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Rapid Determination of Actinides in Emergency Food Samples

S. L. Maxwell, B.K. Culligan, A. Kelsey-Wall and P. J. Shaw

Savannah River National Laboratory
Aiken, SC

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Background

- Need for rapid radiochemical methods
  - Emergency response
    - IND, RDD, nuclear accident
    - Large numbers of samples
      - environmental and bioassay analyses
    - Rapid turnaround times

What about food?

- Rapid food analyses may be needed if an IND, RDD or nuclear accident occurs
- Refractory particles may be present
- Needed rugged yet rapid analyses
  - What is available?

Fukushima Impact on Food Chain

- Radiation fallout from the wrecked Fukushima nuclear plant poses a growing threat to Japan's food chain as unsafe levels of cesium found in beef on supermarket shelves were also detected in more vegetables and the ocean
  - Japan has no centralized system to check for radiation contamination of food, leaving local authorities and farmers conducting voluntary tests. Products including spinach, mushrooms, bamboo shoots, tea, milk, plums and fish have been found contaminated with cesium and iodine as far as 360 kilometers from Dai-ichi.
  - Hay contaminated with as much as 690,000 becquerels a kilogram, compared with a government safety standard of 300 becquerels, has been fed to cattle. Cattle with unsafe levels of the radioactive element were detected in four prefectures, the health ministry said July 23.

Japan's Food-Chain Threat Multiplies as Fukushima Radiation Spreads

By Aya Takada - **JUL 25, 2011 4:59 AM ET**

http://www.bloomberg.com/news/2011-07-24/threat-to-japanese-food-chain-multiplies-as-cesium-contamination-spreads.html

Japan Food Concerns

- Kimie Nozaki, a mother of three children living 60 kilometers from the crippled Fukushima nuclear reactors, said she doesn't trust the government's testing program for radiation-contaminated food.
- The main thing here is restoring confidence in the food supply. If people don't have confidence in the food supply, that can cause as many problems as the reality." There's no centralized checking system and many small farms aren't tested, Taku Ohara, an official in the ministry's inspection and safety division said.
- "It's difficult to take test samples from all farms because there are too many," he said. "We have asked local governments to cover each of the farming regions and monitor them evenly."

http://www.bloomberg.com/news/2011-06-15/japan-s-piecemeal-radiation-testing-heightens-concerns-over-safety-of-food.html

Literature

- Bari, A., Khan, A.J., Semkow, T.M., Syed, U.-F., Roselan, A., Haines, D.K., Roth, G., West, L. and Arndt, M. (2011) Rapid screening of radioactivity in food for emergency response, Applied Radiation and Isotopes 69, 834–843
  - screening was done using an acid leaching technique combined with gross alpha/gross beta method
  - achieved good recoveries for spiked samples using gas flow proportional counting.
  - was not specific for actinide isotopes and does not address refractory particles that may be present as a result of a radiological event.

Literature

- Evans, P., Elahi, S., Lee R. and Fairman, B. (2003) A rapid and accurate method for the determination of plutonium in food using magnetic sector ICP-MS with an ultra-sonic nebulizer and ion chromatography, J. of Environ. Monit. 5, 175-179
  - used magnetic sector ICP-MS and ion chromatography
  - digested in concentrated nitric acid using closed vessel microwave digestion (limited to ~0.5 g aliquots)
  - chromatographic separation 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 using hydrogen peroxide, but there seemed to be a negative impact on Am recoveries when this was added
    - hydrogen peroxide was necessary to achieve good recoveries for Pu and Np
  - a timeline was given where Pu (excluding Pu-238) 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

Literature

- Mellado, J., Llaurado, M. and Rauret G. (2002) Determination of actinides and strontium in fish samples by extraction chromatography, Analytical Chimica Acta, 458, No.2, 367-374
  - UTEVA Resin, TRU Resin and Sr-Resin
  - samples from 5 to 40 grams were analyzed with recoveries that were often less than 40%.
  - fish reference material IAEA-414 was analyzed with and without calcination
  - Low recoveries
    - 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.

