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Rapid determination of actinides in emergency food samples

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Abstract A new rapid method for the determination of actinides in food samples has been developed at the Savannah River Site Environmental Lab (Aiken, SC, USA) that can be used for emergency response or routine food samples. If a radiological dispersive device or improvised nuclear device event occurs, there will be a urgent need for rapid analyzes of many different environmental matrices, as well as food samples, to support dose mitigation and protect general populations from radioactivity that may enter the food chain. The recent accident at Fukushima nuclear power plant in March, 2011 reinforces the need to have rapid analyzes for radionuclides in environmental and food samples. The new method to determine actinides in food samples utilizes a furnace ashing step, a rapid sodium hydroxide fusion method, a lanthanum fluoride matrix removal step, and a column separation process with stacked TEVA, TRU, and DGA resin cartridges. The furnace ashing and rapid fusion steps are performed in relatively inexpensive, reusable zirconium crucibles. Alpha emitters are prepared using rare earth micro precipitation for counting by alpha spectrometry. The method showed high chemical recoveries and effective removal of interferences. The determination of actinides in food samples can be performed in less than 8 h for 10 g samples with excellent quality for emergency samples using short count times. Larger food samples (100 g) may be processed in 24 h or less. The rapid fusion technique is a rugged sample digestion method that ensures that any refractory actinide particles are effectively digested. This method can be used to meet the derived intervention level guidelines recommended by the U.S. Food and Drug Administrations.

Keywords Rapid · Separation · Plutonium · Actinides · Food · Emergency

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Introduction

There is an increasing need to develop faster analytical methods for emergency response, including emergency environmental, and food samples [1–3]. There are a number of analytical methods reported that use ion exchange/extraction chromatography plus alpha spectrometry to determine actinides in environmental and food samples.

Bari et al. [4] reported a rapid screening method for radioactivity in food samples. The screening was done using an acid leaching technique combined with gross alpha/gross beta method that achieved good recoveries for spiked samples using gas proportional counting. This screening method was not specific for actinide isotopes and does not address refractory particles that may be present as a result of a radiological event.

Evans et al. [5] 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 1.5 M 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 h of receipt. To achieve low-level detection limits, however, an ultrasonic desolvation sample introduction system combined with the magnetic sector ICP-MS was required.

Mellado et al. [6] described a new method to determine actinides and strontium in fish samples using UTEVA Resin, TRU Resin and Sr-Resin. Samples from 5 to 40 g were analyzed with recoveries that were often less than 40%. The fish reference material IAEA-414 was analyzed with and without calcination. For the calcinated samples (5 g of ashes), the recovery values were about 45% for Pu and about 15% for Am, while the values obtained without calcination (5 g of dry sample) were 20% for Pu and 2% for Am. For U, the best recovery value was obtained for samples without calcination, about 32%, while for samples with calcination the value was about 19%. The authors noted that Am recoveries seemed to be very dependent on the sample intake and sample pretreatment, and that this was likely related to the relatively low retention of Am on TRU Resin.

Based on a survey of the literature, there is still a need for a rapid, simple method that provides effective digestion and chemical yields for determination of actinide isotopes in food samples.

A rapid vegetation method was reported by this laboratory [3] to separate and determine actinides in emergency vegetation samples using sodium hydroxide fusion. A similar analytical approach was taken for food samples. The importance of having a rugged digestion method for refractory particles on environmental and food samples is well-known [7]. If refractory particles resulting from an improvised nuclear device (IND) or 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, Np, Am, Cm, and U isotopes in food samples has been developed in the Savannah River Site Environmental Lab (Aiken, SC, USA). This new approach has reduced the sample preparation time for food samples to ~6 h, including furnace ashing, fusion, preconcentration, and column separation steps. This method can be used in emergency response situations or for routine analysis. The samples were analyzed using a rapid sodium hydroxide fusion, followed by precipitation steps including a lanthanum fluoride matrix removal step, followed by a stacked multistage column consisting of TEVA + TRU + DGA Resins. Lanthanum, which follows Am on TRU and DGA Resins, was removed on DGA Resin using a dilute nitric acid rinse. Lanthanum was separated effectively from Am and Cm on DGA Resin. Vacuum box technology was used to allow rapid flow rates and a stacked resin cartridge approach was employed to reduce separation times. Alpha sources are prepared using cerium fluoride micro precipitation 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.

