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Rapid Fusion Method for Determination of Plutonium Isotopes in Large Rice Samples

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Abstract

A new rapid fusion method for the determination of plutonium in large rice samples has been developed at the Savannah River National Laboratory (Aiken, SC, USA) that can be used to determine very low levels of plutonium isotopes in rice. The recent accident at Fukushima Nuclear Power Plant in March, 2011 reinforces the need to have rapid, reliable radiochemical analyses for radionuclides in environmental and food samples. Public concern regarding foods, particularly foods such as rice in Japan, highlights the need for analytical techniques that will allow very large sample aliquots of rice to be used for analysis so that very low levels of plutonium isotopes may be detected. The new method to determine plutonium isotopes in large rice samples utilizes a furnace ashing step, a rapid sodium hydroxide fusion method, a lanthanum fluoride matrix removal step, and a column separation process with TEVA Resin™ cartridges. The method can be applied to rice sample aliquots as large as 5 kg. Plutonium isotopes can be determined using alpha spectrometry or inductively-coupled plasma mass spectrometry (ICP-MS). The method showed high chemical recoveries and effective removal of interferences. The rapid fusion technique is a rugged sample digestion method that

ensures that any refractory plutonium particles are effectively digested. The MDA for a 5 kg rice sample using alpha spectrometry is $7E-5$ mBq g^{-1} . The method can easily be adapted for use by ICP-MS to allow detection of plutonium isotopic ratios.

Introduction

On March 11, 2011, a catastrophic earthquake occurred about 130 km off northeastern Japan. This triggered a gigantic tsunami, which caused serious damage to the electrical system of the Fukushima Daiichi nuclear power plants (DNPP). As a result, the nuclear reactor cooling systems failed, resulting in hydrogen explosions in the Unit 1 and 3 reactors on March 12 and 14, respectively. On March 15, additional explosions happened in the Unit 4 reactor building and the Unit 2 reactor. These explosions of the Fukushima DNPP caused significant releases of radionuclides into the atmosphere. [1]

The Savannah River National Laboratory (SRNL) performed analyses on soil and air filter samples received from Japan in April, 2011 as part of a U.S. Department of Energy effort to provide assistance to the government of Japan, following the nuclear event at Fukushima DNPP. Of particular concern was whether it was safe to plant rice in certain areas (prefectures) near Fukushima. Samples included soil from farmland surrounding the Fukushima reactors and air monitoring samples of national interest, including those collected at the U.S. Embassy and American military bases.

Samples were analyzed for a wide range of radionuclides, including ^{89}Sr , ^{90}Sr , gamma-emitting radionuclides, and plutonium, uranium, americium and curium isotopes. The rapid radiochemical analyses provided to the government of Japan and the U.S. Department of Energy provided information that assisted with timely evaluation of personnel exposure hazards, identification of the nuclear power plant radiological source term and plume deposition, and assisted the government of Japan in assessing any

environmental and agricultural impacts associated with the nuclear event. Air filter samples were reported within 24 hours of receipt using rapid techniques published previously. [2] The rapid reporting of high quality analytical data arranged through the U.S. Department of Energy Consequence Management Home Team was critical to allow the government of Japan to readily evaluate radiological impacts from the nuclear reactor incident to both personnel and the environment. [3]

The recent accident at Fukushima Nuclear Power Plant in March, 2011 reinforces the need to have rapid, efficient analysis capabilities to determine radionuclides not only in environmental samples, but food samples as well. The U.S. Food and Drug Administration (FDA) has provided guidance regarding accidental contamination of foods to U.S. state and local agencies so that protective actions may be taken. The FDA Derived Intervention Level (DIL) for $^{238}\text{Pu} + ^{239}\text{Pu} + ^{241}\text{Am}$ is 2 Bq/kg (2 mBq g⁻¹ or 0.054 pCi g⁻¹). [4] The DILs were calculated to help protect even the most vulnerable segments of the population by limiting radiation dose from ingestion. Rapid and effective analysis methods are critical to allow responsible officials to apply protection actions.

