Rapid Method to Determine Plutonium Isotopes in Steel Samples

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Abstract

The rapid measurement of plutonium isotopes in steel samples is very important in the event of a radiological emergency as well as for the characterization of nuclear decommissioning samples. A new method for the determination of plutonium isotopes in steel samples has been developed at the Savannah River Environmental Laboratory. The new method employs a rugged acid digestion method that includes hydrofluoric acid, followed by a single preconcentration step to rapidly preconcentrate the plutonium isotopes and remove most of dissolved steel sample matrix. A fusion option improves ruggedness when soil or concrete is present and can be implemented after steel dissolution. The Pu isotopes are separated using an extraction chromatographic resin and measured by alpha spectrometry. The method can also be adapted for measurement by inductively-coupled plasma mass spectrometry. This approach has a sample preparation time for steel samples of 6-8 hours.

Introduction

During a national radiological emergency, the laboratories providing analytical support will be faced with an overwhelming number of environmental and bioassay samples. Many of the environmental samples with likely consist of urban matrices, building materials such as concrete, brick or asphalt. If a radiological event occurs such as a radiological dispersive device (RDD), an Improvised Nuclear Device

(IND) or a nuclear accident such as the accident at the Fukushima Nuclear Power Plant in March, 2011, the use of rapid methods will be essential to quickly assess the scope and impact of the event. If such an emergency occurs, there will be an urgent need for rapid radiochemical analyses to support dose mitigation and environmental clean-up. [1,2,3,4] In addition to other environmental samples, steel samples from building debris or remaining structures must to be analyzed quickly to ascertain the radiological content. It is very important to couple rapid, effective sample digestion and preconcentration techniques with rapid, innovative column purification methods so that building material samples can be analyzed for radiological contaminants quickly. The use of vacuum-assisted separations and stacked resin cartridges containing highly selective extractant-coated chromatographic resins allows rapid sequential separations of multiple analytes in an emergency. This includes recently published methods for soil, concrete, limestone and marble. [5, 6] These radiochemical methods are both rapid and reliable, offering highly defensible quality.

There is also an emerging need for rapid, reliable cost-effective methods to support decommissioning of older nuclear facilities, especially in Europe. A significant reduction in very high decommissioning costs by the development and implementation of vastly improved measurement techniques is necessary. [7] The application of new, streamlined radiochemical techniques to nuclear decommissioning samples or other routine environmental samples can reduce labor costs and facilitate improved analytical efficiencies. Furthermore, the defensibility of results is very important not only in a radiological emergency but also for nuclear decommissioning samples. Effective sample dissolution is paramount. The ruggedness of the dissolution technique used is very important, and it is well-known that acid leaching alone may not completely digest refractory particles, particularly ones dispersed in an explosion. [6, 9,10] Consistent with this need, a fusion method for 10-20 g soil and concrete samples was recently published by this laboratory. [8] While sodium hydroxide fusion has been used with great success for soil, concrete, asphalt, vegetation and other solid samples, steel samples cannot adequately dissolved sodium hydroxide fusion alone. However, once the steel sample is effectively digested first with acid, the fusion can be applied to digest residual soil, concrete or refractory residues remaining. A rigorous acid digestion method for steel was investigated, with and without hydrofluoric acid, along with a secondary fusion of the acid digested residue for enhanced ruggedness.

Hou et al. surveyed a wide range of analytical separation methods for Pu in waters and environmental solid samples [11]. Methods included varied combinations of ion exchange and/or extraction chromatographic techniques. Chemical recoveries for Pu typically varied between 40-85%. Improvements in chemical yield should help to reduce detection limits and improve overall method ruggedness.

Tavčar et al. [12] reported a method to determine actinides in up to 10g soil and sediment samples by leaching samples with strong nitric acid, filtration, evaporation. The residue was redissolved in 1M HNO_3, and following valence adjustment, the acid concentration was increased to 8M HNO_3. Samples were loaded onto Dowex 1x8 anion resin, and Pu was eluted using 9M HCl with iodide ion present as a reductant. Np was eluted with 4M HCl. The chemical yields for Pu and Np were ~60% and ~40%, respectively. The acid leach used in this method would not effectively digest refractory particles that may be present in the sample.

A new method has been developed at the Savannah River Environmental Laboratory to measure Pu isotopes in steel samples. The method employs preconcentration technology that effectively manages the high iron content resulting from the dissolution of the steel sample, and keeps the sample preparation volumes small so that rapid column separation can be achieved.

Experimental

Reagents

The extraction chromatography resin employed in this work is TEVA Resin® (Aliquat ™ 336), TRU-Resin® (octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) in tri-n-butylphosphate (TBP) from Eichrom Technologies, Inc., (Lisle, Illinois, USA) and Triskem International (Bruz, France). Nitric, hydrochloric and hydrofluoric acids were prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS (American Chemical Society) reagent grade. Radiochemical isotope standards ^{242}Pu and ^{238}Pu were obtained from Eckert Zeigler Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 74 mBq mL^{-1} for this work.

Procedures

Column preparation. TEVA Resin was obtained as 2 mL cartridges. Small particle size (50-100 μm) resin was employed, along with a vacuum extraction system (Eichrom Technologies). The small particle size coated support, with enhanced surface area, improves column separation efficiencies. Flow rates of ~1-2 drops sec^{-1} were typically used for this work, slower on sample loading and final elution steps, faster for the rinses used to remove sample matrix interferences. To facilitate enhanced removal of interferences, column reservoirs and connector tips in the lid were changed after sample loading and prior to the final elution of plutonium isotopes.

Sample Preparation. Figure 1 shows the sample preparation flowchart for Pu isotopes in steel samples. 304 stainless steel disks (~18% chromium, ~8% nickel) weighing approximately 1g were used for this testing. Most of the tests were performed using 1 or 2g steel, but one test was carried out using 5g of 304 stainless steel. Pu isotopes were added to each steel sample to test the method performance. To test the ruggedness of the steel digestion for refractory particles, MAPEP 24 soil aliquots (~0.25 g) were also added to the steel sample aliquots in some of the tests. The MAPEP soil samples were provided by Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA. MAPEP 24 soil standard was chosen because the soil contains refractory ^{239}Pu in the soil. Successful analysis would indicate analytical method ruggedness and applicability when refractory particles are present.