The U.S. Food And Drug Administration (FDA) has provided guidance regarding accidental contamination of foods to state and local agencies so that protective actions may be taken. The FDA derived intervention level (DIL) for ^{238}Pu + ^{239}Pu + ^{241}Am is 2 Bq/kg (2 mBq/g or 0.054 pCi/g) [8]. 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 essential to allow responsible officials to apply protection actions.

This new method to determine actinides in food samples provides a typical MDA of ~0.2 mBq/g for a 10 g sample and 2 h 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 h count time and a 10 g sample, an MDA of 0.04 mBq/g can be achieved.

Experimental

Reagents

The resins employed in this work are TEVA Resin® (Aliquat™336), TRU Resin® (tri-*n*-butylphosphate (TBP) and octyl (phenyl) *N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO)), and DGA Resin (*N*,*N*,*N*′,*N*′,-tetraoctyldiglycolamide), available from Eichrom Technologies, Inc., (Lyle, Illinois, USA) [9–11]. 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 ^{242}Pu, ^{243}Am, and ^{232}U that were obtained from Eckert Ziegler/Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 0.37 Bq mL^{-1} were employed to enable yield corrections. ^{244}Cm was obtained from Eckert Ziegler/Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 0.37 Bq mL^{-1}. ^{232}U tracer was prepared to be self-cleaning, removing its ^{228}Th daughter using barium sulfate precipitation [12].

Procedures

Column preparation

TEVA, TRU, and DGA Resin columns were obtained as cartridges containing 2 mL of each resin from Eichrom Technologies, Inc. Small particle size (50–100 μm) 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 ~2–3 mL min^{-1}. Faster flow rates may be used, but may result in slight reductions to chemical yields.

Sample preparation

To test for ruggedness regarding refractory isotopes, a small amount of MAPEP 18 (Mixed Analyte Performance Evaluation Program) soil standard was added to the food samples. The MAPEP samples were provided by Department Of Energy (DOE)–Radiological And Environmental Sciences Laboratory (RESL), Idaho, USA. MAPEP 18 soil standard was chosen because the ^{239}Pu present in this soil was made refractory by DOE-RESL by heating to 900 °C. Apples and squash were chopped into small pieces in a food processor. Five replicate 10 g aliquots of the various food samples were added to 250 mL zirconium crucibles. To spike the samples with actinide isotopes, either 200 or 400 mg of MAPEP 18 soil standard were added. In addition, ^{244}Cm standard (31.4 mBq) and ^{237}Np (37.0 mBq) were also added to the five spiked replicate samples. If an IND or 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. To test the method with larger food samples, 100 g apple aliquots were added to 1 L glass beakers along with 200 mg of MAPEP 18 soil standard, ^{244}Cm standard (31.4 mBq) and ^{237}Np (37.0 mBq).

Figure 1 shows the rapid fusion and precipitation steps used to digest the samples and preconcentrate the actinides from the alkaline fusion matrix. For the 10 g aliquots, tracers were added to each crucible and the crucibles were dried on a hotplate. For the 100 g aliquots the samples were ramped to 550 °C, ashed for 12 h and the ash was transferred to 250 mL Zr crucibles. The beakers were rinsed with concentrated nitric acid and the rinse was added to the Zr crucibles. 5 mL of 30 wt% hydrogen peroxide was added to each crucible and the ashed samples were dried on a hot plate. The crucibles were heated again in the furnace for ~10 minutes at 600 °C to ensure complete ashing of the food sample. After removing the crucibles from the furnace, 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 ~15 min.

After removing the crucibles from the furnace, the crucibles were cooled for about 10 min, 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. 125 mg of Fe (added as Fe $(NO_3)_3$) and 5 mg of La (as La $(NO_3)_3$) 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.

Four milliliters of 1.25 M $Ca(NO_3)_2$ and 5 mL of 3.2 M $(NH_4)_2HPO_4$ 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. 5 mL of 10% $TiCl_3$ were added to each tube and mixed well. The samples were cooled in an ice bath to room temperature for ~10 min. The tubes were centrifuged at 3,500 rpm for 6 min and the supernatant was discarded. The remaining solids were dissolved in a total volume of ~60 mL of 1.5 M HCl. This solution was diluted to ~170 mL with 0.01 M HCl. After dilution, 1 mg of La (as La $(NO_3)_3$) was added to each sample. To ensure no actinides were in the hexavalent state and facilitate complete precipitation, 3 mL of 10% titanium chloride were added to each sample. 22 mL of 28 M HF were added to each sample. The samples were placed on ice for ~10 min to reduce solubility and centrifuged for 10 min at 3,500 rpm.

