Ultra-low level plutonium isotopes in the NIST SRM 4355A (Peruvian Soil-1)

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ABSTRACT

For more than 20 years, countries and their agencies which monitor radionuclide discharge sites and storage facilities have relied on the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4355 Peruvian Soil. Its low fallout contamination makes it an ideal soil blank for measurements associated with terrestrial-pathway-to-man studies. Presently, SRM 4355 is out of stock, and a new batch of the Peruvian soil is currently under development as future NIST SRM 4355A. Both environmental radioanalytical laboratories and mass spectrometry communities will benefit from the use of this SRM. The former must assess their laboratory procedural contamination and measurement detection limits by measurement of blank sample material. The Peruvian Soil is so low in anthropogenic radionuclide content that it is a suitable virtual blank. On the other hand, mass spectrometric laboratories have high sensitivity instruments that are capable of quantitative isotopic measurements at low plutonium levels in the SRM 4355 (first Peruvian Soil SRM) that provided the mass spectrometric community with the calibration, quality control, and testing material needed for methods development and legal defensibility.

The quantification of the ultra-low plutonium content in the SRM 4355A was a considerable challenge for the mass spectrometric laboratories. Careful blank control and correction, isobaric interferences, instrument stability, peak assessment, and detection assessment were necessary. Furthermore, a systematic statistical evaluation of the measurement results and considerable discussions with the mass spectroscopy metrologists were needed to derive the certified values and uncertainties. The one sided upper limit of the 95% tolerance with 95% confidence for the massic ^{239}Pu content in SRM 4355A is estimated to be 54,000 atoms/g.

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1. Introduction

Significant world-wide contamination with anthropogenic radionuclides has occurred through nuclear weapons testing, discharge from manufacturing and reprocessing facilities, and waste dumping by a number of technologically advanced countries. Nuclear waste storage facilities will inevitably deteriorate and may release further large quantities of radionuclides into the environment.

SRM 4355 (Peruvian Soil) has been serving the radioanalytical community as an anthropogenic radionuclide blank soil. The certified ^{239}Pu+^{240}Pu massic activity was certified at 7.5 μBq ^{239}Pu/g. The SRM has been used by radioanalytical laboratories as a general soil blank, and as a soil matrix that could be spiked with known amounts of anthropogenic radionuclides as a quality control material, and to validate mass spectrometric plutonium methods and verify long-term stability of the radiometrology system.

However, SRM 4355 is now out of stock and an effort to provide another blank soil SRM is underway (SRM 4355A). The first radionuclide to be assessed is plutonium by ultra-low level thermal ionization (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS). While the plutonium content in SRM 4355A was expected to be as low as that for SRM 4355, it was suspected that the content could be even lower because of the

remote location where this material was collected. The metrological challenge for the participating mass spectrometry laboratories would include extreme control over ultra-low counting rates, analytical blank, isobaric interferences, instrument stability, and peak assessment. The results of the metrological effort are summarized in this paper.

2. Peruvian soil samples

One thousand kilograms of Peruvian soil were collected from the Middle Western coastal deserts of Peru at about 20 cm depth. The material was radiation sterilized with 40 kGy of ^{60}Co gamma radiation, and shipped to the NIST. Air-jet pulverization reduced the mean particle size to approximately 10 µm, and then 250 kg were "V" cone blended. The blended material was then bottled in 100 g aliquots and re-sterilized with a minimum of 40 kGy of ^{60}Co gamma radiation.

Three randomly chosen bottles of material were shipped, along with an ampoule of gravimetrically diluted ^{242}Pu tracer solution that was gravimetrically prepared from SRM 4334H, to each of five participating laboratories with instructions to dry the material at 40 °C overnight before conducting plutonium measurements. The laboratories were further instructed to use their method of choice, to provide independent assessments of the massic concentration of the plutonium in the soil.

3. Summary of sample dissolution, separation, and measurement procedures

Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials and equipment identified are necessarily the best available for the purpose.