A rapid method to analyze 10 -100 gram food samples was reported recently by this laboratory. [5] This new method to determine actinides in food samples provides a typical MDA of ~0.2 mBq g⁻¹ for a 10 g sample and 2 hour count time for each of the actinide isotopes cited in the DIL. The method is flexible and longer count times can be used to lower MDA levels as needed. For example, for a 16 hour count time and a 100 g sample, an MDA of 0.004 mBq g⁻¹ can be achieved. This method has been approved for use by the U.S. Food Emergency Response Network (FERN). Following the nuclear incident at Fukushima DNPP, the need to screen food and environmental samples rapidly with reliable results was seen firsthand.

Zheng et al [6] reported the detection of plutonium isotopes in soil samples collected in close proximity to the DNPP. This excellent work reports the isotopic evidence for the release of plutonium into the atmosphere and deposition on the ground in northwest and south of the Fukushima DNPP in the 20–30 km zones. The researchers conclude that the high activity ratio of $^{241}\text{Pu}/^{239+240}\text{Pu}$ (> 100) from the Fukushima DNPP accident highlights the need for long-term ^{241}Pu dose assessment, and the ingrowth of ^{241}Am . This will allow estimation of reactor damage and impact the strategy of decontamination.

Public concern regarding foods, particularly rice in Japan, highlights the need for analytical techniques that will allow very large sample aliquots of rice to be used for analysis. Large sample aliquots must be analyzed to achieve the very low detection limits needed. While methods that meet Derived Intervention Level (DIL) requirements are essential, methods that can be performed with even lower detection limits are needed due to public sensitivities, especially in Japan. The average person in Japan consumed 56.6 kg rice in 2007, so an effective radioanalytical techniques to facilitate confirmation that rice in Japan is free of plutonium contamination at very low levels would be very important.

[7]

Evans et al [8] reported a method for determination of food using magnetic sector ICP-MS and ion chromatography. The food samples were digested in concentrated nitric acid using closed vessel microwave digestion and were limited to ~0.5 g aliquots. A chromatographic separation was performed using a mobile phase of 1.5M nitric acid and 0.01 mM dipicolinic acid and a divinylbenzene-polystyrene substrate. Valence state oxidation for plutonium was performed using hydrogen peroxide, but there seemed to be a negative impact on Am recoveries when this was added. The hydrogen peroxide was necessary to achieve good recoveries for Pu and Np. A timeline was given where Pu in

food samples could be analyzed within 3 hours of receipt. To achieve low level detection limits, however, an ultrasonic desolvation sample introduction system combined with the magnetic sector ICP-MS was required.

To meet very low detection limits, much larger rice aliquots need to be taken. Based on a survey of the literature, there is still a need for a method that provides effective digestion and chemical yields for determination of plutonium isotopes in very large rice samples.

The importance of having a rugged digestion method for refractory particles on environmental and food samples is well-known. [9] If refractory particles resulting from nuclear accident are present in food or environmental samples, having an analysis method with a rugged digestion method will be even more important.

A new method to determine Pu isotopes in large rice samples has been developed in the Savannah River National Laboratory (Aiken, SC, USA). While furnace ashing and wet-ashing steps needed to destroy the large amount of organics present may take about 1 week to complete, the rapid fusion, preconcentration and column separation steps are very rapid. After ashing the rice samples, the samples were analyzed using a rapid sodium hydroxide fusion, followed by iron/titanium hydroxide and a lanthanum fluoride matrix removal steps, followed by separation of Pu isotopes using a single 2 ml TEVA Resin cartridge for each kg of rice. To lower the MDA, the purified eluents from each 1 kg sample were combined for final measurement. Vacuum box technology was used to allow rapid flow rates to reduce separation times. Alpha sources are prepared using cerium fluoride microprecipitation for counting by alpha spectrometry. This new method showed high chemical recoveries and effective removal of interferences. The fusion, unlike fusions that are performed one at a time over a blast burner, can be performed simultaneously in a furnace or furnaces.

Experimental

Reagents

The resin employed in this work is TEVA Resin[®] (Aliquat[™]336) available from Eichrom Technologies, Inc., (Lyle, Illinois, USA) [11]. Nitric 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 reagent grade. Radiochemical isotope tracers ²⁴²Pu that were obtained from Eckert Ziegler/Analytcs, Inc. (Atlanta, GA, USA) and diluted to ~ 0.37 Bq ml⁻¹ were employed to enable yield corrections.