Each sample was placed in a 250 mL Teflon beaker and spiked with a ^{242}Pu tracer. A ^{236}Pu tracer could have been used to allow the simultaneous collection and purification of ^{237}Np but this was not done in this study. [13] Twenty milliliters of 12M HCl, 5 mL 15.8M HNO_3, and 5 mL 28M HF were added to each beaker and the samples were digested to dryness on a hot plate on medium heat to avoid any splattering. After the samples were taken to dryness, 10 mL 12M HCl, 1 mL 15.8M HNO_3, and 1 mL 28M HF were added to each beaker and the samples were evaporated to dryness on a hot plate. Finally, 5 mL 12M HCl and 3M HNO_3-0.25M H_3BO_3 were added to each beaker to remove fluoride. This step was found to facilitate complete removal of the sample residue from the beaker. The contents of each beaker were evaporated to dryness on a hot plate.

To dissolve the sample residue, 25 mL 1M HCl was added to each beaker. Each sample was warmed on a hot plate to dissolve the residue and the dissolved sample was transferred to a 225 mL centrifuge tube. The dissolution and transfer with 25 mL 1M HCl were repeated two more times, warming each beaker as needed. Each sample was diluted in the 225 mL tube to 170 mL with 0.01M HCl and mixed well. To precipitate the Pu from the dissolved steel sample, 5 mg lanthanum, 2 mL 1.25M calcium nitrate and 2 mL 20% $TiCl_3$ were added to each 225 mL tube. After mixing each sample tube well, the tubes were cooled in ice bath for ~15-20 minutes to facilitate complete precipitation. Each sample was centrifuged at 3500 rpm for 6 minutes and the supernate was discarded. Each sample precipitate was redissolved in 7 mL 3M HNO_3-0.25M boric acid and transferred to a 50 mL centrifuge tube. To rinse the 225 mL tube, 7 mL

3M HNO_3 and 7 mL 2M $Al(NO_3)_3$ were added and the rinses were transferred to each 50 mL tube. Each 50 mL sample tube was mixed well, warmed briefly in a hot bath and centrifuged to check for any solids. The sample liquid was transferred to a new 50 mL tube to remove any residual solids.

Figure 2 shows a fusion option that can be used for additional digestion rigor when a steel sample is mixed with soil or concrete or when refractory particles may be present. Samples were placed into 250mL low form zirconium crucibles. Twenty milliliters of 12M HCl and 5 mL 15.8M HNO_3 were added to each crucible and the samples were digested to dryness on a hot plate on medium heat. HF was omitted in this option because it will attack the zirconium crucibles. After the samples were taken to dryness, 10 mL 12M HCl and 1 mL 15.8M HNO_3 were added to each beaker and evaporated to dryness on a hot plate. Sodium hydroxide pellets were added and the sample was fused and processed similar to the fusion described previously [5], except that no additional Fe was added. In this fusion option, an initial precipitation is performed using iron and titanium hydroxide enhanced with calcium phosphate to remove the high levels of hydroxide. Following the initial precipitation, the samples are dissolved in dilute HCl and a calcium fluoride precipitation was performed to remove the Fe, Ti and silicates.

While this new method will need to be validated for effectiveness on other types of steel, no adverse sample matrix impact from variations in the chromium, nickel, carbon and other constituent content is expected. No problems are anticipated since iron, the key matrix component in steel, is effectively removed during the final precipitation step, and chromium, nickel, carbon and the other constituents do not interfere with the TEVA Resin separation methods. [14]

Column separation for Plutonium. Plutonium is separated using a 2 mL TEVA Resin cartridge, using vacuum box flow. The TEVA Resin method used is similar to what was published for the determination of actinides in limestone and marble samples. [5] After cooling the samples to room temperature, a valence adjustment was performed on the load solution by adding 1.25 mL 1.5M ascorbic acid. Typically 1mg Fe is added along with ascorbic acid to facilitate Pu reduction, but since a small amount of residual Fe was present in the load solution from the steel sample, no extra Fe was added. Following a three minute wait to ensure reduction of plutonium to Pu(III), 1 mL 3.5M $NaNO_2$ was added to oxidize plutonium to Pu(IV). After waiting 10 minutes, the sample load solutions were loaded onto a 2 mL TEVA Resin column at approximately 1 drop per second. Sample tubes were rinsed with 5 mL 3M HNO_3 which was transferred to the TEVA Resin column and allowed to pass through the resin at ~1-2 drops per second.

It has been found that U (VI) can be partially reduced to U (IV) during the valence adjustment steps, with Fe(II) and ascorbic acid present. As a result a fraction of the uranium present may be retained on TEVA Resin despite the addition of nitrite ions to oxidize Pu(III) to Pu(IV). While Pu(III) oxidation to Pu(IV) with nitrite in nitric acid is nearly instantaneous, waiting 10 minutes or longer after adding the sodium nitrite facilitates re-oxidation of U(IV) to U(VI). Adding a small amount (50 µL) of 30% hydrogen peroxide to the 3M HNO_3 tube rinse also helps ensure than any uranium that may have been reduced to U(IV) (possibly also due to traces of Ti(III) remaining from the precipitation step) is reoxidized to U(VI), and not retained on the TEVA Resin. While additional uranium decontamination will be achieved during cerium microprecipitation source preparation, uranium contamination could be a problem if electrodeposition is used. It is also desirable to remove U very effectively if inductively-coupled plasma mass spectrometry (ICP-MS) will be used to measure ^{239}Pu, since ^{238}U can lead to isobaric interference in the ^{239}Pu assay.

Each TEVA Resin column was rinsed with 15 mL of 3M HNO_3 at ~2 drops per second, followed by Th elution with 20 mL 9M HCl at 1-1.5 drops per second. After the elution of Th from TEVA Resin, a column rinse of 5 mL 3M HNO_3 at ~2 drops per second to reduce any extractant bleed-off. Pu is eluted at ~1 drop per second with 20 mL of 0.1M HCl-0.05M HF-0.01M $TiCl_3$ for measurement by alpha spectrometry. Ti (III) reductant helps remove Pu from TEVA Resin as Pu(III). When electrodeposition of the purified eluents will be employed, sodium formaldehyde sulfoxylate (rongalite) reductant or hydroxylamine hydrochloride should be used instead of $TiCl_3$, as these reductants are compatible with ICP-MS instrumentation.