3.1. Los Alamos National Laboratory (LANL)

Three bottles of NIST SRM 4355A Peruvian soil were received. They came identified by the following numbers: 311, 1186, and 1857. Eight aliquots of approximately 5 g each were selected. Three aliquots were sampled from bottles 311 and 1857, and two aliquots were made from bottle 1186. The aliquots were weighed in tared 100 mL quartz tubes. The tubes were then plugged with quartz wool and reweighed. The tubes were heated in a muffle furnace at 40 °C for 24 h to obtain the dry weight. The tubes were then ramped to 550 °C and heated for 5 h to remove any organic material. Samples were transferred from the quartz tubes to 100 mL beakers with 3 M HCl and H_2O. The tubes were leached further by heating them with 3 M HCl and transferring these solutions. The samples were then carefully dried. Samples were dissolved using nitric, hydrofluoric, and perchloric acids using a ^{1}Teflon^{TM}-beaker-hot plate technique and fumed to a cake. The resulting cake was redissolved in 3 M HCl. These steps were repeated twice more on the residues until only a very small amount of brown residue was obtained. The final stock solution mass was ~180 g. Aliquots of ~70 g 3 M HCl of the stock solution,

corresponding to about 2 g of the NIST SRM each, were taken for mass spectrometry. Six of the eight aliquots were spiked with ^{244}Pu (~2×10^9 atoms/g) and ^{236}Np (~2×10^7 atoms/g). The other two aliquots were analyzed without spikes. The spikes and samples were equilibrated by drying down with 3 mL perchloric acid and 50 mg Nd carrier, and Np was removed from Pu by anion exchange separations. Resin bead sources were prepared for mass spectrometry and the samples were analyzed by TIMS using a VG^{TM} Sector 54 mass spectrometer. Ion counting ratios were collected in sequence on the Daly pulse ion collector.

3.2. Laurence Livermore National Laboratory (LLNL)

Samples were weighted in quartz tubes, dried, re-weighed, and then ashed at 650 °C for 4 h in a muffle furnace. They were transferred to Teflon^{TM} jars with HNO_3 and the quartz tubes were policed with a HNO_3-weak HF solution. ^{244}Pu was added as an internal spike. More HF was added and the samples were digested in sealed jars. The samples were uncovered, and $HClO_4$ was added and evaporated. The HNO_3–HF was again added and the samples were digested in the sealed jars. Perchloric acid was again added and fumed off. The samples were transferred to Pyrex^{TM} with HNO_3 and evaporated to $HClO_4$ fumes. Sufficient $HClO_4$ was then added to dissolve precipitates then evaporated away. This acid fuming process was to eliminate fluorine completely. The remaining material was converted by drying twice with HNO_3. The residues were refluxed in 8 M HNO_3, centrifuged and the supernatants were loaded on AG1 × 8 (100–200 mesh) columns. The columns were rinsed with 8 M HNO_3, rinsed with 9 M HCl, and Pu eluted with a 9 M HCl–HI mixture. The eluent was dried twice with HNO_3. The samples were dissolved in 9 M HCl and loaded on smaller AG1 × 8 (100–200 mesh) columns and rinsed. Plutonium was eluted with 9 M HCl–HI which was taken to dryness twice with HNO_3. The samples were dissolved in 3 M HNO_3 plus a few microliters of saturated $NaNO_2$, loaded onto 0.3 mL resin bed EiChrom TEVA^{TM} columns and rinsed with 3 M HNO_3. Plutonium was eluted with 0.1 M HCl–0.005 M HF followed by a 15:1 solution of 0.1 M HCl–HI (ca. 15:1) and evaporated to dryness. The Pu separations were repeated on the TEVA^{TM} columns and the samples were analyzed by Multi Collision-ICPMS.

The mass spectrometry analyses were made by peak hopping 239–240–242 on the axial Daly pulse-counting detector. Although the IsoProbe^{TM} 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 were collected in 30 cycles of 5 s integrations or for a total of 150 s at each mass. Data reduction for these samples was done by summing the entire signal at each mass as total counts in 150 s. 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 expanded measurement uncertainties ($k = 2$) on the net counts at each mass, and these uncertainties were used in the combined uncertainties (u_c). The uncertainties are not "total" combined uncertainties, because, for one thing, no corrections for instrumental mass bias have been applied to these data. The uncertainty propagated from the multiplicative correction factor is less than 1%. This mass bias correction and the uncertainty associated with it are both small in relation to the magnitude of the uncertainties from counting statistics.