Procedures

Column preparation. TEVA Resin columns were obtained as cartridges containing 2 ml of each resin from Eichrom Technologies, Inc.. Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies) that will handle 24 samples at a time. Flow rates of 1-3 ml min⁻¹ were typically used. Sample loading and final elution steps were typically 1 ml min⁻¹ while rinse steps were ~ 2 to 3 ml min⁻¹.

Sample Preparation. To test for ruggedness regarding refractory plutonium isotopes, a small amount of MAPEP 12 (Mixed Analyte Performance Evaluation Program) soil standard was added to the large rice samples. The MAPEP samples were provided by Department of Energy (DOE) – Radiological and Environmental Sciences Laboratory (RESL), Idaho, USA. MAPEP 12 soil standard was chosen because the ²³⁹Pu

present in this soil was made refractory by DOE-RESL by heating to 900°C. If an Improvised Nuclear Device (IND), Radiological Dispersive Device (RDD) or nuclear accident occurs, it is important to have a method rugged enough to provide total digestion not only of the food sample but also any refractory radioactive particles present. Rice aliquots of 1 kg and 1.5 kg were processed in 2 L glass beakers.

Figure 1 shows the furnace fusion and precipitation steps used to digest the samples and preconcentrate the plutonium from the alkaline fusion matrix. The 1-1.5kg rice aliquots were ramped to 350°C for 5 hours, then ramped to 550°C and ashed for 12 hours. The samples were carefully wet-ashed on a hotplate by adding concentrated nitric acid and 30 wt% hydrogen peroxide. The samples were heated to dryness on a hot plate and placed into the furnace. The samples were ramped immediately to 525-550°C for 6-12 hours, as needed. The heating and wet-ashing steps were repeated until the black charred solids were small enough to transfer to 250 ml Zr crucibles. The beakers were rinsed with concentrated nitric acid and the rinse was added to the Zr crucibles. Heating and wet-ashing steps were repeated for short periods of times until the dried solids were a lavender color (no charred black color was present). After removing crucibles from the hotplate, 15 g NaOH were added to each crucible. The crucibles were covered with a zirconium lid and placed into a furnace already heated to 600°C for ~ 20 to 30 minutes.

After removing the crucibles from the furnace, the crucibles were cooled for about 10 minutes, water was added to each and the crucibles were heated on a hot plate to dissolve and transfer the solids to 225 ml centrifuge tubes. The residual solids were removed from the crucibles by adding water and heating the crucibles further on the hot plate as needed. One hundred and twenty-five milligrams of Fe (added as Fe (NO₃)₃) and ten milligrams of La (as La (NO₃)₃) were added to each 225 ml centrifuge tube prior to

transferring the alkaline solution and solids from the crucibles into the tubes. The samples were diluted to 180 ml with water and cooled in an ice bath to room temperature.

Two milliliters of 1.25M $\text{Ca}(\text{NO}_3)_2$ and one milliliter of 3.2M $(\text{NH}_4)_2\text{HPO}_4$ were added to each tube and each was capped and mixed well. The Ca^{2+} and PO_4^{3-} ions were added to enhance recoveries. Six milliliters of 10% TiCl_3 were added to each tube and mixed well. The tubes were centrifuged at 3500 rpm for 6 minutes and the supernatant was discarded. The remaining solids were dissolved in a total volume of ~80-100 ml of 1.5 M HCl. This solution was diluted to ~170 ml with 0.01M HCl and 5 ml of 10% titanium chloride were added to each sample. Twenty-two milliliters of 28M HF were added to each sample. The samples were centrifuged for 10 minutes at 3500 rpm.

The supernatant was discarded and the residual solids containing the actinides were dissolved in 5 ml of warm 3M HNO_3 -0.25M H_3BO_3 , 6 ml of 7M HNO_3 and 7 ml of 2 M $\text{Al}(\text{NO}_3)_3$ and 3 ml 3M HNO_3 . The aluminum nitrate was previously scrubbed to remove trace uranium by passing approximately 250 ml of 2M aluminum nitrate through a large column (Environmental Express, Mount Pleasant, SC, USA) containing 7 ml of UTEVA Resin (Eichrom Technologies) at ~10 to 15 ml per minute. The columns were prepared from a water slurry of the UTEVA Resin. The dissolved samples were transferred to 50 ml tubes, warmed in a hot block as needed to facilitate dissolution and centrifuged at 3500 rpm to remove any traces of solids. The load solutions were allowed to cool to room temperature.