Cerium fluoride microprecipitation was used to prepare the purified samples for measurement by alpha spectrometry. Fifty micrograms of Ce (as Ce(III) nitrate standard), 0.5 mL 30wt% H_2O_2 and 1 mL 28 M HF were added to each Pu eluent. The hydrogen peroxide ensures additional removal of any uranium present, by ensuring oxidation of U(IV) to U(VI). After waiting 15 minutes, the solution was filtered using a 25 mm polypropylene filter (0.1 µm pore size disposable Eichrom Resolve™ filter funnel). Each sample tube was rinsed with ~5 mL deionized water, adding the rinse to the filter. After the entire sample was filtered, ~3 mL of ethanol was added to each filter to facilitate drying. The filters were heated briefly under a heat lamp to ensure dryness. Samples were counted for 16 hours to ensure sufficient counts were obtained and reduce counting uncertainty to effectively evaluate performance on the spiked samples. In an emergency, shorter count times may be used, with appropriate adjustments to tracer activity levels.

While alpha spectrometry was used in this work to demonstrate the effectiveness of the new method, the method can be successfully adapted for ICP-MS, based on past experience in this laboratory. The sample can be counted for ^{238}Pu by alpha spectrometry and then redissolved from the sample test source filter using warm 3M HNO_3-0.25M boric acid. The dissolved Pu isotopes can be processed quickly through TEVA Resin, eluted and measured by ICP-MS to determine the ^{239}Pu / ^{240}Pu ratio. This “hybrid” approach allows both ^{238}Pu ,^{239}Pu / and ^{240}Pu to be determined, if needed.

The CeF_3 microprecipitation step with hydrogen peroxide present can remove an additional 1000 x ^{238}U, so this approach, in combination with another TEVA Resin separation, can result in extremely high ^{238}U decontamination factors. If the redissolved sample is reprocessed through TEVA Resin, a Pu eluent solution of 0.05M HCl-0.025M HF-0.02M hydroxylamine hydrochloride may be used to allow ICP-MS assay.

For improved ^{238}U removal that will facilitate the measurement of ^{239}Pu and ^{240}Pu by ICP-MS, Pu can be eluted directly from TEVA Resin as Pu^{+3} (with 15-20 mL 3M HNO3-0.1M ascorbic acid-0.02M Fe^{+2}) through a coupled UTEVA Resin cartridge (1mL) onto a stacked DGA Resin cartridge to achieve very high uranium decontamination factors (~$1x10^7$). This eliminates eluting and reloading Pu to TEVA Resin multiple times. After a single elution and rapid clean-up on DGA Resin, Pu isotopes can be eluted from DGA Resin with a 5mL volume of 0.02M HCl-0.005M HF (or also with -0.01M hydroxylamine hydrochloride) and assayed by ICP-MS. [15]

Apparatus

Plutonium isotopic measurements were performed by alpha-particle pulse-height measurements using Passivated Implanted Planar Silicon (PIPS) detectors. The PIPS detectors have an active surface of 450 mm^2. The nominal counting efficiency for these detectors is 28-30%. The distance between the sample and detector surface is ~3 mm.

Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 mL plastic tubes were used. Two boxes were connected to a single vacuum source by using a T-connector and individual valves on the tubing to each box.

Results and Discussion

Table 1 shows the individual results for the determination of Pu isotopes in five 2 g steel samples spiked with ^{238}Pu using this rapid method, the TEVA Resin separation and alpha spectrometry. The average $^{239/240}$Pu result was 37.7 mBq smp^{-1}, with a 1.9% bias and SD (standard deviation) of 1.6 7 mBq smp^{-1}. The average tracer recovery for ^{242}Pu was 89.3% ± 2.3% (SD). The high ^{242}Pu tracer recoveries and excellent results for $^{239/240}$Pu versus known values indicate the robust nature of the sample preparation and measurement steps. The Full Width Half Maximum (FWHM) results for the ^{242}Pu tracer peaks show good alpha peak resolution. The uncertainties for the individual $^{239/240}$Pu results were typically ± 7-8% (1 SD), with a 16 hour count time. Shorter count times may be used in a radiological emergency, with higher tracer activity levels added to minimize counting uncertainty for the tracer used.

Table 2 shows the individual results for the determination of Pu isotopes in four 2 g steel samples spiked with 0.25g MAPEP 24 soil containing refractory Pu-239/240 using this rapid method with hydrofluoric acid not included. The Pu was separated using TEVA Resin separation and measured by alpha spectrometry. The average $^{239/240}$Pu result was 1.094 mBq smp^{-1}, with a 95.5% bias and SD (standard deviation) of 0.38 mBq smp^{-1}. The average tracer recovery for ^{242}Pu was 89.4% ± 7.3% (SD). The very low $^{239/240}$Pu results show the importance of using HF in the steel digestion step when refractory Pu is present.

Table 3 shows the individual results for the determination of Pu isotopes in six 2 g steel samples spiked with 0.25g MAPEP 24 soil containing refractory Pu-239/240 using this rapid method with hydrofluoric acid included. The Pu was separated using TEVA Resin separation and measured by alpha spectrometry. The average $^{239/240}$Pu result was 23.36 mBq smp^{-1}, with a -4.7% bias and SD (standard deviation) of 0.93 mBq smp^{-1}. The average tracer recovery for ^{242}Pu was 98.9% ± 6.6% (SD). The high ^{242}Pu tracer recoveries and excellent results for $^{239/240}$Pu versus known values indicate the robust nature of this rapid method with HF included in the acid digestion. The Full Width Half Maximum (FWHM) results for the ^{242}Pu tracer peaks show good alpha peak resolution. The uncertainties for the individual $^{239/240}$Pu results were typically ± 7-8% (1 SD), with a 16 hour count time.

Table 4 shows the individual results for the determination of Pu isotopes in five 1 g steel samples plus 0.5g concrete. The samples were spiked with 0.25g MAPEP 24 soil containing refractory Pu-239/240 and analyzed using this rapid method using the sodium hydroxide fusion option. The Pu isotopes were separated using TEVA Resin separation and measured by alpha spectrometry. The average $^{239/240}$Pu result was 24.4

mBq smp^{-1}, with a -0.2% bias and SD (standard deviation) of 1.6 7 mBq smp^{-1}. The average tracer recovery for ^{242}Pu was 98.9% ± 6.6% (SD). The high ^{242}Pu tracer recoveries and excellent results for $^{239/240}$Pu versus known values indicate the robust nature of this rapid method using the fusion option. The Full Width Half Maximum (FWHM) results for the ^{242}Pu tracer peaks show good alpha peak resolution. The uncertainties for the individual $^{239/240}$Pu results were typically ± 7-8% (1 SD), with a 16 hour count time.