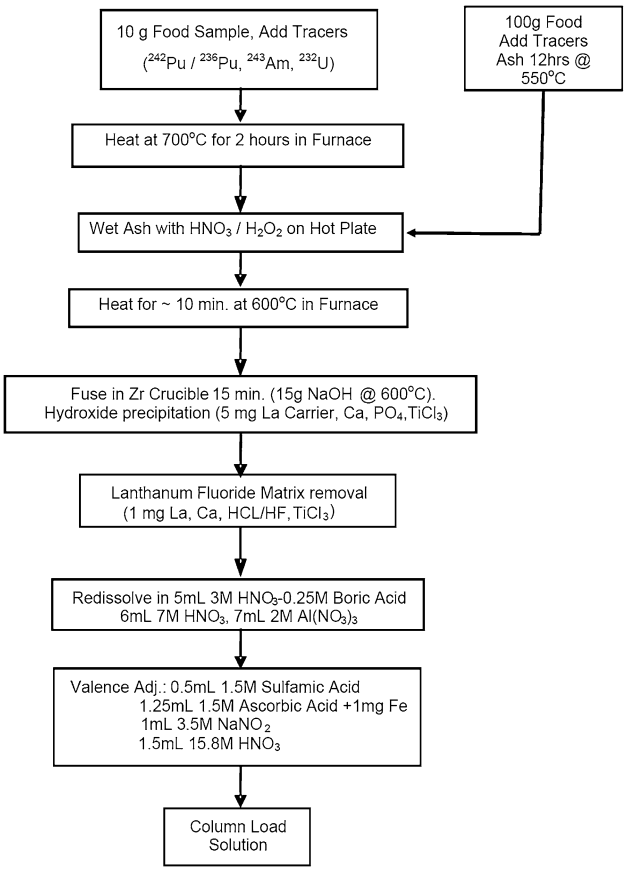

Fig. 1 Rapid fusion method for food samples

The supernatant was discarded and the residual solids containing the actinides were dissolved in 5 mL of warm 3 M HNO_3–0.25 M H_3BO_3, 6 mL of 7 M HNO_3 and 7 mL of 2 M $Al(NO_3)_3$ and 3 mL of 3 M HNO_3. The aluminum nitrate was previously scrubbed to remove trace uranium by passing approximately 250 mL of 2 M 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 min^{-1}. The columns were prepared from a water slurry of the UTEVA Resin. The solids were transferred to 100 mL Teflon beakers during this step and warmed to redissolve the solids. The dissolved samples were transferred to 50 mL tubes and centrifuged at 3,500 rpm to remove any traces of solids.

A valence adjustment was performed on the load solution by adding 0.5 mL of 1.5 M sulfamic acid and 1.25 mL of 1.5 M ascorbic acid with a 3 min wait step to reduce plutonium to Pu^{3+}. Np was assayed along with Pu in the purified Pu fraction using ^{236}Pu tracer. Traces of Fe (converted to Fe^{2+} by ascorbic acid) are present in the column load solution as carryover from the iron-hydroxide precipitation. To enhance reduction of Np to Np^{4+}, additional Fe was added (0.2 mL of 5 mg Fe/mL) to increase the Fe^{2+} levels slightly. If Np assay is not required, the Fe does not need to be added. Following the reduction step, 1 mL of 3.5 M $NaNO_2$ was added to oxidize plutonium to Pu^{4+}. After this oxidation step, 1.5 mL of 15.8 M HNO_3 was added to each sample to increase the nitrate concentration. This enhances Am/Cm retention and reduces Ca retention on DGA Resin.

Column separation

The stacked TEVA, TRU, and DGA Resin cartridge separation was similar to what has been reported previously [3]. Figure 2 shows the column separation method used, which was designed to separate Pu, Np, U, Am, and Cm for assay. The method is flexible and can be modified if only some of these actinides are needed. For example, for Pu (or Pu/Np), only TEVA Resin is used. For Pu and Am (or Am/Cm) isotopes, a TEVA + DGA stacked column can be used. For U, only TEVA + TRU Resins are required. For this study, however, the separation method was used to separate all these actinides sequentially.

