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Plutonium in Peruvian Soil Project Report

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Pu in Peruvian Soil Project Report

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Abstract

The ^{239}Pu concentration of the NIST Peruvian soil is less than 1 femtogram per gram (fg/g). The greatest ^{239}Pu concentration measured using the ^{242}Pu isotope dilution tracer supplied by NIST was 0.93 fg/g and the minimum was 0.04 fg/g. The simple mean of six spiked analyses is 0.50 fg/g and the error-weighted mean is 0.64 fg/g, but if the results are weighted by the spike recovery then the ^{239}Pu concentration is 0.37 fg/g. These results for ^{239}Pu are not corrected for analytical blank. A spiked reagent and processing blank gave the equivalent of 0.47 fg/g when calculated on the basis of a 5 gram sample. If this blank is subtracted from the three 5 gram samples that were analyzed, then none of these three results are distinguishable from zero. If the blank is scaled appropriately and subtracted from the three 10 gram samples, then none of the ^{239}Pu concentrations are greater than 0.7 fg/g. The upper limit of 1 fg/g for ^{239}Pu is conservative. An isobar at mass 240 of highly variable intensity interfered with the analysis of ^{240}Pu, and no reliable results for ^{240}Pu/^{239}Pu were obtained.

Introduction

An upper limit on the ^{239}Pu concentration in NIST Peruvian Soil 4355A is the only information that can be extracted from the analyses made at LLNL. Due to various difficulties, only 14 of the 25 analyses requested for the experimental protocol were completed. These analyses were one spike-only, six spiked samples and seven un-spiked samples. Although it appears that a signal from ^{239}Pu was detected above background levels for the 6 spiked analyses, the net signal at mass 239 was negative for two of the un-spiked samples. While the net signal at mass 240 was positive for all samples, it was anomalously and unrealistically high relative to mass 239 in 12 of the 13 samples measured, indicating an isobaric interference.

The plutonium isotopic analyses were made with an IsoProbe multi-collector ICP-MS. While the sensitivity of the IsoProbe is very good, the instrument detection limits for the actinides are limited by on-mass background peaks of complex and poorly understood origin. For these analyses, the sensitivity for Pu was approximately 30 cps/ppq (ppq being femtogram/gram of solution) and the aspiration rate was 60 µL/min, which is a total efficiency of slightly more than 1%. All of the plutonium analyses reported here have been corrected for instrumental background as measured on a sample of the acid used to dilute the samples for analysis.

Results

The analyses reported here were made by peak hopping 239-240-242 on the axial Daly pulse-counting detector. Although the IsoProbe has the capability of simultaneous multi-collection in pulse-counting mode using continuous dynode multipliers, the backgrounds on these multipliers are higher than on the Daly detector, and using a single detector avoids the problem of cross calibrating the different pulse-counting detectors. Data was collected in thirty cycles of 5 second integrations or for a total of 150 seconds at each mass. Data reduction for these samples was done by summing the entire signal at each mass as total counts in 150 seconds. Backgrounds were measured on blank acid using the same data collection methodology as for the samples, and these "blank counts" were subtracted from the sample counts. Poisson counting statistics were used to calculate the 2-sigma uncertainties on the net counts at each mass, and these uncertainties were used in the combined uncertainties (u_c) reported in Table 2. The uncertainties are not "total" combined uncertainties, because, for one thing, no corrections for instrumental mass bias have been applied to these data. The magnitude of the multiplicative correction factor for $^{240}Pu/^{239}Pu$ is generally about 0.995 (0.5%), and the uncertainty propagated from this correction is less than 1%. This mass bias correction and the uncertainty associated with it are both trivial relative to the magnitude of the uncertainties from counting statistics.

Table 1. Measured $^{240}Pu/^{239}Pu$

Experiment Run number	NIST Peruvian Soil 4355A		^{242}Pu spike Added (g)	^{240}Pu / ^{239}Pu	
	Bottle number	grams		Value	Uncert., 2σ
0	N/A	0	0.7133	1.138	0.225
2	1609	10.0098	1.1012	0.910	0.083
3	1609	10	0	1.380	0.121
4	8	5.0024	0.7158	5.052	0.947
5	1609	5.0229	0.7158	29.264	48.881
8	8	5	0	0.311	0.023
12	1333	5.0018	0.7158	2.498	0.251
14	1333	5	0	< 0	4.400
16	8	10	0	1.532	0.206
17	8	10.0013	1.1012	1.852	0.287
20	8	5	0	2.795	0.452
22	1333	5	0	2.406	0.287
23	1609	5	0	< 0	0.591
24	1333	9.9945	1.1002	0.966	0.171

Two quality control solutions were prepared from NBL certified Pu standards and were analyzed as unknowns with each batch the Peruvian soil samples. The CRM 137 solution was about 24.5 fg Pu/mL with $^{240}Pu/^{239}Pu$ of 0.2409, and the CRM 138 solution was about 9.4 fg Pu/mL with $^{240}Pu/^{239}Pu$ of 0.0862. The analyses of these solutions are shown in Figure 1 with the lines representing the certified isotopic compositions of the standards. The variations in net counts show the variation in instrumental sensitivity during on different days. All of the CRM 137 $^{240}Pu/^{239}Pu$ analyses lie within their uncertainty (2σ, from counting statistics) of the certified value. The analyses of CRM

138 are more variable, as is expected due to the lower counts, with two having lower $^{240}Pu/^{239}Pu$ values than certified.