Table 5 shows the individual results for the determination of Pu isotopes in four 5 g steel samples spiked with ^{238}Pu. The acid digestion method was scaled up with increased acid volumes, and 500 mL centrifuge tubes were used to accommodate the larger volumes. After digestion and preconcentration, the TEVA Resin separation was used along with alpha spectrometry to measure the Pu isotopes. The average ^{238}Pu result was 38.3 mBq smp^{-1}, with a 3.4% bias and SD (standard deviation) of 1.0 mBq smp^{-1}. The average tracer recovery for ^{242}Pu was 92.1% ± 14.3% (SD). The average ^{242}Pu tracer recoveries and excellent results for $^{239/240}$Pu versus known values indicate the robust nature of method, even with a 5g steel aliquot.. The variations in the tracer recover likely result from the more difficult sample matrix with 5g of steel digested. The Full Width Half Maximum (FWHM) results for the ^{242}Pu tracer peaks show good alpha peak resolution. The uncertainties for the individual $^{239/240}$Pu results were typically ± 7-8% (1 SD), with a 16 hour count time.

Figure 3 shows an example of the spectra of Pu isotopes in a 2g steel sample. The ^{242}Pu tracer recovery was 91.9% and the Full Width Half Maximum (FWHM) was 33 keV, showing acceptable alpha peak resolution and good tracer recovery. The ^{239}Pu peak labeled on the spectra represents ^{239}Pu plus ^{240}Pu, since these isotopes have overlapping alpha energies.

The MDA (Minimum Detectable Activity) for Pu isotopes using this method with measurement by alpha spectrometry was calculated according to equations prescribed by Currie: [16]

$$\text{MDA} = [2.71+4.65\sqrt{B}]/\ (CT*R*V*Eff*\mathbf{A}*0.060)$$

where B = Total Background counts, = BKG (rate) * sample count time ; CT = sample count time (min) R = Chemical Recovery; V = Sample aliquot **(**g) ; EFF = Detector Efficiency ; A = Isotopic abundance (in most cases this will be ~1) ; 0.060 = conversion from dpm to mBq.

The MDA (minimum detectable activity) for the alpha spectrometry results can be adjusted as needed, depending on the sample aliquot and count time. For a 2g steel aliquot, the method MDA for the plutonium isotopes with a 16 hour count time is ~250 uBq g^{-1}.

While the fusion option provides additional ruggedness for this method, it does add processing time. In an emergency, the aqua regia plus HF acid digestion method would likely be acceptable, unless very high fired Pu was present. In the MAPEP 24 soil preparation, the Pu was taken up to ~900°C to form refractory Pu by the Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA. For high fired material such as ^{238}Pu oxide used as radioisotope thermoelectric generator, the fusion option should be utilized. [17] This study does illustrate why a simple nitric acid leach of the steel surface alone and processing of the leachate for Pu without HF attack may give highly unreliable results, if refractory Pu is present. It should be noted that it would be very easy to include other actinides in this steel method using the sequential separation techniques described previously. [5, 6]

Conclusions

A new rapid method to determine plutonium isotopes in steel samples has been developed that effectively digests steel samples (or steel plus concrete) for samples received in a radiological emergency or form routine nuclear decommissioning samples. The new method features a rapid preconcentration and separation of Pu isotopes with high chemical yields and effective removal of interferences. The method digests the samples with ruggedness and is very flexible, allowing several different measurement options.

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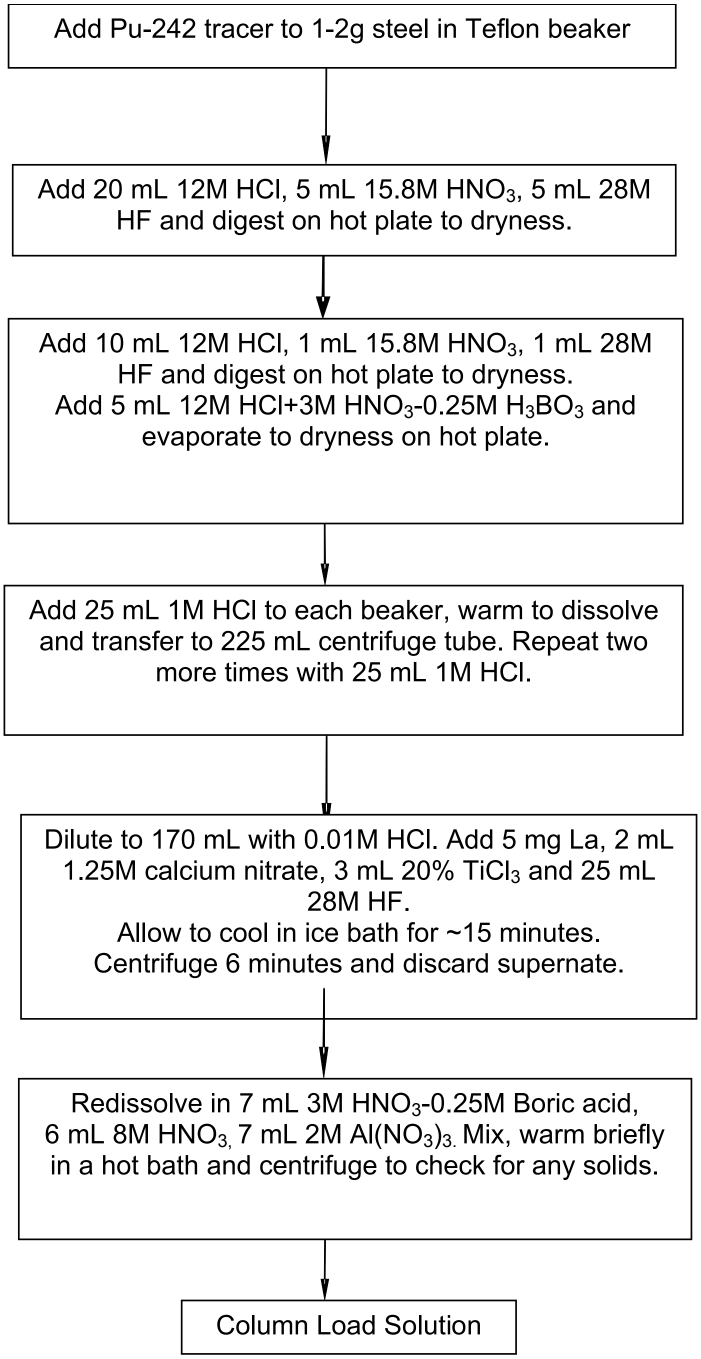
Figure 1 Steel Dissolution with Pu Isotopes Sample Preparation Method



Add Pu-242 tracer to 1-2g steel in Teflon beaker

Add 20 mL 12M HCl, 5 mL 15.8M HNO_3, 5 mL 28M HF and digest on hot plate to dryness.