Apparatus

Plutonium, neptunium, americium, curium, and uranium isotopic measurements were performed by alpha-particle pulse-height measurements using passivated implanted planar silicon (PIPS) detectors. The PIPS detectors have an

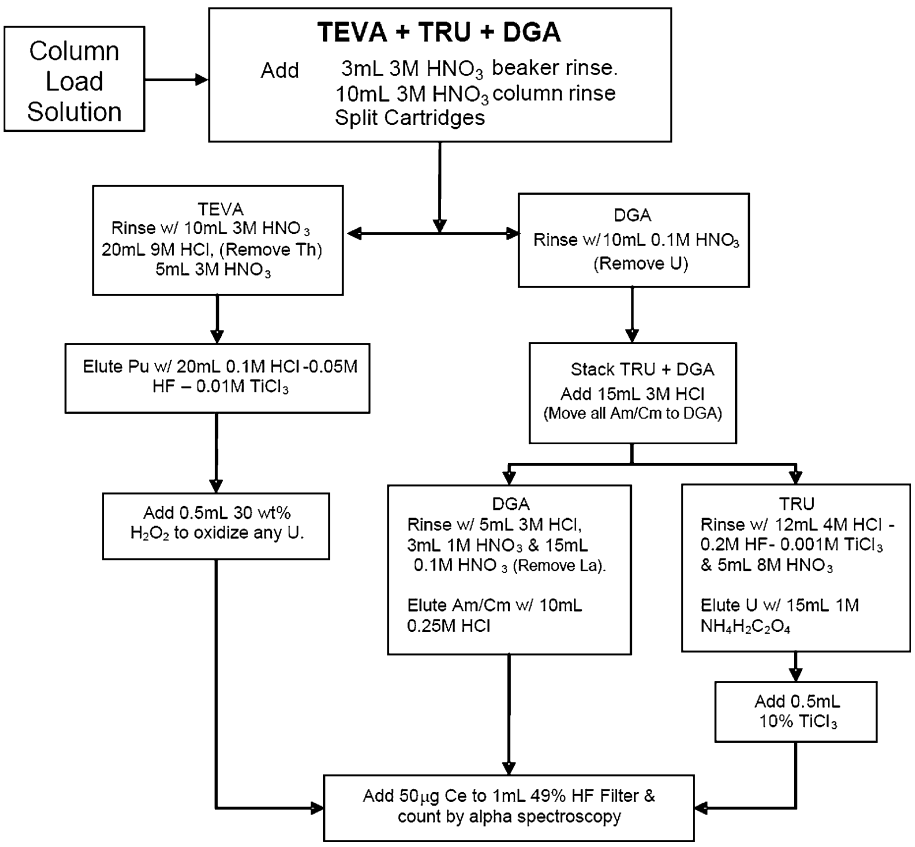

Fig. 2 Rapid sequential column separation method for food samples

active surface of 450 mm^2. The nominal counting efficiency for these detectors is 0.30. The distance between the sample and detector surface is $\sim$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 ^{238}Pu, ^{239}Pu, and ^{237}Np in five 10 g food samples using this rapid separation method and alpha spectrometry. The results were corrected for ^{236}Pu tracer yield. The average ^{238}Pu result for the 10 g baby food samples was 28.9 mBq smp^{-1}, with a -0.7% bias and 1 SD (standard deviation) of 1.3 mBq smp^{-1}. The average ^{239}Pu result was 33.2 mBq smp^{-1}, with a -7.9% bias and 1 SD of 3.5 mBq smp^{-1}. The average ^{237}Np result was 34.0 mBq smp^{-1}, with a -8.1% bias and 1 SD of 2.1 mBq smp^{-1}. The high ^{236}Pu tracer recoveries and excellent results for the analytes versus known values indicate the sample preparation and measurement steps for the baby food samples were effective. The average tracer recovery for ^{236}Pu was 93.5 $\pm$ 7.5% at 1 SD. The ^{237}Np results had a slight negative bias, perhaps due to the slightly lower *k'* of Np on TEVA Resin compared to Pu in 3 M HNO_3, however this bias was acceptable for emergency response and would have even passed MAPEP program bias limits of $\pm$20% for routine analysis.