A valence adjustment was performed on the load solution by adding 0.5 ml 1.5M sulfamic acid and 1.25 ml 1.5M ascorbic acid with a three minute wait step to reduce plutonium to Pu^{3+} . To enhance the reduction of plutonium, 2 mg Fe was added (0.4 ml of 5 mg Fe/ml as iron nitrate) just prior to adding ascorbic acid to enhance reduction

kinetics. Following the reduction step, 1 ml 3.5M NaNO₂ was added to oxidize plutonium to Pu⁴⁺.

Column separation. The TEVA Resin cartridge separation was similar to what has been reported previously, except when sample aliquots larger than 1 or 1.5 kg are required, the purified eluents from each replicate are combined, and filtered as CeF₃. [5] This creates an ease of handling and facilitates higher chemical yields. Figure 2 shows the rapid column separation method. In this work, the plutonium isotopes were determined using alpha spectrometry.

If Pu isotopic measurements by ICP-MS are desired, a Pu eluent solution of 0.05M HCl-0.025M HF-0.02M hydroxylamine hydrochloride may be used instead of 0.1M HCl-0.05M-0.01M TiCl₃ eluent solution used in this work. The eluent solution containing hydroxylamine hydrochloride has been found to work effectively for ICP-MS applications. Even though the kinetics of this reduction of Pu⁺⁴ to Pu⁺³ are not as rapid as using Ti⁺³, the rate of reduction is sufficient during the 15 minute elution time to facilitate effective Pu removal from TEVA Resin. By employing this alternate eluent solution that does not contain Ti, even the sensitive highly sensitive APEX/SF-ICP-MS analytical system used by researchers such as Zheng et al and Epov et al [6, 10, 11] may be employed for extremely low detection limits of Pu isotopes.

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 mm². The nominal counting efficiency for these detectors is 0.25. The distance between the sample and detector surface is ~3mm.

Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 ml plastic tubes were used.

Results and Discussion

Table 1 shows the individual results for the determination of ^{238}Pu in eight 1 kg rice samples using this rapid separation method and alpha spectrometry. The results were corrected for ^{242}Pu tracer yield, with an average yield of 86.8% (4.1% 1SD). The average ^{238}Pu result for the 1 kg rice samples was 10.5 mBq kg^{-1} , with a -0.7% bias and 1SD (standard deviation) of 0.7 mBq kg^{-1} . The tracer yields were excellent considering the multiple furnace steps and difficulty associated with processing 1 kg of rice.

Table 2 shows the ^{239}Pu results for the eight 1 kg rice samples. The average ^{239}Pu result was 11.8 mBq kg^{-1} , with a -5.6% bias and 1SD of 1.0 mBq kg^{-1} . The results for the refractory ^{239}Pu analyte measurements were very good. Comparison with the ^{239}Pu known value indicates that the sample preparation and measurement steps for the large rice samples are very rugged.

Table 3 shows the results for the determination of ^{239}Pu in 5 kg rice samples using alpha spectrometry. The first sample listed was processed by combining the final purified eluents from five 1 kg replicate samples onto the same cerium fluoride micro-precipitate, while samples 2 and 3 were prepared by combining purified eluents from four 1.25 kg replicate samples. The average ^{242}Pu tracer yield was 73.4%, slightly lower than expected. The lower tracer yields were perhaps due to slight losses when eluents were combined and cerium fluoride precipitation was performed on the combined replicate eluents. To the combined eluent volume from the 4 or 5 replicates, $100 \mu\text{g Ce}$, $2 \text{ ml } 30 \text{ wt}\% \text{ H}_2\text{O}_2$ and $5 \text{ ml } 28\text{M HF}$ were added to combine the Pu isotopes onto a single 25mm polypropylene filter for counting. This step could likely be optimized further for higher

yields, but >70% yield is still good for a 5 kg rice sample. This loss might not have occurred if eluents were evaporated for final combination for ICP-MS assay, although tracer yields could be less when 1.25 kg rice aliquots are processed and combined instead of 1 kg aliquots.