Approach

- Could we apply rapid fusion technology we have used for NRIP emergency vegetation samples to food ?
  - Previous method: furnace, wet-ash, acid leach digestion
    - Residual ash/solids
    - Lower tracer recoveries
  - Now: furnace, wet-ash, *rapid fusion*
  - Why: eliminate lower, inconsistent yields and improve quality
  - TEVA Resin +TRU Resin + DGA Resin, then Sr Resin
  - CeF_3 microprecipitation-alpha spectrometry
  - Sr-89/90- gas proportional counting
    - Gravimetric recovery-Sr carrier (4mg)
  - Results in <8 hours

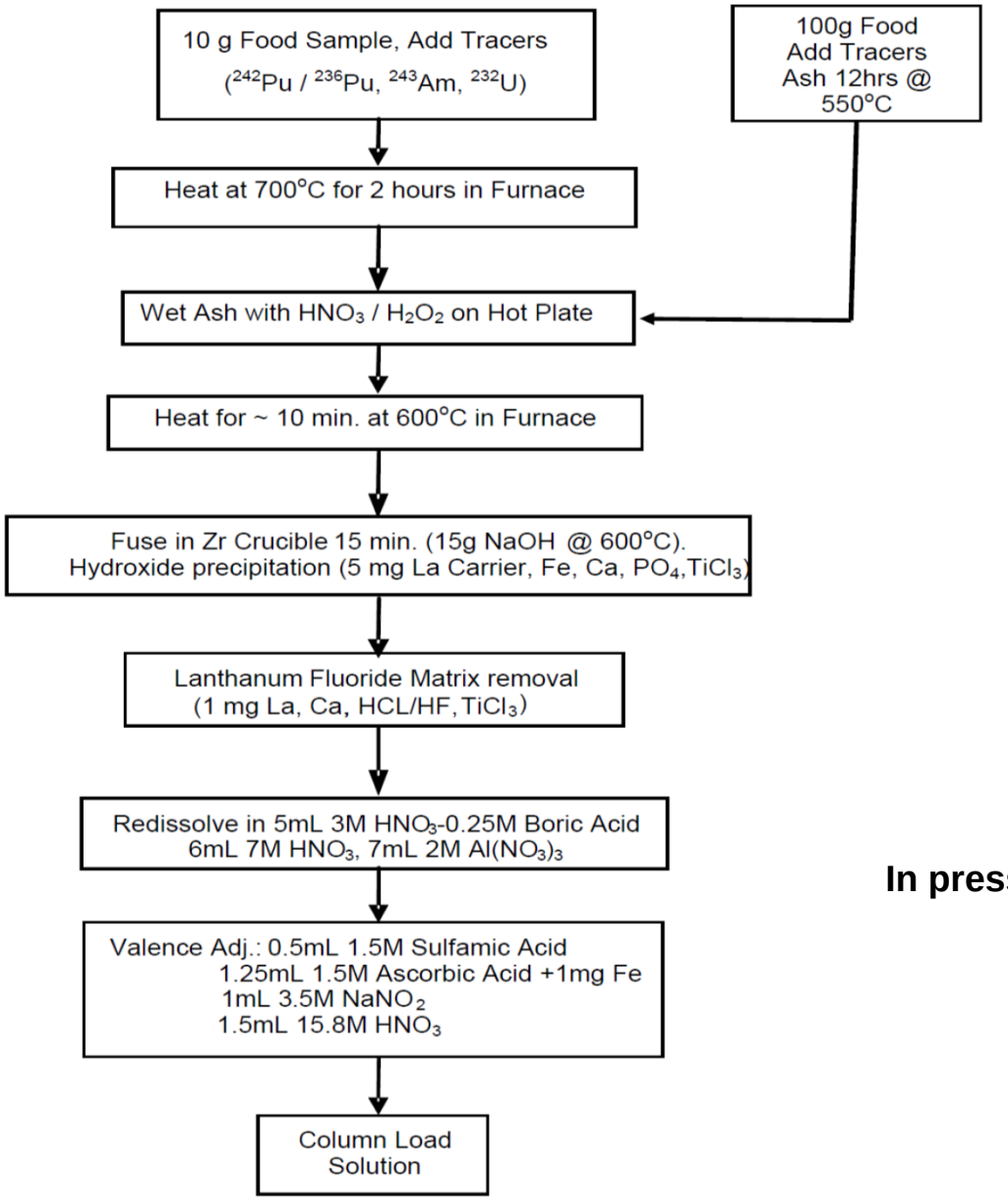
Maxwell, S., Culligan, B. and Noyes, G., Rapid Separation of Actinides and Radiostrontium in Vegetation Samples, J. Radioanal. Nucl. Chem, (2010), 286:273–282