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3.3. Oak Ridge National Laboratory (ORNL)

Soil samples were weighed into an acid-leached porcelain crucible. The filled crucibles were placed in an oven for at least 24 h at 40 °C, cooled in a desiccator, and reweighed to obtain dry weight values. The crucibles were then returned to the furnace and heated at 600 °C for approximately 8 h to destroy soil organic compounds. The weight loss for organic ashing cycle was $1.8 \pm 0.1\%$. Ashed soils were transferred from crucibles to Teflon^{TM} beakers. The crucibles were rinsed with several portions of aqua regia for a total of 50 mL. The soils were mixed for about 10 min in the aqua regia before the ORNL ^{244}Pu spike was added. Sixty-five microliters of ORNL ^{244}Pu, equivalent to 2.5 pg Pu, were weighed in a Teflon^{TM} vial to five significant digits. A total of 50 mL HF was added to the spiked samples. The beakers were covered and heated for two days before the solutions were dried down. Fifty milliliters of HF was again added to each residue, heated overnight, and evaporated. At this point remaining organic compounds in the samples were destroyed by adding 10 mL concentrated HCl and 45 mL 30% H_2O_2 (very slowly) under modest heat to maintain control over the reaction. The samples were digested overnight and then dried. The residues were digested twice with 20 mL HCl, followed by three digestions with 50 mL concentrated HNO$_3$. The treated residues were brought up in 90 mL 1 M HNO$_3$ and heated for 4 h to dissolve the majority of solids. Approximately 0.35 g H_3BO_3 and 0.1 g $NaNO_2$ were added to the cooled solutions. After 30 min the solutions were centrifuged to remove small amounts of white residue. Ten milligrams of La carrier were then added to the stirred samples as the co-precipitation agent. The acidity of the samples was reduced to pH 4 with concentrated NH$_4$OH, then further reduced to pH 9 with $(NH_4)_2CO_3$. After overnight stirring, the precipitate was collected by centrifugation. The precipitates were washed twice with 40 mL NH$_4$OH at pH 9 to remove entrained contaminants. The washed precipitate was dissolved in 6 mL concentrated HNO$_3$, and then diluted with 20 mL 0.45 M HNO$_3$ to reduce the acidity for subsequent column chemistry. The acidified samples were again centrifuged to remove any undissolved material that might plug the chemical separation columns. Each dissolved sample was processed through three successive TEVA^{TM} Eichrom columns. TEVA^{TM} columns were conditioned with 12 mL 3 M HNO$_3$ to reduce the amount of column stationary phase that might bleed into the final plutonium fractions. The dissolved samples were treated with 0.5 g $Al(NO_3)_3$ and 0.3 g NaNO$_2$ and loaded onto the TEVA^{TM} columns. The columns were washed with 15 mL 3 M HNO$_3$. Three milliliters of 9 M HCl was then added to convert the columns to the chloride form. Plutonium was eluted with 12 mL 0.1 M HCl–0.06 M HF–0.4 M HI. The purified Pu fractions were dried down in a HEPA-filtered evaporation box. Residues were twice dissolved in 50 μL aqua regia, then 25 μL 8 M HNO$_3$ with 25 μL 30% H_2O_2 to destroy any organic compounds that may have bled from the TEVA^{TM} column. The residues were brought up in 1 mL 3 M HNO$_3$; the Pu fractions were further purified using two additional TEVA^{TM} columns. Finally, the residues were heated at 600 °C for several hours to assure complete destruction of column organics. The treated samples were brought up in 0.7 mL 2% HNO$_3$ and warmed lightly to dissolve the Pu fraction. The final samples were submitted for analysis.

Samples are introduced to the ICP-MS at a rate of 100 μL/s. A two-step routine was used to acquire sample count data. In the first step the plutonium isotopic composition of each sample is acquired for 100 s in the static mode on multi-ion counters (MICs). This is followed by a second step in which the count rate for uranium in the sample is collected for 20 s on a Faraday cup (FC). The FC and MIC detectors are aligned to maximize ion count rate

using NBL CRM 137 plutonium isotopic standard. The same standard is used to match the gain sensitivity among the MIC detectors. Two percent nitric acid solution was analyzed using the same data acquisition protocol before each sample or standard to acquire background counts at each mass position. A 60 s wash with 2 M HNO$_3$–0.15 M HF and a 60 s rinse with 5% HNO$_3$–0.01 M HF are used to clean the instrument transfer lines between each sample.