It is also possible to split the eluent from samples and count part by samples by alpha spectrometry and part by alpha spectrometry to allow measurement of relatively short-lived ^{238}Pu isotope more effectively. Another option is to redissolve the sample from the cerium fluoride filter, after initial alpha counting of short-lived Pu isotopes, using warm 3M HNO_3 -0.25M H_3BO_3 and reprocess the dissolved sample through TEVA Resin, eluting with an ICP-MS friendly eluent if sample splitting would result in an unacceptable MDA level.

The MDA (Minimum Detectable Activity) for the actinide isotopes by alpha spectrometry were calculated according to equations prescribed by Currie: [11]

$$\text{MDA} = [3 + 4.65\sqrt{B}] / (\text{CT} * \text{R} * \text{W} * \text{Eff} * 0.060)$$

Where B = Total Background counts, = BKG (rate) * BKG Count time

CT = sample count time (min)

R = Chemical Recovery

W = Sample aliquot (g)

Eff = Detector Efficiency

0.060 = conversion from dpm to mBq

In low-level counting, where a zero background count is quite common, the constant 3 is used to prevent an excessively high false positive rate.

The MDA (minimum detectable activity) for the alpha spectrometry results can be adjusted as needed, depending on the sample aliquot and count time. This method

provides a typical MDA of $\sim 7.4 \times 10^{-5}$ mBq/g for a 30 hour count time and 5 kg sample.

Figure 3 shows an example of the spectra of Pu isotopes in a large rice sample aliquot. The ^{242}Pu tracer recovery was 92.8% and the Full Width Half Maximum (FWHM) was 30.6 keV, showing acceptable alpha peak resolution and good tracer recovery. The ^{239}Pu peak labeled on the spectra represents $^{239}\text{Pu} + ^{240}\text{Pu}$, since these isotopes have overlapping alpha energies.

New resin cartridges were used for each analysis to minimize any chance of cross-contamination of samples or unexpected degradation of performance, which can occur over time and may be different than the anticipated reuse rate depending on real world sample matrix variation.

The initial sample ashing step for 1 to 1.25 kg food aliquots takes about a week. Smaller amounts of rice can be processed much more quickly, but for this work the focus was achieving very low MDA levels. The rapid fusion method plus precipitation steps takes about 1.5 hours, followed by Pu separation steps that take about 2 hours to complete. It is also possible to apply ICP-MS measurement technology if desired, with slight changes in column eluate solutions to ensure compatibility with the ICP-MS, such as using hydroxylamine hydrochloride as a reductant in the eluent solution instead of Ti^{3+} [12, 13]. It is likely this approach can also be applied to other large food types as well, but due to the high consumption rate of rice East Asia and public sensitivities to food contamination after the Fukushima DNPP incident, this work focused solely on rice samples.

Conclusions

A new rapid fusion method to determine Pu isotopes in 1 to 5 kg rice samples has been developed that allows the separation of these isotopes with high chemical yields and effective removal of interferences. The rapid fusion technique is fast and rugged,

demonstrating very good recoveries of MAPEP standards which contain refractory ^{239}Pu . ICP-MS, including the sensitive highly sensitive APEX/SF-ICP-MS analytical system, may be used if a Pu eluent solution is employed containing hydroxylamine hydrochloride instead of Ti^{+3} .

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Table Captions

Table 1	Spiked Pu -238 in Rice Results -1kg samples
Table 2	Spiked Pu -239 in Rice Results -1kg samples
Table 3	Spiked Pu -239 in Rice Results -5 kg samples

Table 1 Spiked Pu -238 in Rice Results -1 kg samples

Sample ID	²⁴² Pu Yield (%)	²³⁸ Pu Reference Value (pCi kg ⁻¹)	²³⁸ Pu Reference Value (mBq kg ⁻¹)	Measured Value (mBq kg ⁻¹)	Difference (%)	MDA (mBq g ⁻¹)	Reference
1	88.9	0.287	10.6	11.8	11.0	3.7 E-4	MAPEP 12
2	91.5	0.287	10.6	10.1	-4.3	3.7 E-4	MAPEP 12
3	92.8	0.287	10.6	10.0	-5.2	3.7 E-4	MAPEP 12
4	81.0	0.287	10.6	10.3	-3.1	3.7 E-4	MAPEP 12
5	83.8	0.287	10.6	10.2	-4.0	3.7 E-4	MAPEP 12
6	85.1	0.287	10.6	11.1	5.0	3.7 E-4	MAPEP 12
7	87.1	0.287	10.6	9.9	-7.0	3.7 E-4	MAPEP 12
8	83.7	0.287	10.6	10.8	2.0	3.7 E-4	MAPEP 12
Avg	86.8			10.5	-0.7		
SD	4.1			0.7			
% RSD	4.7			6.2			