FDA Requirements

- 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
- FDA Derived Intervention Level (DIL) for ^{238}Pu+ ^{239}Pu + ^{241}Am is 2 Bq/kg (2 mBq/g or 0.054 pCi/g).
  - 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.

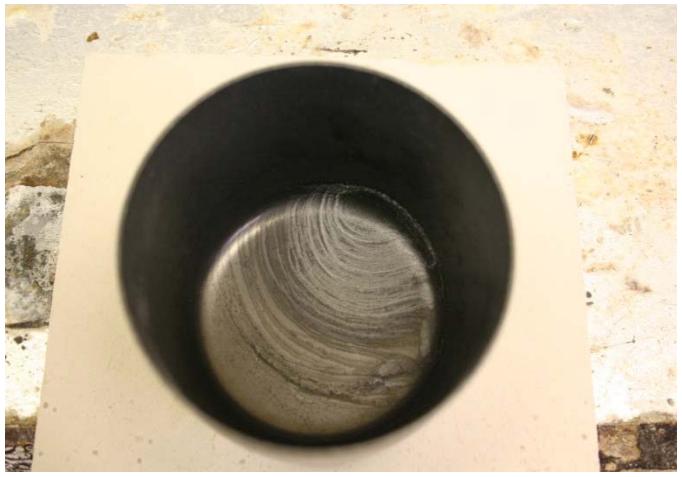
  - U.S Department of Health and Human Services, Food and Drug Administration, Accidental Radioactive Contamination of Human Food and Animal Feeds: Recommendations for State and Local Agencies, Center for Devices and Radiological Health, August 13, 1998, http://www.fda/cdrh

