unknown, but GEL will continue to investigate.

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(a) Summaries are taken from GEL (2010).

RELEVANT PROCEDURES AND CORRESPONDENCE

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Antonio, C. L. 2012. "Results of the PNL Excreta Bioassay Quality Control Oversight Program for October 1, 2011 through December 31, 2011." Letter Report, Pacific Northwest Laboratory, Richland, Washington. (Available from the Hanford Radiological Records Historical File.)

ATTACHMENT A

THE IMPLICATION TO BIOASSAY PROTOCOLS FOR WORKERS RECEIVING CHELATION THERAPY DUE TO INTAKES OF PLUTONIUM MIXTURES

The Hanford Internal Dosimetry Program (IDP) suggests chelation therapy at committed effective dose levels likely to be equal to or greater than 20 mSv (20 rem). The most effective chelation therapy for plutonium and americium isotopes is DiethyleneTriaminePentaAcetate (DTPA) with trisodiumcalcium (or zinc). The chemical form for DTPA is Na_3Ca (or $Zn)C_{14}H_{18}N_3O_{10}$. DTPA combines with the heavy metal to form complexes. These DTPA-heavy metal complexes are excreted by the kidney into the urine, thus preventing the radioactive substances from reaching and depositing in the bone or liver. Ca-DTPA is ~10 times more effective than Zn-DTPA within the first 24 h, after the first 24-h Zn-DTPA is as effective as Ca-DTPA. DTPA can reduce dose by 80% for soluble forms if given within 24 h, but <25% after intake of insoluble compounds. Mode of Treatment for adults: 1 g of DTPA in 5 ml slow IV push over 3 to 4 min.

Urine bioassays are obtained to assess the efficacy of the initial DTPA treatment and as a basis to consider further therapy. The duration of the chelation therapy depends on the amount of internal deposition and the individual response to the treatment.

In one gram of DTPA there are about $1x10^{21}$ molecules of DTPA. In the first 24 hr following therapy more than 99% of the DTPA would be excreted, leaving less than 0.5% in the plasma, or $6x10^{18}$ molecules of DTPA. Knowing that DTPA binds to the heavy americium and plutonium metals, will DTPA interfere with the radiochemistry and if so to what degree? That is, is a separate analytical procedure for urine samples containing DTPA needed? To test the current analysis procedure, IDP submitted eight samples spiked with plutonium and americium as well as Ca-DTPA or ZN-DTPA. Table 1 shows the sampling protocol.

METHOD

Table 1. Sample Protocol for 1500 ml Urine Samples

Sample Protocol			
DTPA	^{241}Am (mBq)	^{239,240}Pu (mBq)	Analytical Procedure
0.5 g Ca-DTPA	16.7	16.7	Wet ash and evaporate to dryness prior to co-ppt
0.5 g Ca-DTPA	16.7	16.7	Wet ash and evaporate to dryness prior to co-ppt
0.5 g Ca-DTPA	16.7	16.7	Co-ppt prior to evaporation and wet ashing
0.5 g Ca-DTPA	16.7	16.7	Co-ppt prior to evaporation and wet ashing
0.5 g Zn-DTPA	16.7	16.7	Wet ash and evaporate to dryness prior to co-ppt
0.5 g Zn-DTPA	16.7	16.7	Wet ash and evaporate to dryness prior to co-ppt
0.5 g Zn-DTPA	16.7	16.7	Co-ppt prior to evaporation and wet ashing
0.5 g Zn-DTPA	16.7	16.7	Co-ppt prior to evaporation and wet ashing

The current procedure for routine analytical Urinalysis program is:

1. The urine sample is adjusted to pH $\leq$ 2 using HNO_3
2. Appropriate tracers are added (^{243}Am or ^{242}Pu)
3. The analytes, plutonium and americium, are pre-concentrated using a calcium phosphate precipitation.
4. **Organic material is then destroyed and the analytes are dissolved through a process of evaporation and wet ashing.**
5. Chemical separations are performed via ion exchange or organic extraction.
6. Analytes are then prepared for alpha spectrometry counting using a rare earth fluoride coprecipitation.

RESULTS

The results are shown in Figures 1 and 2. The first 4 samples were analyzed using the current procedure of pre-concentrating the actinides prior to the destruction of organics. All the samples showed detection for ^{239}Pu and ^{241}Am, and the yields for the plutonium analysis averaged 86%, however, the yields for the americium analysis were only 40%, with a range of 31% - 54%. The procedure was revised so that the destruction of the organic material was performed prior to the pre-concentration of the actinides.

Revised procedure for samples containing high levels of DTPA:

1. The urine sample is adjusted to pH $\leq$ 2 using HNO_3
2. Appropriate tracers are added (^{243}Am or ^{242}Pu)
3. **Organic material is destroyed and the analytes are dissolved through a process of evaporation and wet ashing.**
4. The analytes, plutonium and americium, are then pre-concentrated using a calcium

phosphate precipitation.
5. Chemical separations are performed via ion exchange or organic extraction.
6. Analytes are then prepared for alpha spectrometry counting using a rare earth fluoride coprecipitation.

The remaining 4 samples were analyzed under the revised procedure and the yield recovery for the plutonium analysis continued to be acceptable at 86% but there was a significant improvement in the americium analysis with an average yield of 97.5%.
The MDA was evaluated for ^{238}Pu, and it was acceptable at less than 48% of the required detection level. The relative bias and precision for ^{239}Pu and ^{241}Am were likewise acceptable based on the analysis results of all 8 samples. However, to ensure that tracer yields meet the criteria, a revision to the current procedure was made stating that if a sample contains DTPA that the destruction of the organic material is to be performed prior to the pre-concentration of the actinides.

CONCLUSION:

DTPA complexes are slow to decompose and without completely destroying the organic material the DTPA complexes will not be pre-concentrated in the calcium phosphate precipitate. In addition, americium is more tenaciously bound to DTPA than plutonium at pH 2.

CHANGES IN THE APPROACH TO ANALYZE BIOASSAY SAMPLES CONTAINING DTPA

Destruction of organic material will need to be performed prior to preconcentration of sample for samples containing DTPA. The lab will need to be notified of bioassay samples containing DTPA so they could implement the revised procedure. Samples not containing DTPA will continue to be analyzed using the routine monitoring procedures.

For small sample volumes this would not impact processing times, however, larger sample volumes will take longer to process. Priority processing turnaround times should not be affected but longer processing times will be expected for Emergency and Expedite processing.

APPENDIX A

QUALITY CONTROL SAMPLE RESULTS
(Historical File Only)

APPENDIX B

GEL QUALITY CONTROL SAMPLE REPORT SUMMARY

(Historical File Only)

APPENDIX C

QUALITY CONTROL INTERCOMPARISON PARTICIPATION RESULTS
(Historical File Only)