Data reduction includes correcting the counts at mass 239 for the presence of uranium hydride. Additionally, a mass bias correction is performed by running isotopic standard NBL CRM 137 at a concentration of 0.5 pg/g before and after the sample in question, and averaging the response of both standards for each isotopic ratio. The averaged values of the measured ratios of the bias standards are divided by the certified values to determine the bias correction. The mass bias for mass 239 is assumed to be a value of one. Counts at remaining masses are multiplied by the average mass bias value to correct the count data. The isotopic composition of the spiked samples, together with that of the ORNL ^{244}Pu spike, is input into the isotope dilution computations.

3.4. Pacific Northwest National Laboratory (PNNL)

Soils were weighed out into 250 mL glass beakers and were dried at 40 °C to obtain the dry weight of the aliquots. After obtaining dry weights, the soil aliquots were muffled at 600 °C to remove most organic matter. The mass difference following this treatment was approximately 3%. After cooling and weighing, soils were quantitatively transferred to 400 mL Teflon^{TM} beakers and digested by heating with a series of inorganic acids, including concentrated HNO$_3$, HCl, HF, and HClO$_4$. The final soil digestate solution was diluted gravimetrically to approximately a 200 mL volume using 1.2 M HCl. Approximately 2 g soil-equivalent aliquots of each of the digestates were sampled for processing and analysis. ^{244}Pu tracer was added to each aliquot plus the chemical process blank, and was equilibrated with the sample by heating to near dryness with concentrated HClO$_4$. The separations chemistry procedures developed at PNNL for low-level Pu samples have been reported elsewhere (Beasley et al., 1998a–c; Dai et al., 2001, 2002; Kelley et al., 1999). Briefly, they entail concentrating the Pu by co-precipitation with neodymium oxalate and ferric hydroxide solids, then purifying by use of two anion-exchange columns. Preparation of the source for analysis by a triple-stage TIMS is then achieved by concentrating the Pu into a single anion-exchange bead through a series of equilibration steps from successively smaller volumes.

3.5. Savannah River National Laboratory (SRNL)

The soil samples were weighed and then dried overnight at 105 °C, allowed to cool to room temperature, and reweighed. No net changed in weight was observed in any of the samples. They were then ashed at 525 °C for at least 8 h, cooled, and reweighed. The weight losses on ashing were generally about 0.1% or less. The chemical processing was based on work by Moreno et al. (1997). The samples were transferred by weight to 250 mL Teflon^{TM} beakers. They were slurried with 25 mL of 1 N HNO$_3$. Aliquots of the NIST supplied spike containing 3×10^{10}–5×10^{10} atoms (2–3 mBq) of ^{242}Pu were transferred to each beaker by weight. All acids used in the chemistry were Fisher^{TM} Optima^{TM} Grade diluted with Type I water and stored in Teflon^{TM} bottles. A 50 mL portion of concentrated HF was added to each beaker and they were evaporated to dryness on a hotplate. The HF addition and evaporation was repeated once more. Three, 50 mL portions of

concentrated HNO_3 were successively added to each sample and evaporated. A 50 mL portion of concentrated HCl and 3 g of boric acid were then added to each sample and evaporated to dryness. Three 10 mL portions of concentrated HNO_3 were added to each residue and evaporated to dryness. The sample was dissolved in 70 mL of 1 N HNO_3 and centrifuged. The clear solutions were returned to beakers and about 0.5 g of sodium nitrite was added to each solution and were heated to stabilize the Pu in the +4 state. The plutonium was co-precipitated with iron hydroxide from ammonium hydroxide/ammonium carbonate solution and centrifuged. The mixed hydroxides were dissolved in about 25 mL of 8 N HNO_3. The plutonium fractions were purified by separation on an 15 mL anion exchange column from 8 N HNO_3. The column was washed repeatedly with 8 N HNO_3 to remove iron and other impurities. The column was washed with 8 N HCl to remove thorium and convert the column to chloride form. The plutonium was eluted from the column with ammonium iodide in 8 N HCl. The residue was digested several times with 8 N HNO_3 and the plutonium was re-adsorbed onto a second 5 mL anion column. The washings with HNO_3 and HCl were repeated and the plutonium was again eluted with ammonium iodide in 8 N HCl. All samples were run through a last anion column separation from HNO_3 on a 1 mL column. The plutonium was removed from the column with 3 mL of concentrated HBr directly into a small, conical Teflon^{TM}