Actinides in Food

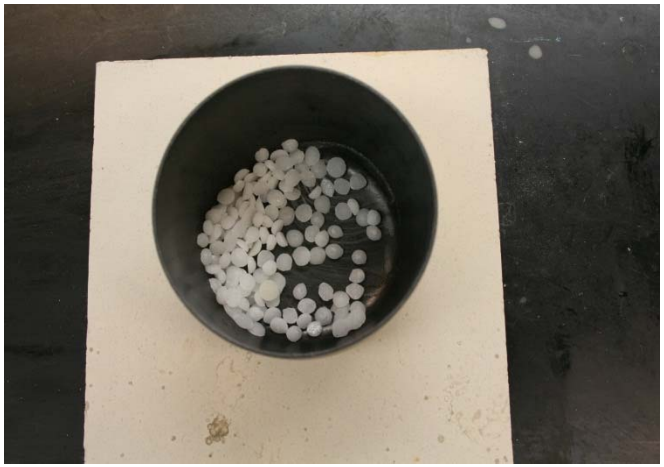


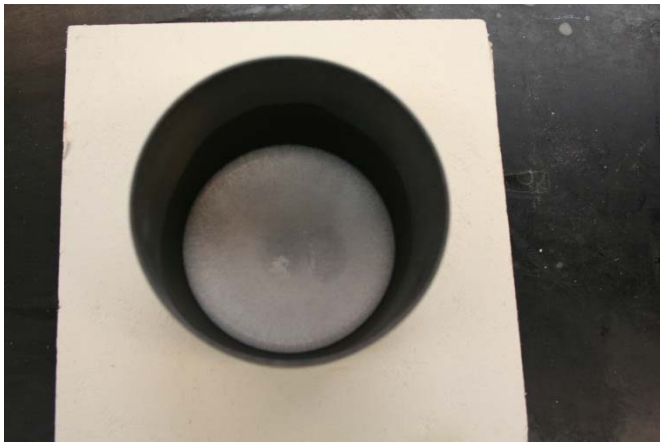
In press JRNC

Rapid Furnace Heating of Food Aliquots

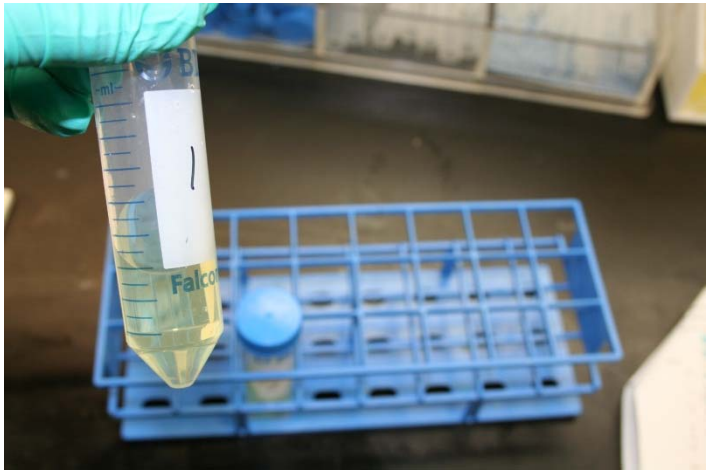


Rapid Sodium Hydroxide Fusion

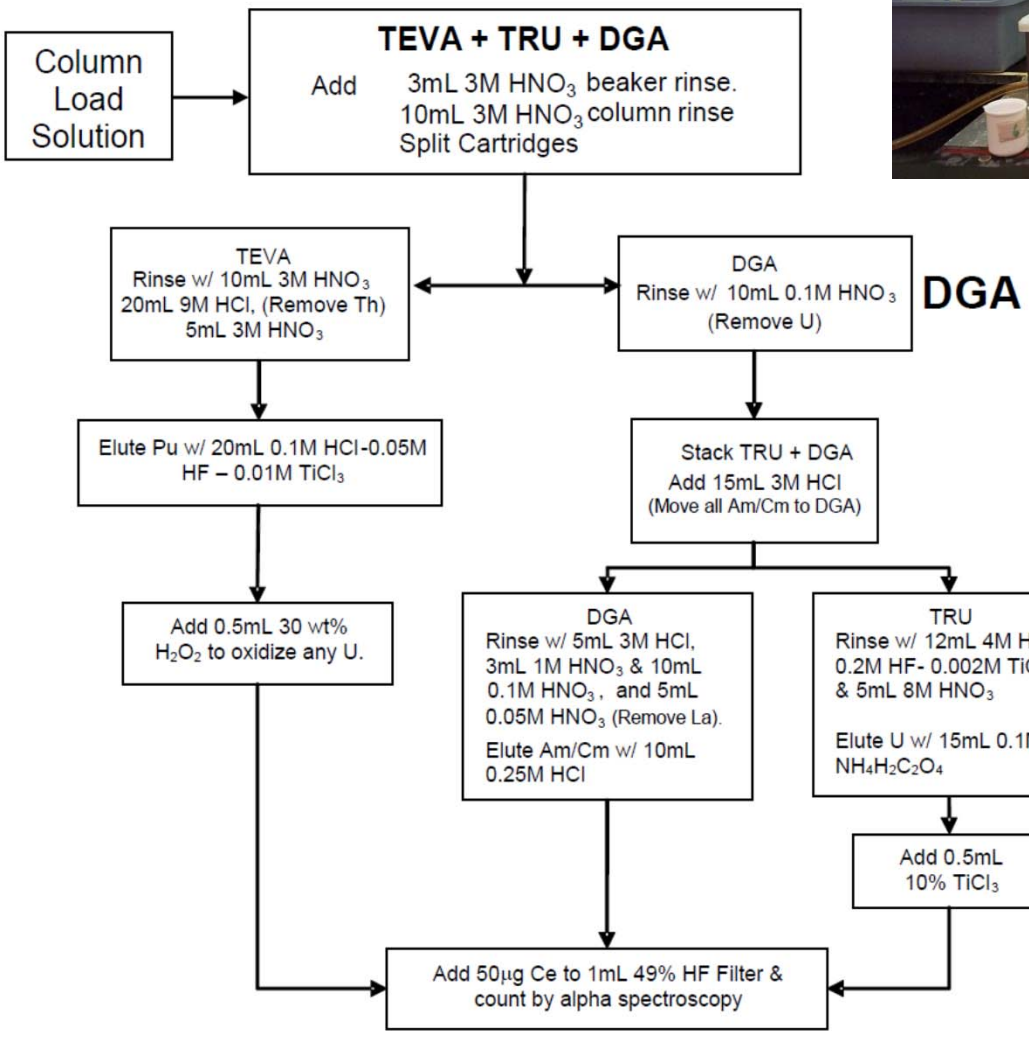




Preconcentration Steps



Rapid Column Separation



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Pu and Np Results for 10g food aliquots

	Sample ID	^{236}Pu Yield (%)	^{238}Pu Measured mBq Smp^{-1}	^{239}Pu Measured mBq Smp^{-1}	^{237}Np Measured mBq Smp^{-1}
10g baby food N=5	Avg.	93.5	28.9	33.2	34.0
	1SD	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
10g apple sauce N=5	Avg.	96.2	14.2	18.7	36.0
	1SD	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
10g apples N=5	Avg.	97.5	29.0	35.7	32.7
	1SD	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
10g squash N=5	Avg.	97.5	29.4	33.7	30.4
	1SD	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