Add 10 mL 12M HCl, 1 mL 15.8M HNO_3, 1 mL 28M HF and digest on hot plate to dryness.
Add 5 mL 12M HCl+3M HNO_3-0.25M H_3BO_3 and evaporate to dryness on hot plate.

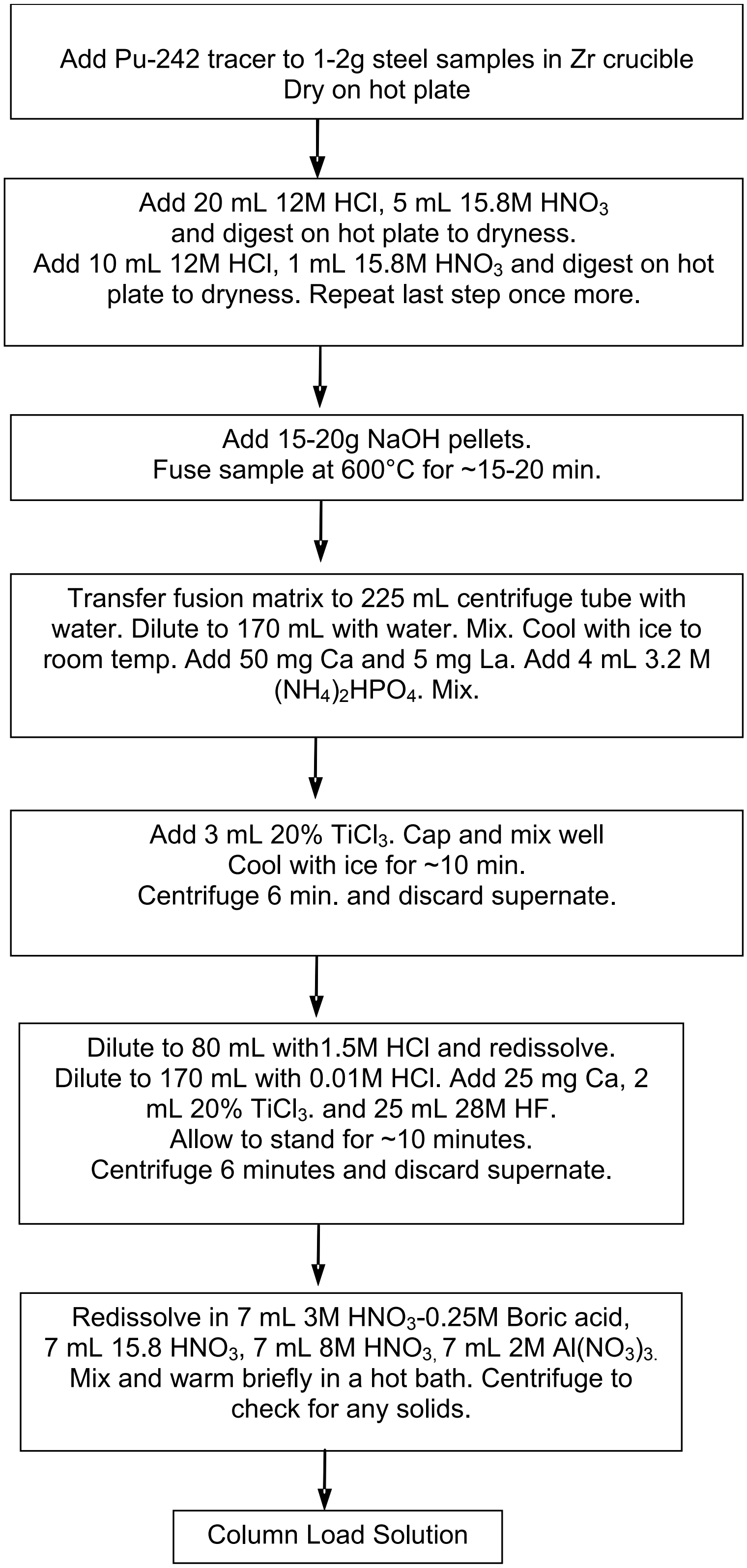
Add 25 mL 1M HCl to each beaker, warm to dissolve and transfer to 225 mL centrifuge tube. Repeat two more times with 25 mL 1M HCl.

Dilute to 170 mL with 0.01M HCl. Add 5 mg La, 2 mL 1.25M calcium nitrate, 3 mL 20% $TiCl_3$ and 25 mL 28M HF.
Allow to cool in ice bath for ~15 minutes.
Centrifuge 6 minutes and discard supernate.

Redissolve in 7 mL 3M HNO_3-0.25M Boric acid, 6 mL 8M HNO_3, 7 mL 2M $Al(NO_3)_3$. Mix, warm briefly in a hot bath and centrifuge to check for any solids.

Column Load Solution

Figure 2 Steel Dissolution with Pu Isotopes Fusion Option



Add Pu-242 tracer to 1-2g steel samples in Zr crucible
Dry on hot plate

Add 20 mL 12M HCl, 5 mL 15.8M HNO_3
and digest on hot plate to dryness.
Add 10 mL 12M HCl, 1 mL 15.8M HNO_3 and digest on hot plate to dryness. Repeat last step once more.

Add 15-20g NaOH pellets.
Fuse sample at 600°C for ~15-20 min.

Transfer fusion matrix to 225 mL centrifuge tube with water. Dilute to 170 mL with water. Mix. Cool with ice to room temp. Add 50 mg Ca and 5 mg La. Add 4 mL 3.2 M $(NH_4)_2HPO_4$. Mix.