The results for 10 g apple sauce, apples, and squash samples are also shown with excellent results for ^{238}Pu, ^{239}Pu, and ^{237}Np, with tracer recoveries for ^{236}Pu averaging about 97%. The good results for ^{239}Pu for all samples demonstrate the ruggedness of the rapid fusion method since the ^{239}Pu isotope added was refractory. A larger negative balance for ^{237}Np for the squash samples was observed. It is possible that there was incomplete reduction of Np to Np^{4+}, since, for the squash samples, no additional Fe was added to the column load solution to generate Fe^{2+}, which is very effective in reducing Np. A small amount of Fe ions are present in the column load solution from the $Fe(OH)_2$ precipitation, despite the LaF_3 matrix removal step. This amount may not have been sufficient, however, to fully reduce Np to Np^{4+}, explaining the slight negative bias. One can also use ^{239}Np as an alternate yield monitor if desired.

Table 2 shows the results for the determination of ^{241}Am and ^{244}Cm in the 10 g food samples using alpha spectrometry. The average ^{241}Am result for the apple samples, for example was 49.4 mBq smp^{-1}, with a -2.8%

Table 1 Pu and Np results for 10 g food samples

	Sample ID	^{236}Pu yield (%)	^{238}Pu measured mBq Smp^{-1}	^{239}Pu measured mBq Smp^{-1}	^{237}Np measured mBq Smp^{-1}
10 g baby food $N = 5$	Avg.	93.5	28.9	33.2	34.0
	1 SD	7.5	1.3	3.5	2.1
	% RSD	8.1	4.6	10.7	6.1
	Reference		29.1	36	37
	% Difference		−0.7	−7.9	−8.1
10 g apple sauce $N = 5$	Avg.	96.2	14.2	18.7	36.0
	1 SD	4.2	1.4	2.3	2.0
	% RSD	4.4	9.9	12.1	5.7
	Reference		14.6	18	37
	% Difference		−3.0	4.0	−2.7
10 g apples $N = 5$	Avg.	97.5	29.0	35.7	32.7
	1 SD	11.8	0.9	4.1	1.4
	% RSD	12.1	3.2	11.6	4.1
	Reference		29.1	36	37
	% Difference		−0.5	−0.9	−11.5
10 g squash $N = 5$	Avg.	97.5	29.4	33.7	30.4
	1 SD	5.7	1.1	1.8	2.4
	% RSD	5.9	3.7	5.5	7.9
	Reference		29.1	36	37
	% Difference		1.0	−6.3	−17.8

Table 2 Am and Cm results for 10 g food samples

	Sample ID	^{243}Am yield (%)	^{241}Am measured mBq Smp^{-1}	^{244}Cm measured mBq Smp^{-1}
10 g baby food $N = 5$	Avg.	84.6	49.1	36.5
	1 SD	6.3	0.7	3.1
	% RSD	7.5	1.4	8.4
	Reference		50.9	35
	% Difference		−3.5	4.4
10 g apple sauce $N = 5$	Avg.	88.5	24.8	33.4
	1 SD	3.1	2.1	2.2
	% RSD	3.5	8.5	6.5
	Reference		25.4	35
	% Difference		−2.3	−4.6
10 g apples $N = 5$	Avg.	93.4	49.4	37.2
	1 SD	8.5	3.4	4.8
	% RSD	9.1	6.9	12.9
	Reference		50.8	35
	% Difference		−2.8	6.3
10 g squash $N = 5$	Avg.	88.5	49.8	35.9
	1 SD	3.1	1.8	2.7
	% RSD	3.5	3.7	7.4
	Reference		50.8	35
	% Difference		−2.0	2.6

Table 3 U isotope results for 10 g food samples

	Sample ID	^{232}U yield (%)	^{234}U measured mBq Smp^{-1}	^{238}U measured mBq Smp^{-1}
10 g baby food $N = 5$	Avg.	77.9	55.9	59.0
	1 SD	10.2	3.6	2.3
	% RSD	13.1	6.4	3.8
	Reference		56.8	59.2
	% Difference		−1.5	−0.3
10 g apple sauce $N = 5$	Avg.	88.9	26.6	27.5
	1 SD	2.9	1.3	1.6
	% RSD	3.3	5.1	5.6
	Reference		28.4	29.6
	% Difference		−6.4	−7.1
10 g apples $N = 5$	Avg.	88.9	56.1	55.4
	1 SD	9.7	3.3	4.2
	% RSD	10.9	6.0	7.5
	Reference		56.8	59.2
	% Difference		−1.2	−6.4
10 g squash $N = 5$	Avg.	77.9	54.2	60.5
	1 SD	10.2	2.0	3.3
	% RSD	13.1	3.7	5.5
	Reference		56.8	59.2
	% Difference		−4.6	2.3