vial for filament mounting for TIMS. The chemical recoveries averaged 57% with a standard deviation of 10%. The Nonproliferation Technology Section (NTS) TIMS has been in operation in basically the same mode for the past 30 years. Analytical results on NIST SRMs such as 4350B are essentially identical over that period. The method is summarized in Buesseler and Halverson (1987) and the references contained in this article describe all of the components of the analysis in detail. The system uses a single phototube detector and "mass steps" or scans the mass peaks of interest according to a programmed time sequence. Mass 245.5 is included in the scans as a real-time "background". The measurement time at mass 242 is maintained at 2% of the total time. For a useable analytical data a run using this protocol gives 10^4–10^6 counts for 10 pg of ^{242}Pu.

4. Uncertainty issues

The dominant sources of mass spectrometric measurement uncertainty are due to the statistical detection of pulses from samples, reagent blanks, and background sources due to the extremely low plutonium massic content in the soil. Chemical purification issues were of secondary importance—variable chemical yield, isobaric interferences (e.g., ^{238}UH), incomplete chemical separations of thorium and platinum (when stripped
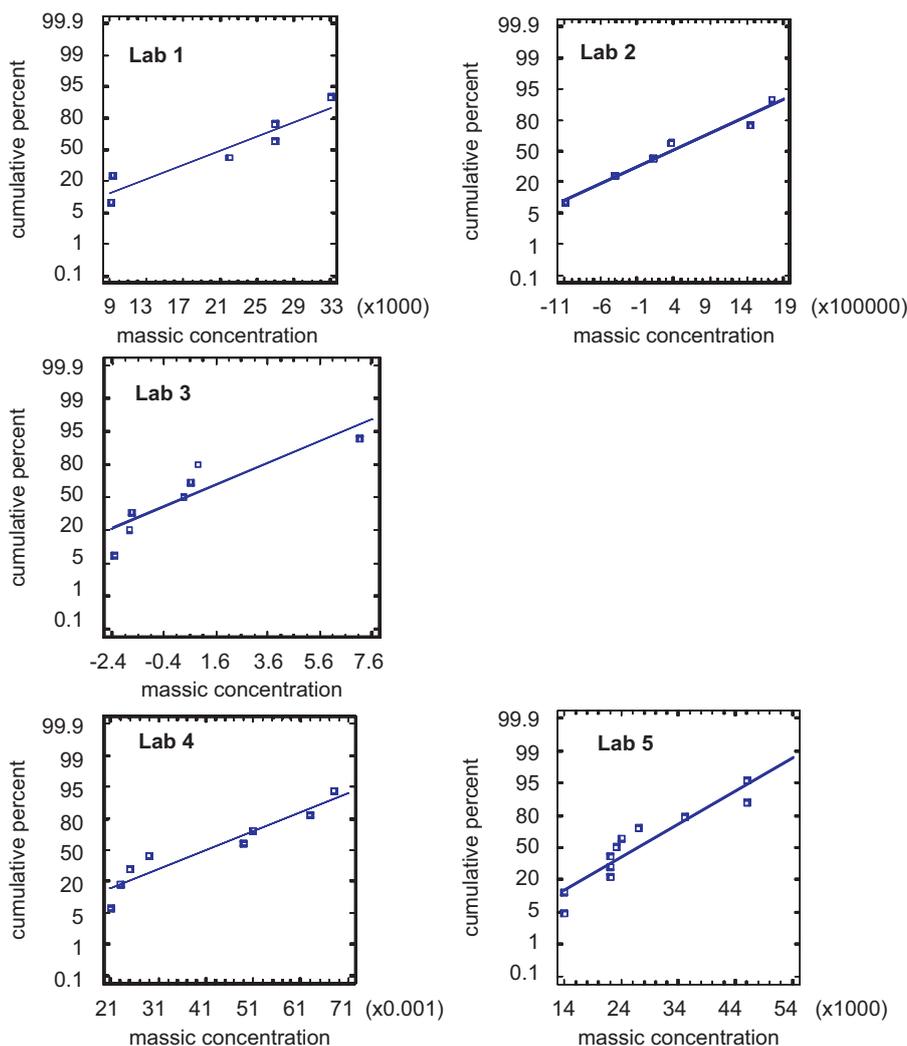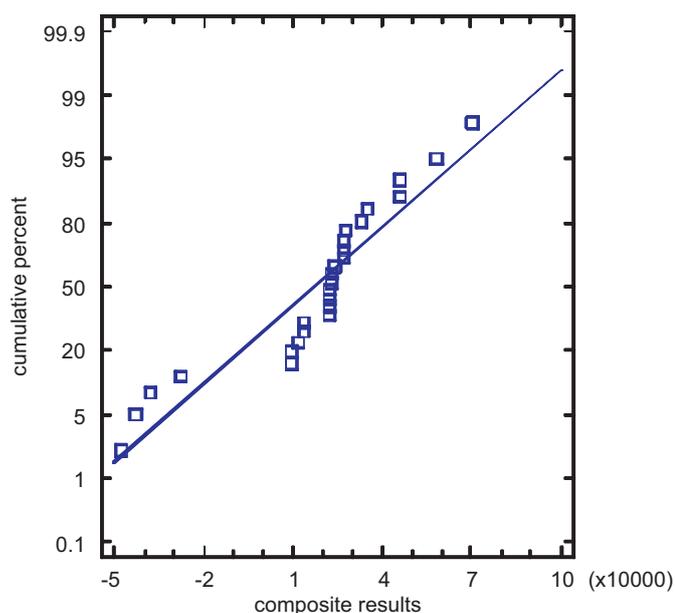