The ^{240}Pu and ^{239}Pu net counts that combined give the ratios in Table 1 are shown graphically in Figure 2. The anomalously high $^{240}Pu/^{239}Pu$ ratios are most likely the result of anomalously high net ^{240}Pu counts, but no more is known about this isobaric interference at mass 240 at the present time.

Figure 1. Analyses of ultra-low level QC standards analyzed with the Peruvian Soils

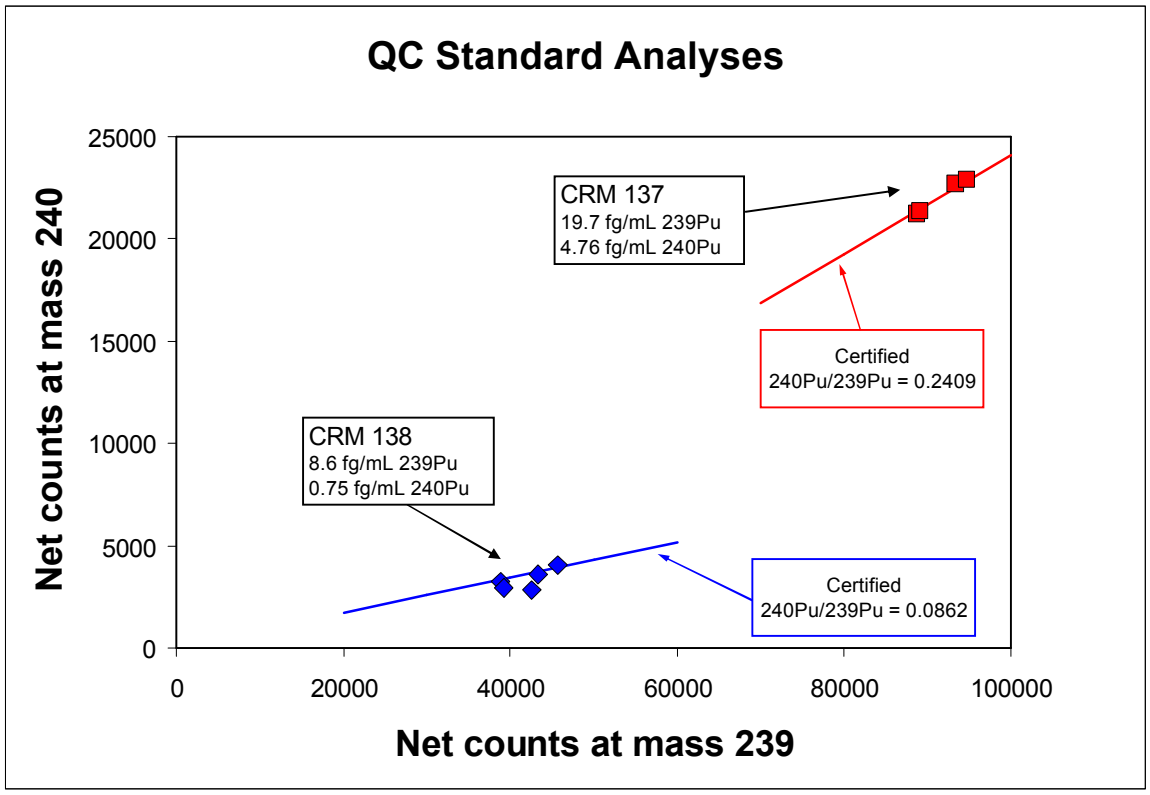
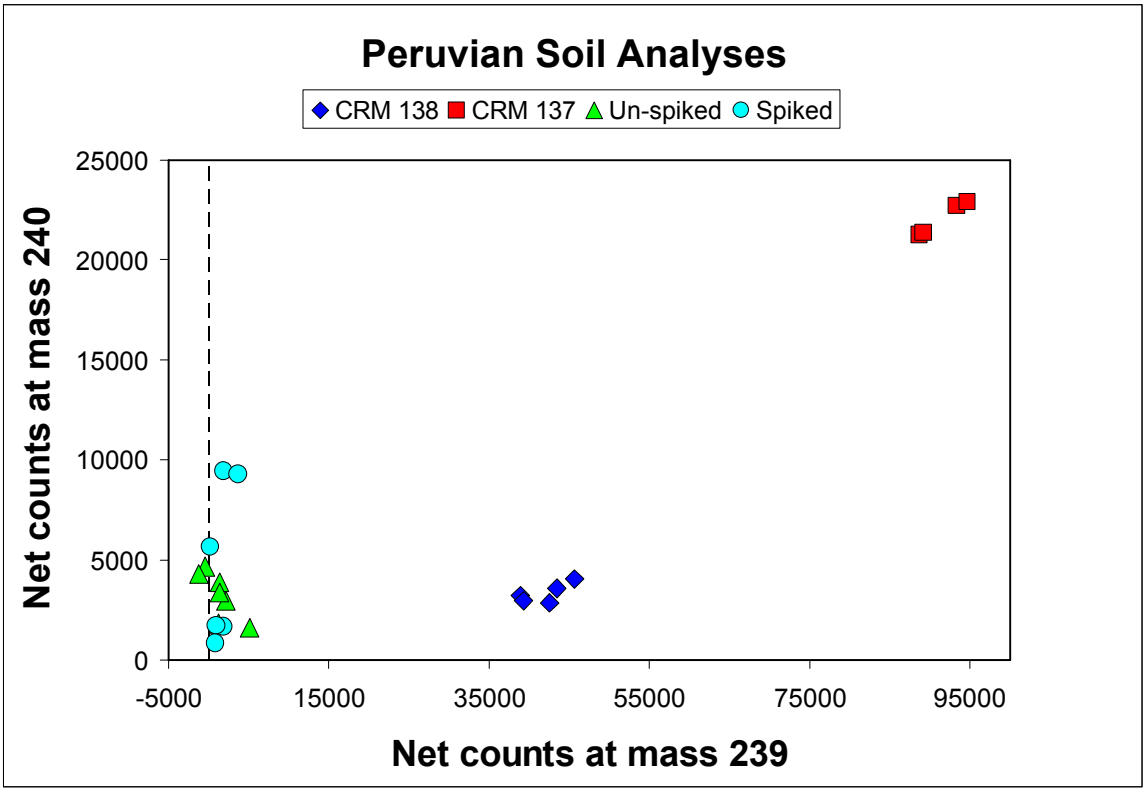