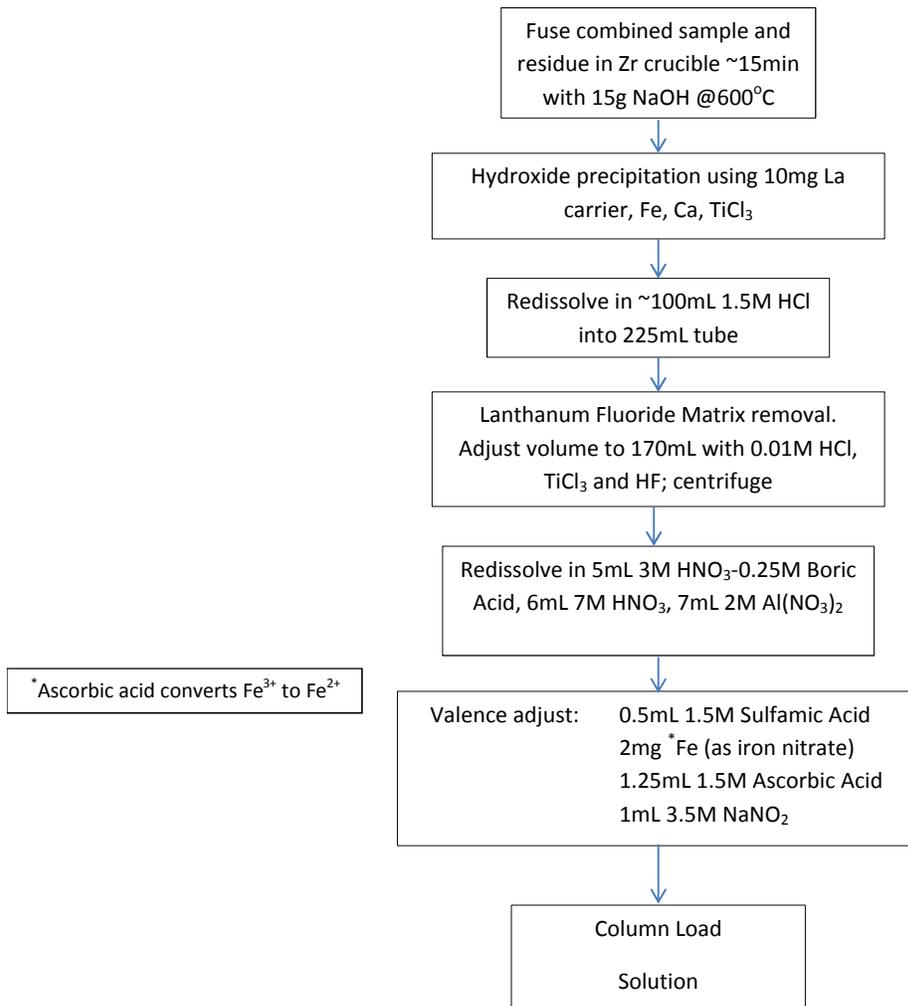
Table 2 Spiked Pu -239 in Rice Results -1 kg samples