bias and 1 SD of 3.4 mBq smp^{-1}. The average ^{244}Cm result was 37.2 mBq smp^{-1}, with a 6.3% bias and 1 SD of 4.8. The average tracer recovery for ^{243}Am for these samples was 93.4 ± 8.5% at 1 SD. The ^{243}Am tracer corrections were applied to the ^{241}Am and ^{244}Cm sample results. This illustrates that under these conditions ^{243}Am works very well as tracer for ^{244}Cm. These results show the effectiveness of the separation and measurements, and illustrate that DGA Resin continues to be an excellent resin for Am/Cm separation from difficult sample matrices. Am^{3+} and Cm^{3+} both have very high *k*' values on DGA Resin. In contrast to TRU Resin, Fe^{3+} has no essentially no adverse impact, making Am/Cm separation on DGA Resin ideal for difficult samples [11].

The results for 10 g baby food, apple sauce and squash samples are also shown with excellent results for ^{241}Am and ^{244}Cm isotopes, with tracer recoveries for ^{243}Am averaging between 85 and 88%.

Table 3 shows the results for the determination of ^{234}U and ^{238}U isotopes in the 10 g food samples using alpha spectrometry. The U isotope results were corrected for ^{232}U tracer yield. The average ^{234}U result for the 10 g apple sauce samples was 26.6 mBq smp^{-1} (1 SD of 1.3 mBq smp^{-1}), with an average bias was −6.4% for ^{234}U. The average ^{238}U result was 27.5 mBq smp^{-1} (1 SD of 1.6 mBq smp^{-1}) with an average bias of −7.1%. The ^{232}U tracer yield was 88.9 ± 2.9% at 1 SD. No corrections were made for any of the actinide isotopes present in unspiked samples because no significant amounts were detected.

The 100 g samples were prepared in a slightly different manner to accommodate the much large sample size. Although 100 g sample aliquots were processed, it is likely than sample aliquots larger than 100 g could have also been prepared. The samples were ashed overnight in large

Table 4 Pu and Np results for 100 g apple samples

Sample ID	^{236}Pu yield (%)	^{238}Pu measured mBq Smp^{-1}	^{239}Pu measured mBq Smp^{-1}	^{237}Np measured mBq Smp^{-1}
1	81.9	29.1	34.2	35.7
2	77.2	30.5	41.4	37.6
3	75.0	29.1	37.7	36.6
4	66.8	33.0	42.5	37.2
5	90.7	28.4	31.4	31.9
Avg.	78.3	30.0	37.4	35.8
1 SD	8.8	1.8	4.7	2.3
% RSD	11.3	6.1	12.5	6.4
Reference		29.1	36	37
% Difference		3.1	4.0	−3.3

1 L glass beakers and then the ash was transferred to the 250 mL Zr crucibles, with beaker rinses added. The chemistry steps after that were identical to the 10 g sample fusion method.

Table 4 shows the individual results for the determination of ^{238}Pu, ^{239}Pu, and ^{237}Np in five 100 g apple samples using alpha spectrometry. The results were corrected for ^{236}Pu tracer yield. The average ^{238}Pu result was 30.0 mBq smp^{-1}, with a 3.1% bias and 1 SD of 1.8 mBq smp^{-1}. The average ^{239}Pu result was 37.4 mBq smp^{-1}, with a 4.0% bias and 1 SD of 4.7 mBq g^{-1}. The average ^{237}Np result was 35.8 mBq smp^{-1}, with a −3.3% bias and 1 SD of 2.3 mBq smp^{-1}. The average tracer recovery for ^{236}Pu was 78.3 ± 8.8% at 1 SD. The tracer recoveries were less than the recoveries for the 10 gram samples but are more than adequate.

Table 5 shows the results for the determination of ^{241}Am and ^{244}Cm in the 100 g apple samples using alpha spectrometry. The average ^{241}Am result was 24.8 mBq smp^{-1}, with a −2.3% bias and 1 SD of 2.1 mBq smp^{-1}. The average ^{244}Cm result was 40.6 mBq smp^{-1}, with a 15.9% bias and 1 SD of 3.2 mBq smp^{-1}. The average tracer recovery for ^{243}Am was 75.7 ± 3.2% at 1 SD. The ^{243}Am tracer corrections were applied to the ^{241}Am and ^{244}Cm sample results. It is not certain why the ^{244}Cm results were biased high, since if any column losses are ever seen on DGA, Cm^{3+} will be lost before Am^{3+} ions. The ^{241}Am was added via the MAPEP soil while the ^{244}Cm was added via pipet. Perhaps there was a problem with the addition of the ^{244}Cm standard for this set of samples. Without sample #3, however, the average bias was only 12%. MAPEP performance testing limits for actinides are ±20% and all the Cm results were still within those limits with the exception of sample #3.