Figure 2. Analyses of the Peruvian Soil samples shown with the QC analyses



While the variation of the signal at mass 240 for the Peruvian soils is problematic, the signal at mass 242 for the spiked samples is much greater than the background level and greater than that for all the un-spiked samples. Although an isobaric interference may be present at either mass 239 or mass 242, it is reasonable to assume that the 239/242 ratios for the spiked samples represent the maximum possible $^{239}Pu/^{242}Pu$ ratios for these samples. The ^{239}Pu concentrations in fg/g for these samples are given in Table 2.

Table 2. ^{239}Pu Concentration Measurements in Peruvian Soil

Experiment Run number	NIST Peruvian Soil 4355A		^{239}Pu femtogram / gram		^{242}Pu Spike Recovery (%)
	Bottle number	grams	Value	u_c, k=2	
2	1609	10.0098	0.928	0.069	6.3
4	8	5.0024	0.313	0.058	35.9
5	1609	5.0229	0.040	0.066	29.3
12	1333	5.0018	0.520	0.050	43.0
17	8	10.0013	0.813	0.116	3.7
24	1333	9.9945	0.384	0.056	7.5

As requested, the samples were dried at 40 degrees C for 24 hours prior to weighing. For nine samples treated in this way the weight loss was 0.08 ± 0.02 %.

The ^{242}Pu spike recoveries for the 5 gram samples were significantly better than those for the 10 gram samples. Considerable time and effort were put into understanding the problem and revising the analytical method to overcome it, but the resources for this

project were expended before the final test samples were analyzed. The only results available are those in Tables 1 and 2.

Perhaps it is significant that the ^{239}Pu concentrations are, on average, lower for the 5 gram samples with better recoveries than for the 10 gram samples. However, there is no reason to exclude the 10 gram samples when evaluating the ^{239}Pu content. Considered together, these six sample analyses give an upper limit of 1 femtogram per gram for the ^{239}Pu concentration of the Peruvian Soil 4355A. Further treatments of these data are summarized in the abstract, and the ^{239}Pu concentrations in atoms/gram are given in the following table.

Table 3. ^{239}Pu concentrations in atoms/g

Experiment Run number	NIST Peruvian Soil 4355A		^{239}Pu atoms / gram		^{242}Pu Spike Recovery (%)
	Bottle number	grams	Value	u_c, k=2	
2	1609	10.0098	2.34E+06	1.75E+05	6.3
4	8	5.0024	7.88E+05	1.46E+05	35.9
5	1609	5.0229	9.99E+04	1.67E+05	29.3
12	1333	5.0018	1.31E+06	1.25E+05	43.0
17	8	10.0013	2.05E+06	2.93E+05	3.7
24	1333	9.9945	9.66E+05	1.42E+05	7.5