Sample ID	²⁴² Pu Yield (%)	²³⁹ Pu Reference Value (pCi kg ⁻¹)	²³⁹ Pu Reference Value (mBq kg ⁻¹)	Measured Value (mBq kg ⁻¹)	Difference (%)	MDA (mBq g ⁻¹)	Reference
1	88.9	0.338	12.5	10.7	-14.4	3.7 E-4	MAPEP 12
2	91.5	0.338	12.5	12.6	0.8	3.7 E-4	MAPEP 12
3	92.8	0.338	12.5	12.4	-0.8	3.7 E-4	MAPEP 12
4	81.0	0.338	12.5	12.2	-2.4	3.7 E-4	MAPEP 12
5	83.8	0.338	12.5	12.8	2.4	3.7 E-4	MAPEP 12
6	85.1	0.338	12.5	12.0	-4.0	3.7 E-4	MAPEP 12
7	87.1	0.338	12.5	11.7	-6.4	3.7 E-4	MAPEP 12
8	83.7	0.338	12.5	10.0	-20.1	3.7 E-4	MAPEP 12
Avg	86.8			11.8	-5.6		
SD	4.1			1.0			
% RSD	4.7			8.3			
Pu-239 is refractory in MAPEP 12							

Table 3 Spiked Pu -239 in Rice Results -5 kg samples

Sample	²⁴² Pu Yield	²³⁹ Pu Reference Value	²³⁹ Pu Reference Value	Measured Value	Difference	MDA	
ID	(%)	(pCi kg ⁻¹)	(mBq g ⁻¹)	(mBq g ⁻¹)	(%)	(mBq g ⁻¹)	Reference
1	72.6	0.1130	0.00418	0.00396	-5.3	7.40E-05	MAPEP 12
2	70.6	0.0904	0.00334	0.00353	5.6	7.40E-05	MAPEP 12
3	76.9	0.0904	0.00334	0.00366	9.6	7.40E-05	MAPEP 12
Avg	73.4			0.00372	3.3		
SD	3.2			0.00022			
% RSD	4.4			5.9			
	#1: 5 x 1 kg samples combined						
	#2: 4 x 1.25 kg samples combined						
	#3: 4 x 1.25 kg samples combined						

Figure 1 Rapid Fusion Method for Large Rice Samples



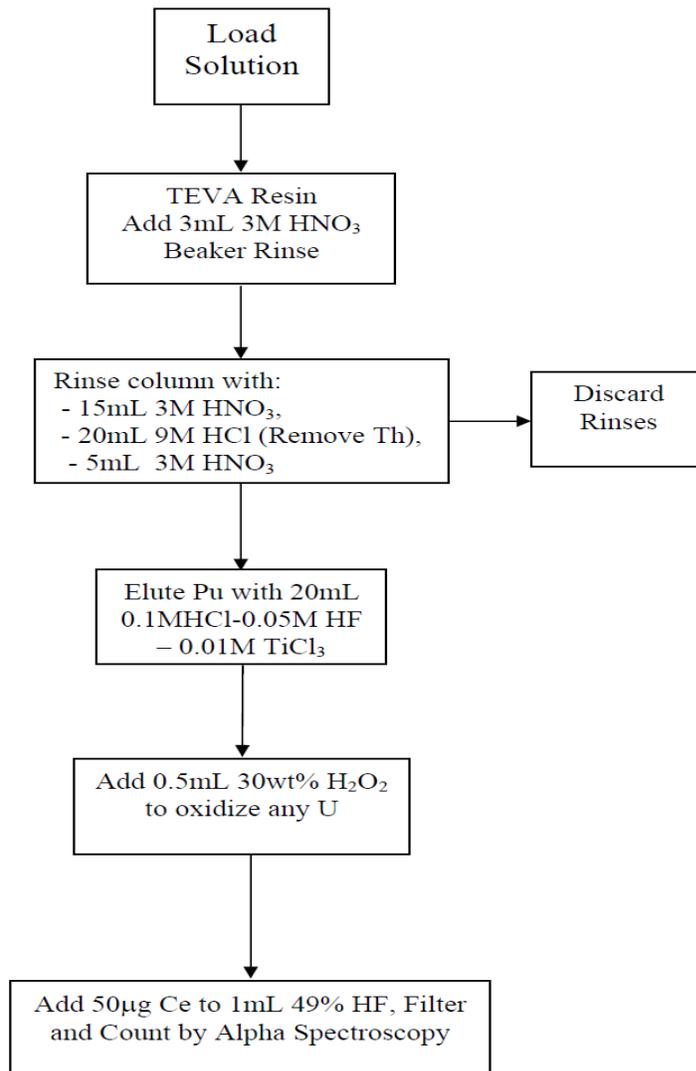


Figure 3 Alpha spectra – Pu Isotopes in Spiked Rice Sample