Add 3 mL 20% $TiCl_3$. Cap and mix well
Cool with ice for ~10 min.
Centrifuge 6 min. and discard supernate.

Dilute to 80 mL with1.5M HCl and redissolve.
Dilute to 170 mL with 0.01M HCl. Add 25 mg Ca, 2 mL 20% $TiCl_3$. and 25 mL 28M HF.
Allow to stand for ~10 minutes.
Centrifuge 6 minutes and discard supernate.

Redissolve in 7 mL 3M HNO_3-0.25M Boric acid,
7 mL 15.8 HNO_3, 7 mL 8M $HNO_{3,}$ 7 mL 2M $Al(NO_3)_{3.}$
Mix and warm briefly in a hot bath. Centrifuge to check for any solids.

Column Load Solution

Figure 3 Alpha Spectra for Pu Isotopes in Steel

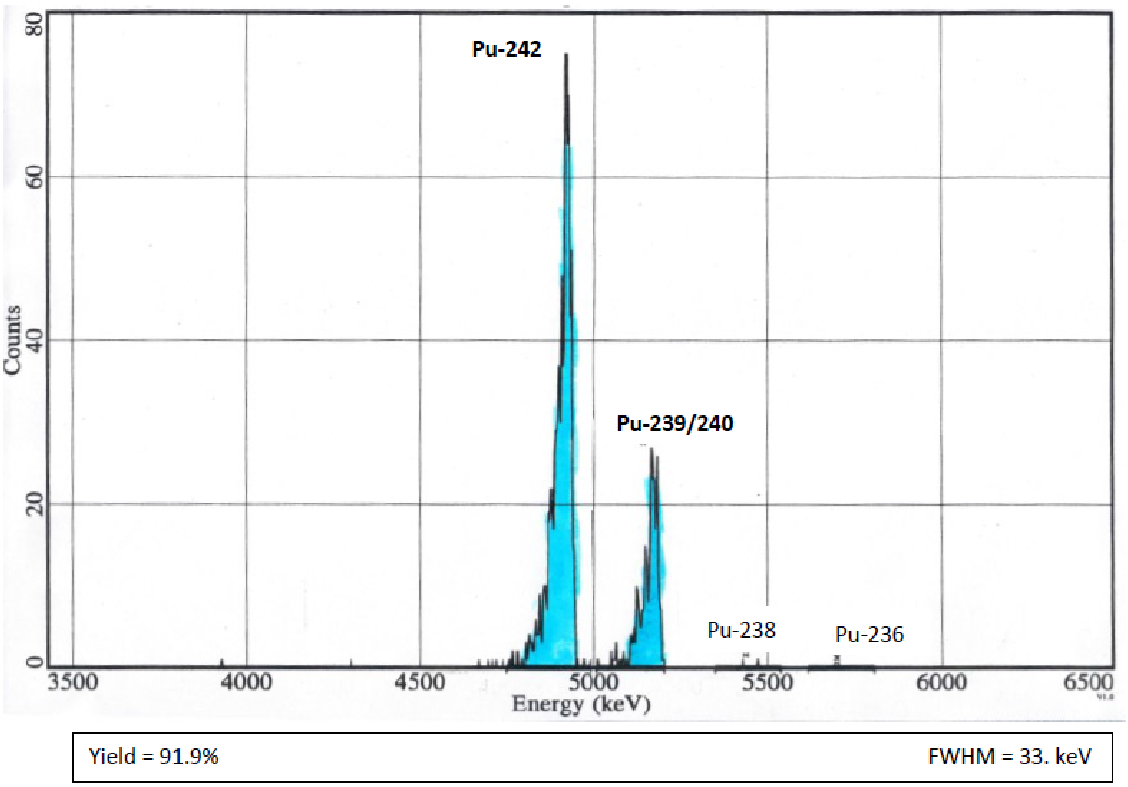
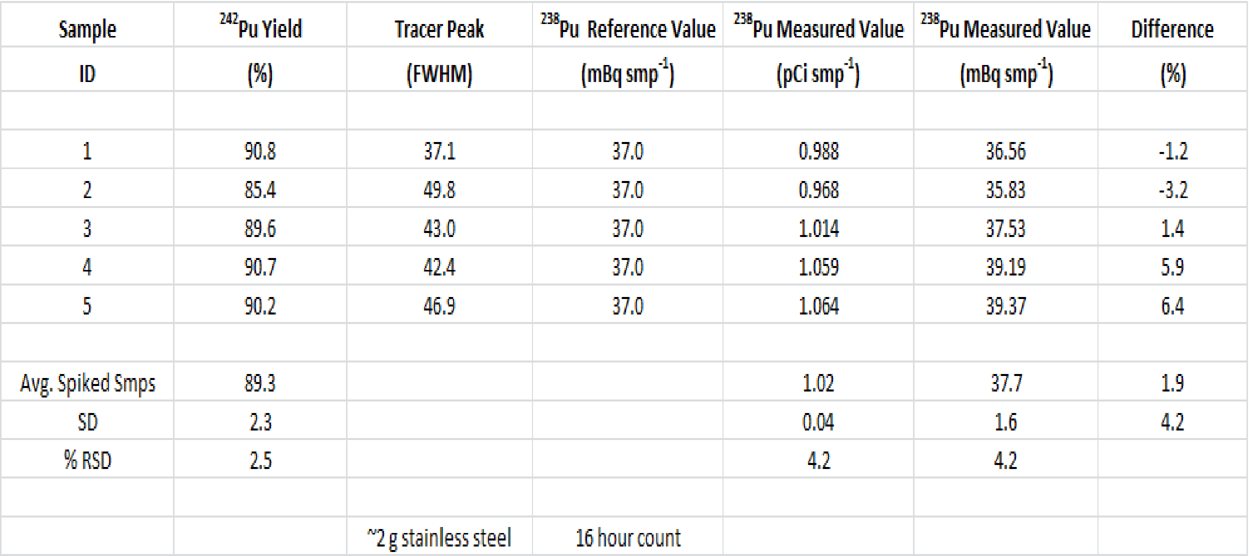
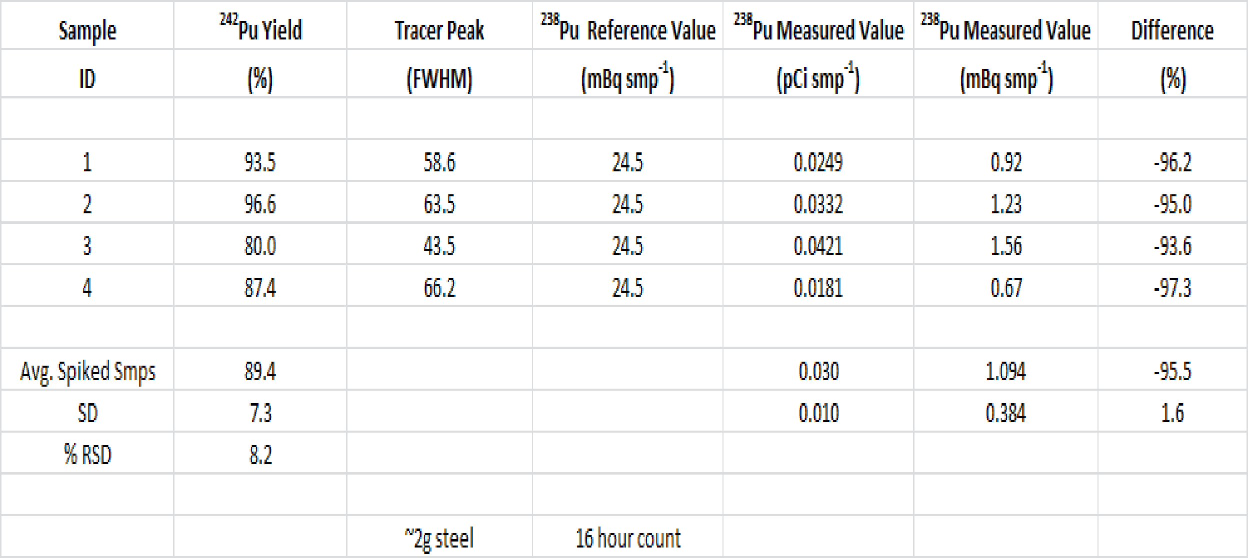