Am and Cm Results for 10g food aliquots

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

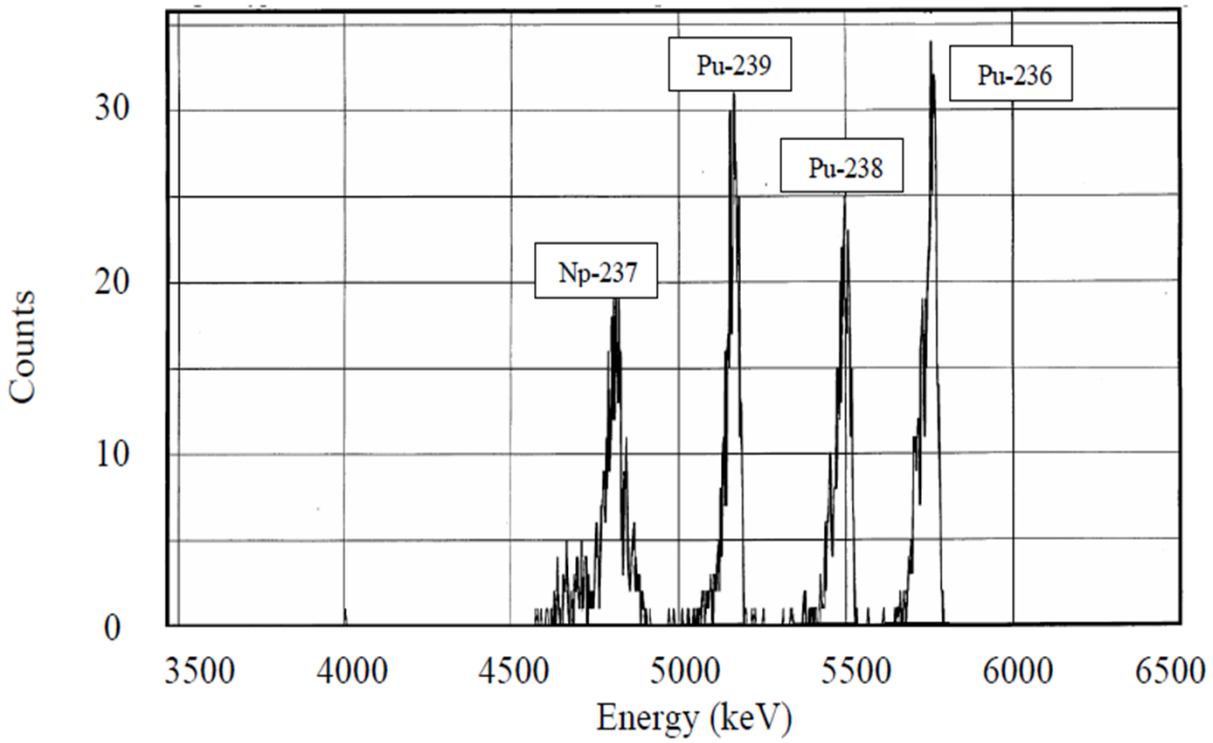
U Isotope Results for 10g food aliquots

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

Pu and Np Results for 100g food aliquots

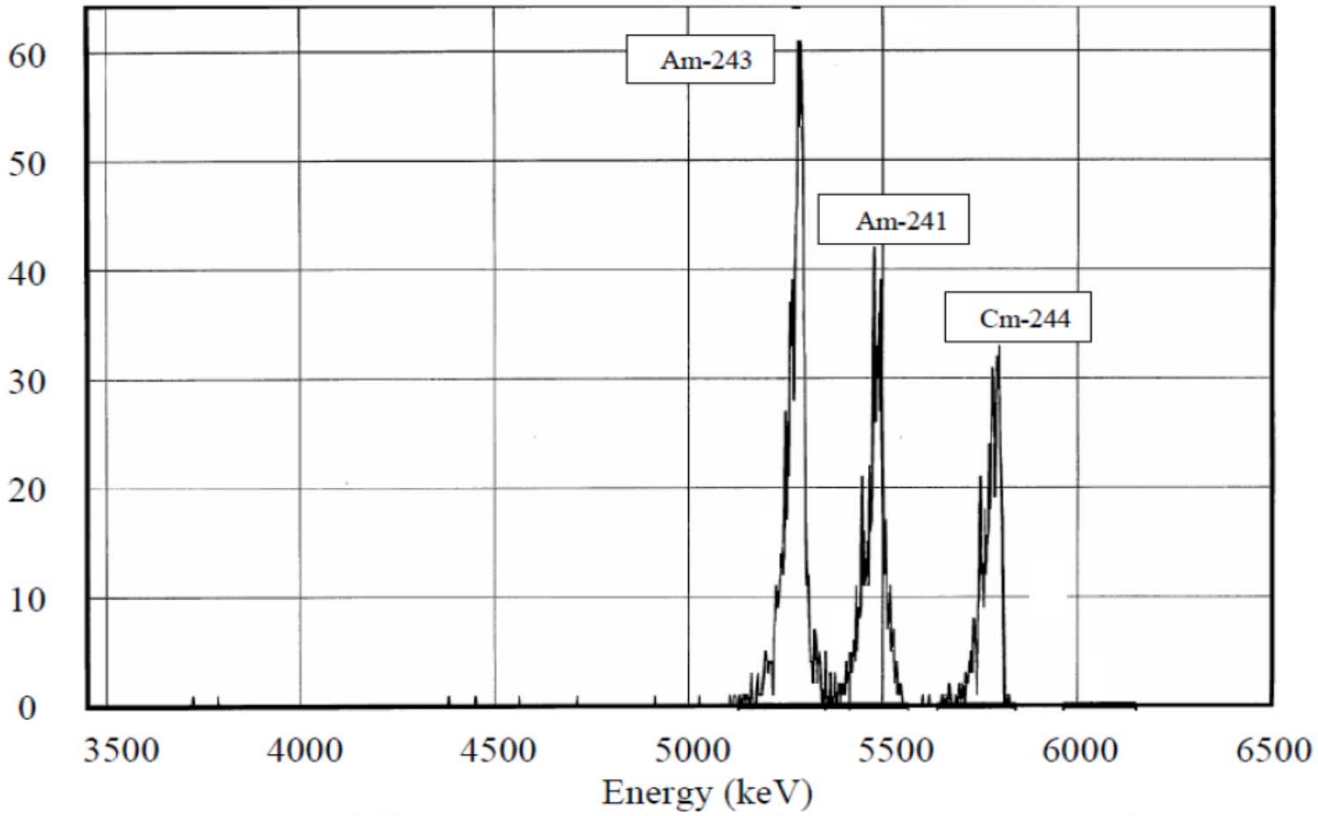
Sample ID	^{236}Pu Yield (%)	^{238}Pu Measured mBq Smp^{-1}	^{239}Pu Measured mBq Smp^{-1}	^{237}Np Measured mBq Smp^{-1}
1	81.9	29.1	34.2	35.7
2	77.2	30.5	41.4	37.6
3	75.0	29.1	37.7	36.6
4	66.8	33.0	42.5	37.2
5	90.7	28.4	31.4	31.9
Avg.	78.3	30.0	37.4	35.8
1SD	8.8	1.8	4.7	2.3
%RSD	11.3	6.1	12.5	6.4
Reference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