Table 6 shows the results for the determination of ^{234}U and ^{238}U isotopes for the five 100 g apple samples using alpha spectrometry. The U isotope results were corrected for ^{232}U tracer yield. The average ^{234}U result was 56.0 mBq smp^{-1} (1 SD of 3.8 mBq smp^{-1}). The average bias for ^{234}U in these samples was −1.4%. The average ^{238}U result was 57.6 mBq smp^{-1} (1 SD of 5.2 mBq smp^{-1}). The average bias for ^{238}U in these samples was −2.7%. The average ^{232}U tracer yield was 71.3 ± 5.4% at 1 SD.

The minimum detectable activity (MDA) for the actinide isotopes by alpha spectrometry were calculated according to equations prescribed by Currie: [13]

$$\mathrm{MDA} = \frac{\left[3 + 4.65\sqrt{\mathrm{B}}\right]}{(\mathrm{CT}^{*}R^{*}W^{*}\mathrm{Eff}^{*}0.060)}$$

where B is the total background counts, = BKG (rate) *BKG count time; CT Sample count time (min); R is the chemical recovery; W is the sample aliquot (g); Eff is the detector efficiency; and 0.060 is the conversion from dpm to mBq.

Table 5 Am and Cm results for 100 g apple samples

Sample ID	^{243}Am yield (%)	Am measured mBq Smp^{-1}	^{244}Cm measured mBq Smp^{-1}
1	79.2	23.5	39.1
2	71.1	24.6	37.4
3	73.9	23.0	45.9
4	77.1	28.4	41.1
5	77.1	24.7	39.5
Avg.	75.7	24.8	40.6
1 SD	3.2	2.1	3.2
% RSD	4.2	8.5	8.0
Reference		25.4	35
% Difference		−2.3	15.9

Table 6 U isotope results for 100 g apple samples

Sample ID	^{232}U yield (%)	^{234}U measured mBq Smp^{-1}	^{238}U measured mBq Smp^{-1}
1	75.0	57.4	58.1
2	66.7	59.6	52.5
3	69.3	51.8	54.4
4	66.7	59.2	66.0
5	78.8	52.2	57.0
Avg.	71.3	56.0	57.6
1 SD	5.4	3.8	5.2
% RSD	7.6	6.7	9.0
Reference		56.8	59.2
% Difference		−1.4	−2.7

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 ~0.2 mBq/g for a 2 h count time and 10 g sample. Longer count times can be used to lower MDA levels as needed. For example, for a 16 h count time and a 10 g sample, an MDA of 0.04 mBq can be achieved. Higher level tracers (e.g., 370 mBq) should be used in conjunction with shorter count times, such as 1–4 h, for more rapid analysis.

The USA FDA provided guidance regarding accidental contamination of foods to state and local agencies so that protective actions may be taken. As stated, the FDA DILs for ^{238}Pu + ^{239}Pu + ^{241}Am is 2 Bq/kg (2 mBq/g or 0.054 pCi/g) [8]. This new method will meet the FDA DIL requirements with 10 g sample aliquots and short count times. Longer count times and larger sample aliquots may be used as needed. Typically, the USA FDA recommends