Table 1 Pu-238 Results for Spiked Steel Samples



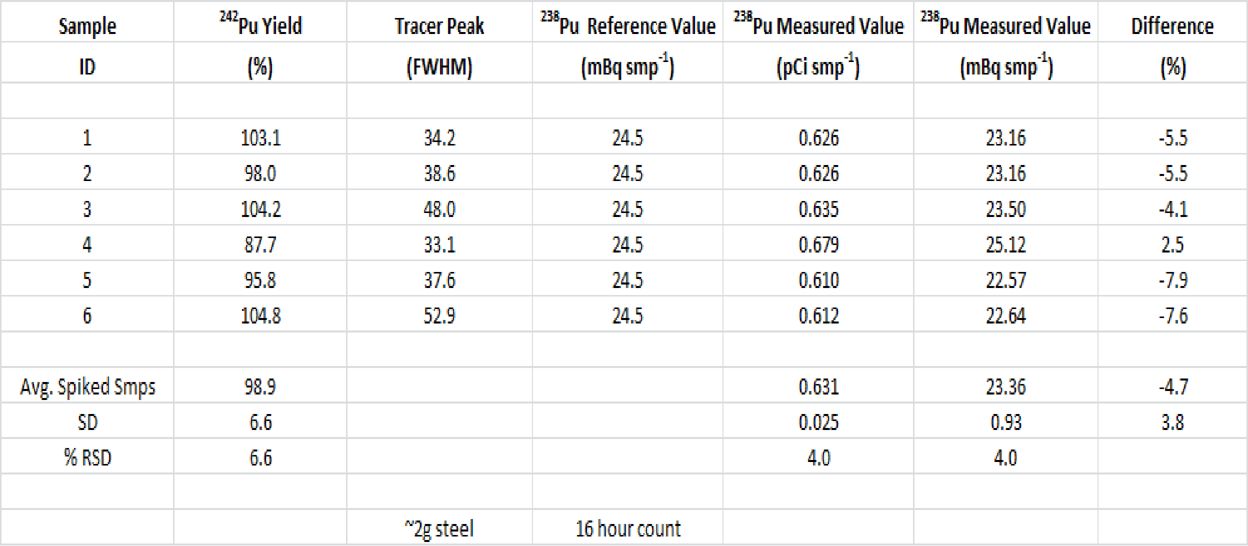
Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{238}Pu Reference Value (mBq smp^{-1})	^{238}Pu Measured Value (pCi smp^{-1})	^{238}Pu Measured Value (mBq smp^{-1})	Difference (%)
1	90.8	37.1	37.0	0.988	36.56	-1.2
2	85.4	49.8	37.0	0.968	35.83	-3.2
3	89.6	43.0	37.0	1.014	37.53	1.4
4	90.7	42.4	37.0	1.059	39.19	5.9
5	90.2	46.9	37.0	1.064	39.37	6.4
Avg. Spiked Smps	89.3			1.02	37.7	1.9
SD	2.3			0.04	1.6	4.2
% RSD	2.5			4.2	4.2	
		~2 g stainless steel	16 hour count			

Table 2 Pu-239/240 Results for Steel Spiked with Refractory Pu MAPEP 24 Soil (no HF)