Pu and Np Alpha Spectra Food Sample



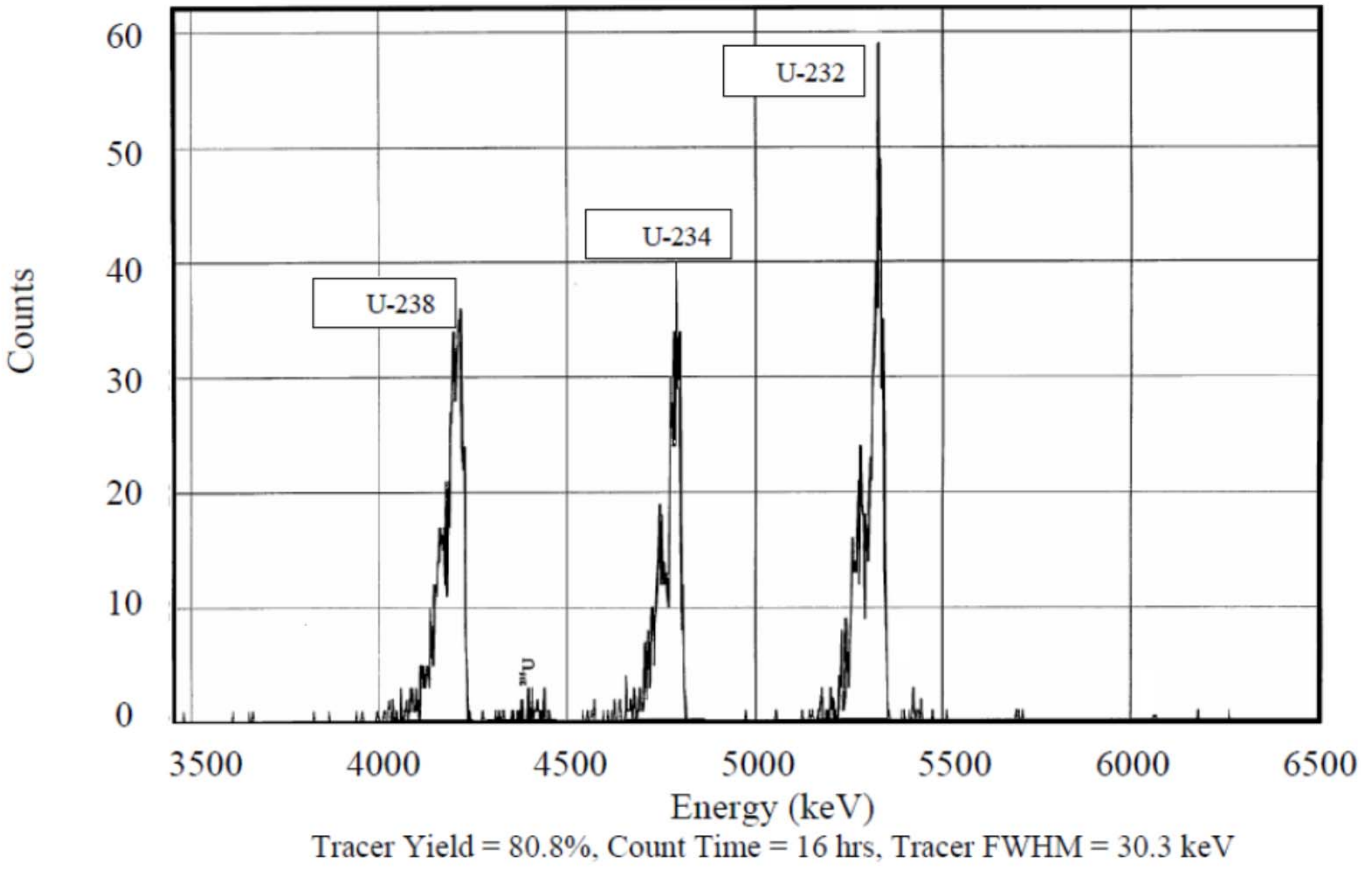
Tracer Yield = 100.5%, Count Time = 16 hrs, Tracer FWHM = 49.3 keV

Am and Cm Alpha Spectra Food Sample



Tracer Yield = 93.2%, Count Time = 16 hrs, Tracer FWHM = 42.6 keV

U Isotope Alpha Spectra Food Sample



Tracer Yield = 80.8%, Count Time = 16 hrs, Tracer FWHM = 30.3 keV

MDA

- U. S. Food and Drug Administration (FDA) provided guidance for accidental contamination of foods to state and local agencies so that protective actions may be taken.
  - FDA derived intervention level (DIL) for 238Pu + 239Pu + 241Am is 2 Bq/kg (2 mBq/g or 0.054 pCi/g).
- SRS method provides a typical MDA of ~0.2 mBq/g for a 10 g food sample and 2 hour count time for each of the actinide isotopes cited in the DIL.
- Method is flexible
  - longer count times can be used to lower MDA levels as needed.
  - For example, for a 16 hour count time and a 10 g sample, an MDA of 0.04 mBq/g can be achieved.
- Typically, the U. S. FDA recommends MDA levels be 1/3 of the DIL.
  - These MDAs are readily achievable using this rapid method.
  - Count times may be extended as needed.

Summary

- Rapid fusion method is effective for food samples
  - Digests refractory particles
  - Good chemical yields
  - Effective removal of interferences
- Meets MDA requirements
  - 10 g can meet FDA DIL
    - FDA derived intervention levels (DIL) for 238Pu + 239Pu + 241Am is 2 Bq/kg (2 mBq/g or 0.054 pCi/g)
  - 100g or more food aliquots can also be processed
  - Can be adapted for ICP-MS using ICP-MS friendly eluents