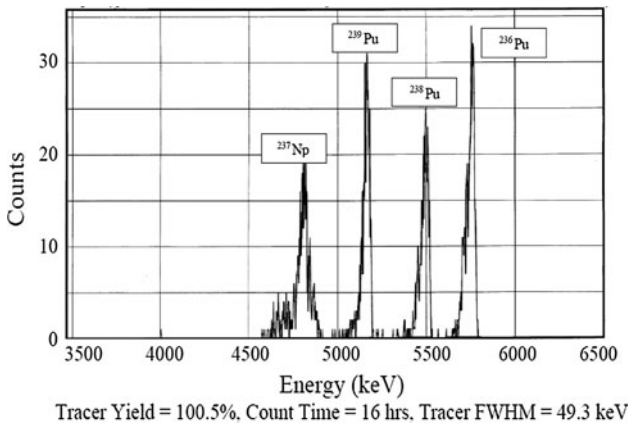

Fig. 3 Alpha spectra–Pu/Np isotopes in spiked food sample

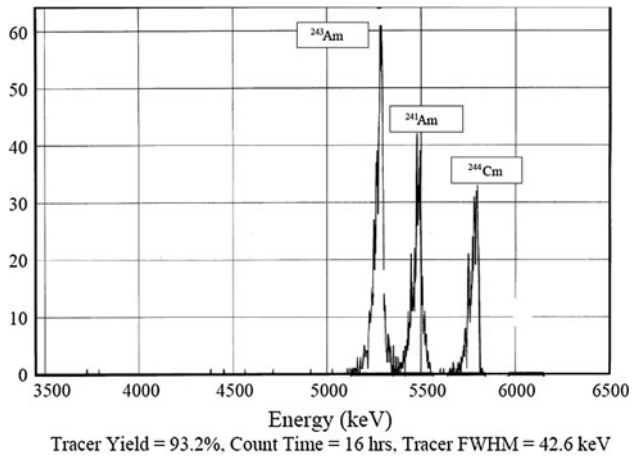

Fig. 4 Alpha spectra–Am/Cm isotopes in spiked food sample

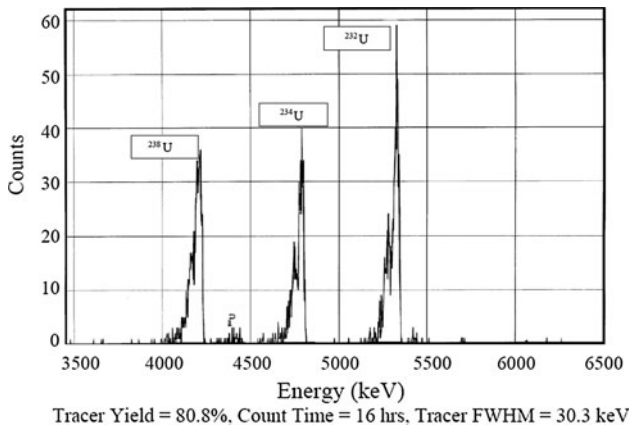

Fig. 5 Alpha spectra–U isotopes in spiked food sample

MDA levels be 1/3 of the DIL. These MDAs are readily achievable using this rapid method.

Figure 3 shows an example of the spectra of Pu isotopes in a food sample. The ^{236}Pu tracer recovery was 100.5% and the full width half maximum (FWHM) was 49.3 keV, showing acceptable alpha peak resolution and good tracer recovery. The ^{239}Pu peak labeled on the spectra represents ^{239}Pu + ^{240}Pu, since these isotopes have overlapping alpha energies. Figure 4 shows an example of the spectra of Am and Cm in a food sample. The ^{243}Am tracer recovery was 93.2% and the FWHM was 42.6 keV, showing acceptable alpha peak resolution and good tracer recovery. Figure 5 shows an example of the Uranium isotope spectra in a food sample. The ^{232}U tracer recovery was 80.8% and the FWHM was 30.3 keV, showing acceptable alpha peak resolution and good tracer recovery.

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. Some laboratories, however, have had success reusing resins.

The initial sample ashing step for 10 g food aliquots takes about 2 h for a batch of ten samples. The rapid fusion method plus precipitation steps takes about 1.5 h, followed by actinide separation steps that take about 2.5–3 h to complete (depending on flow rates used). Samples may be counted by alpha spectrometry for 1–16 h in an emergency or for routine analyzes using appropriate level tracers for the desired count time to minimize counting uncertainty. If an RDD, IND or even a nuclear accident were to occur in an area where food materials must be tested for radioactivity levels, this rapid method can be applied to samples even containing refractory particles with high throughput and reliability. In this work, Pu and Np isotopes were collected together, but they may be effectively separated by moving Pu from TEVA Resin to DGA Resin if that is required. 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 [14–17].

Conclusions

A new rapid method to determine Pu, Np, U, Am, and Cm isotopes in 10 and 100 g food 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. The FDA DIL for ^{238}Pu + ^{239}Pu + ^{241}Am is 2 Bq/kg (2 mBq/g or 0.054 pCi/g) can me met using this method. Larger food aliquots and longer count times may be applied. ICP-MS may also be used with slight variations in column eluents.

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