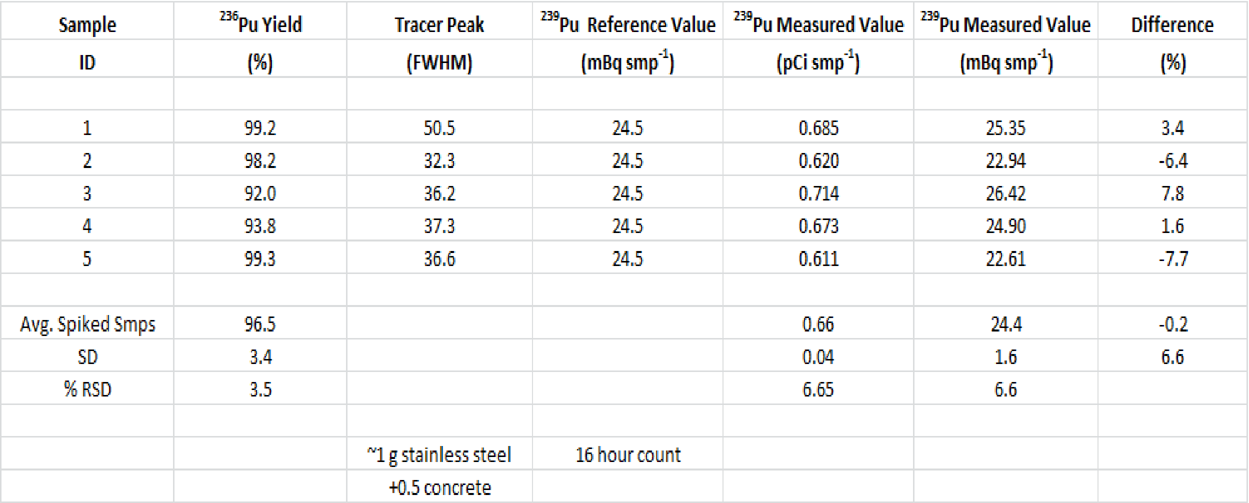
Sample	^{242}Pu Yield	Tracer Peak	^{238}Pu Reference Value	^{238}Pu Measured Value	^{238}Pu Measured Value	Difference
ID	(%)	(FWHM)	(mBq smp^{-1})	(pCi smp^{-1})	(mBq smp^{-1})	(%)
1	93.5	58.6	24.5	0.0249	0.92	-96.2
2	96.6	63.5	24.5	0.0332	1.23	-95.0
3	80.0	43.5	24.5	0.0421	1.56	-93.6
4	87.4	66.2	24.5	0.0181	0.67	-97.3
Avg. Spiked Smps	89.4			0.030	1.094	-95.5
SD	7.3			0.010	0.384	1.6
% RSD	8.2					
		~2g steel	16 hour count			

Table 3 Pu-239/240 Results for Steel Spiked with Refractory Pu MAPEP 24 Soil (with HF)



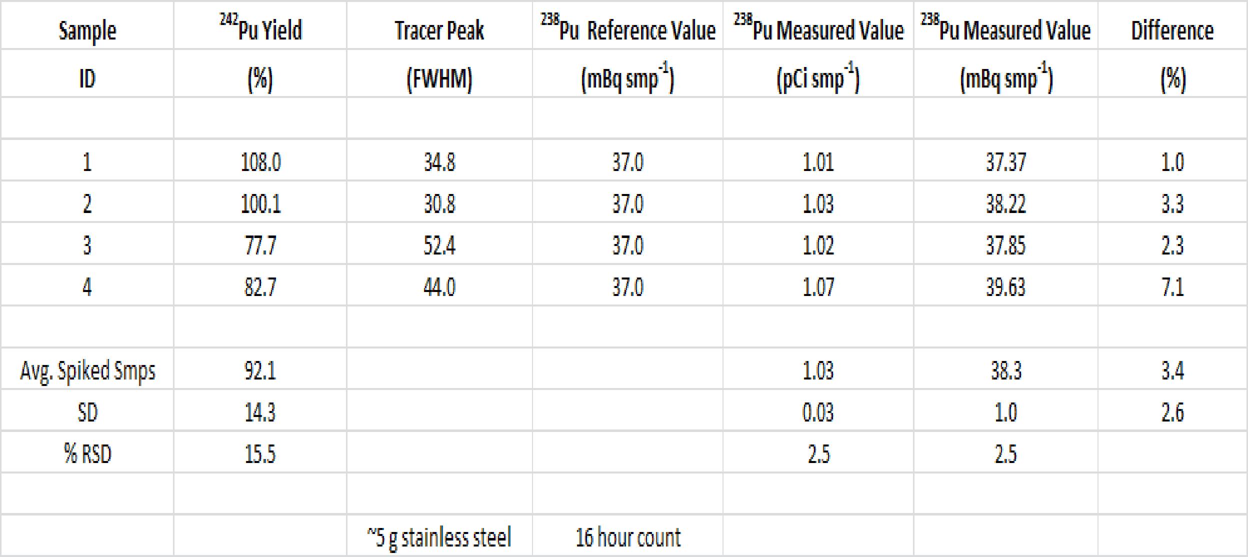
Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{238}Pu Reference Value (mBq smp^{-1})	^{238}Pu Measured Value (pCi smp^{-1})	^{238}Pu Measured Value (mBq smp^{-1})	Difference (%)
1	103.1	34.2	24.5	0.626	23.16	-5.5
2	98.0	38.6	24.5	0.626	23.16	-5.5
3	104.2	48.0	24.5	0.635	23.50	-4.1
4	87.7	33.1	24.5	0.679	25.12	2.5
5	95.8	37.6	24.5	0.610	22.57	-7.9
6	104.8	52.9	24.5	0.612	22.64	-7.6
Avg. Spiked Smps	98.9			0.631	23.36	-4.7
SD	6.6			0.025	0.93	3.8
% RSD	6.6			4.0	4.0	
		~2g steel	16 hour count			

Table 4 Plutonium Results for Steel Samples + Concrete and Refractory Pu Samples (Fusion)



Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Reference Value (mBq smp^{-1})	^{239}Pu Measured Value (pCi smp^{-1})	^{239}Pu Measured Value (mBq smp^{-1})	Difference (%)
1	99.2	50.5	24.5	0.685	25.35	3.4
2	98.2	32.3	24.5	0.620	22.94	-6.4
3	92.0	36.2	24.5	0.714	26.42	7.8
4	93.8	37.3	24.5	0.673	24.90	1.6
5	99.3	36.6	24.5	0.611	22.61	-7.7
Avg. Spiked Smps	96.5			0.66	24.4	-0.2
SD	3.4			0.04	1.6	6.6
% RSD	3.5			6.65	6.6	
		~1 g stainless steel	16 hour count			
		+0.5 concrete				

Table 5 Pu-238 Results for Spiked Steel Samples (5g steel)



Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{238}Pu Reference Value (mBq smp^{-1})	^{238}Pu Measured Value (pCi smp^{-1})	^{238}Pu Measured Value (mBq smp^{-1})	Difference (%)
1	108.0	34.8	37.0	1.01	37.37	1.0
2	100.1	30.8	37.0	1.03	38.22	3.3
3	77.7	52.4	37.0	1.02	37.85	2.3
4	82.7	44.0	37.0	1.07	39.63	7.1
Avg. Spiked Smps	92.1			1.03	38.3	3.4
SD	14.3			0.03	1.0	2.6
% RSD	15.5			2.5	2.5	
		~5 g stainless steel	16 hour count			