Fig. 1. Normal probability plots of individual laboratory measurement of ^{239}Pu atoms/g of Peruvian soil. The abscissas (x-axis) are the ordered massic concentration of the measurements, and the ordinates (y-axis) are the normal order statistic medians.

Fig. 2. Normal probability plots of the composite measurements of ^{239}Pu atoms/g of Peruvian Soil. The abscissa (*x*-axis) is the ordered massic concentration of the measurements, and the ordinate (*y*-axis) is the normal order statistic median.

after alpha-particle spectroscopic measurements). Instrument based issues such as calibration memory, mass bias corrections, variation in detection over measurement runs, and atomic masses and abundances were of tertiary importance.

5. Results

Each of the laboratories reported measurement results of highest confidence. These data are displayed in Fig. 1 as normal probability plots. The abscissa (*x*-axis) depicts the ordered measurement results, and the ordinate (*y*-axis) depicts the normal order statistic medians. A collection of data is consistent with a normal statistical population when they approximate a straight line on the normal probability plot. All of the individual plots are consistent with normal distributions and indicate statistical control over their analytical processes. Initially, all laboratories indicate an upper limit for the ^{239}Pu massic content in the Peruvian Soil (SRM 4355A) to be less than 2.5×10^{6} atoms/g (1 fg/g).

While results from laboratories 3 and 4 are consistent with this upper limit, they are not used for further evaluation of the data because of dominance by the analytical blank. The remaining results were considered as a homogeneous set that could be combined to gain more statistical power and is displayed in Fig. 2

as a composite normal probability plot. This normal probability plot indicated a homogeneous data set. The standard deviation of these measurement results is 13,500 atoms ^{239}Pu/g. Because of the uncertainty in this determination, a one sided upper limit of the 95% tolerance with 95% confidence is estimated to be 54,000 atoms ^{239}Pu/g.

6. Conclusions

Each laboratory invested considerable effort to meet the challenge of making measurements at ultra-low massic concentration of plutonium in the Peruvian Soil (SRM 4355A). While conducting these measurements, extreme care was exercised to assure process control that strengthen the laboratories analytical effectiveness.

The one sided upper limit of the 95% tolerance with 95% confidence for the massic ^{239}Pu content in SRM 4355A is estimated to be 54,000 atoms/g. At this level, the material can be used as a blank material for general anthropogenic radio-nuclide measurements. Furthermore, SRM 4355A can be used for methods development and as soil matrix for spiked QC materials as tools to help establish legal defensibility of measurement results.

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