Isotopic Analysis of Pu in Food by Inductively-Coupled Plasma Mass Spectrometry

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Presentation Outline

- Motivations
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➢ Motivations

- A number of radioactive Pu isotopes are identified as radionuclides of greatest concern for food safety due to their harmful ionizing radiation in association with food consumption
- Rapid detection and quantification of ^{239}Pu and ^{240}Pu in food are required by FDA food safety compliance and emergency response programs
- Need alternative methodology and greater surge capacity to assess extent of food contamination for efficient and effective radiological emergency response
- Pu isotopic composition provides important information for their source identification and enables detailed radiological risk assessment

➢ Objectives

- To develop a robust ICPMS method capable of detecting and quantifying ^{239}Pu and ^{240}Pu in a wide verity of foods
- To develop a isotopic technique enabling accurate measurement of $^{239}Pu/^{240}Pu$ ratio for identification of source of Pu contamination
- To develop a rapid and high-throughput ICPMS method for response to radiological emergency involving Pu
- To adapt agency's radioanalytical methodology to the latest radiochemical separation and atom counting technologies

Experimental Approach

The Pu maximum permissible level for food is 2 Bq/kg, which is extremely difficult to detect without matrix removal, extensive radiochemical separation, and sensitive instrumentation.

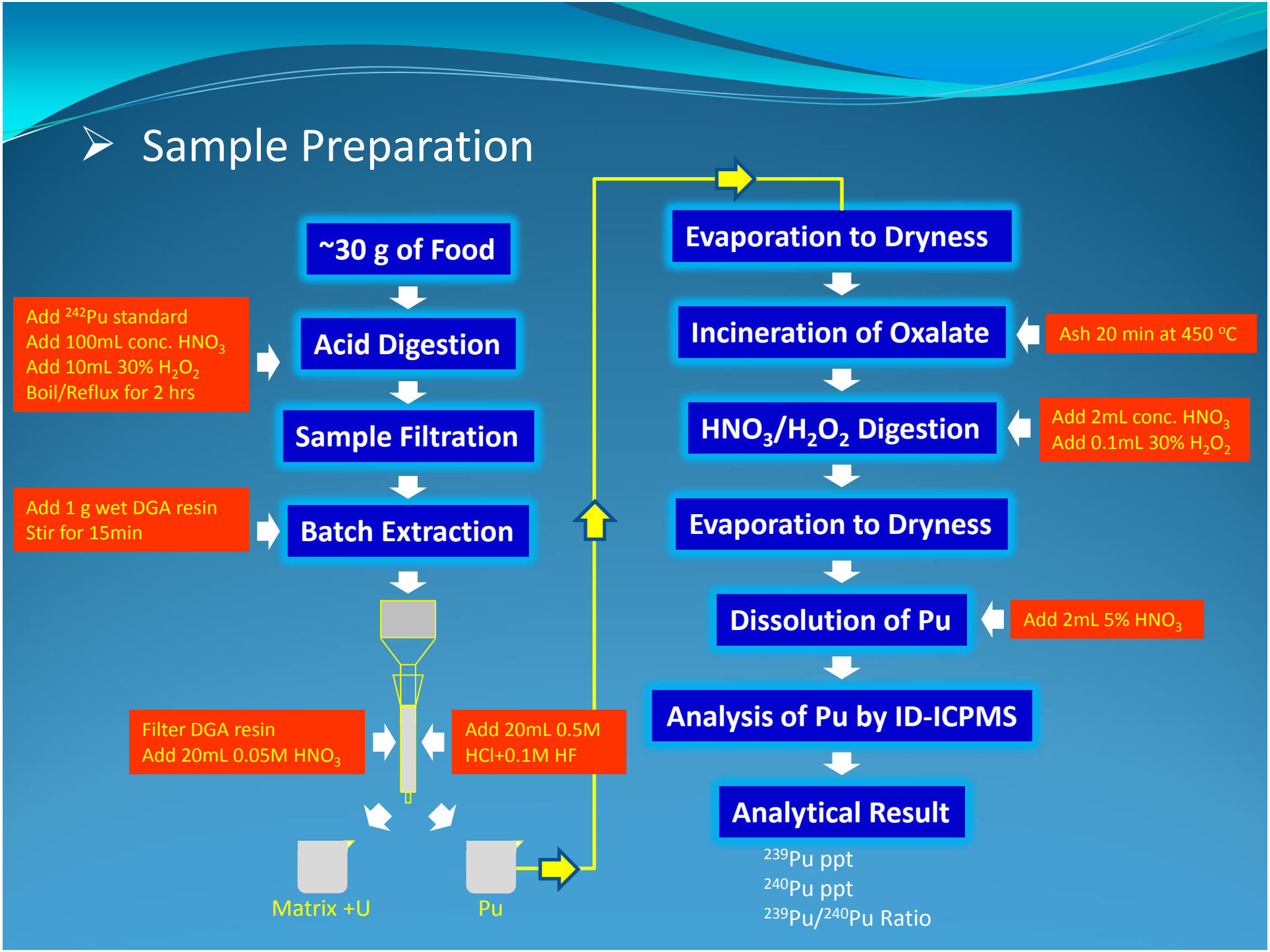
The study plan was formulated with the following in mind:

- Wet digestion of food to rapidly convert Pu into soluble ionic forms
- Use DGA resin to separate Pu from sample matrix and polyatomic interferences
- Broaden method applicability by experimenting with a wide variety of foods including vegetation, meat, dairy, grain, and complex meal
- Apply atom-counting technique instead of radioactive decay counting technique
- Resolve ^{239}Pu and ^{240}Pu radioactivity based on their mass-to-charge ratio rather than their characteristic alpha decay energies

Data Quality Objectives

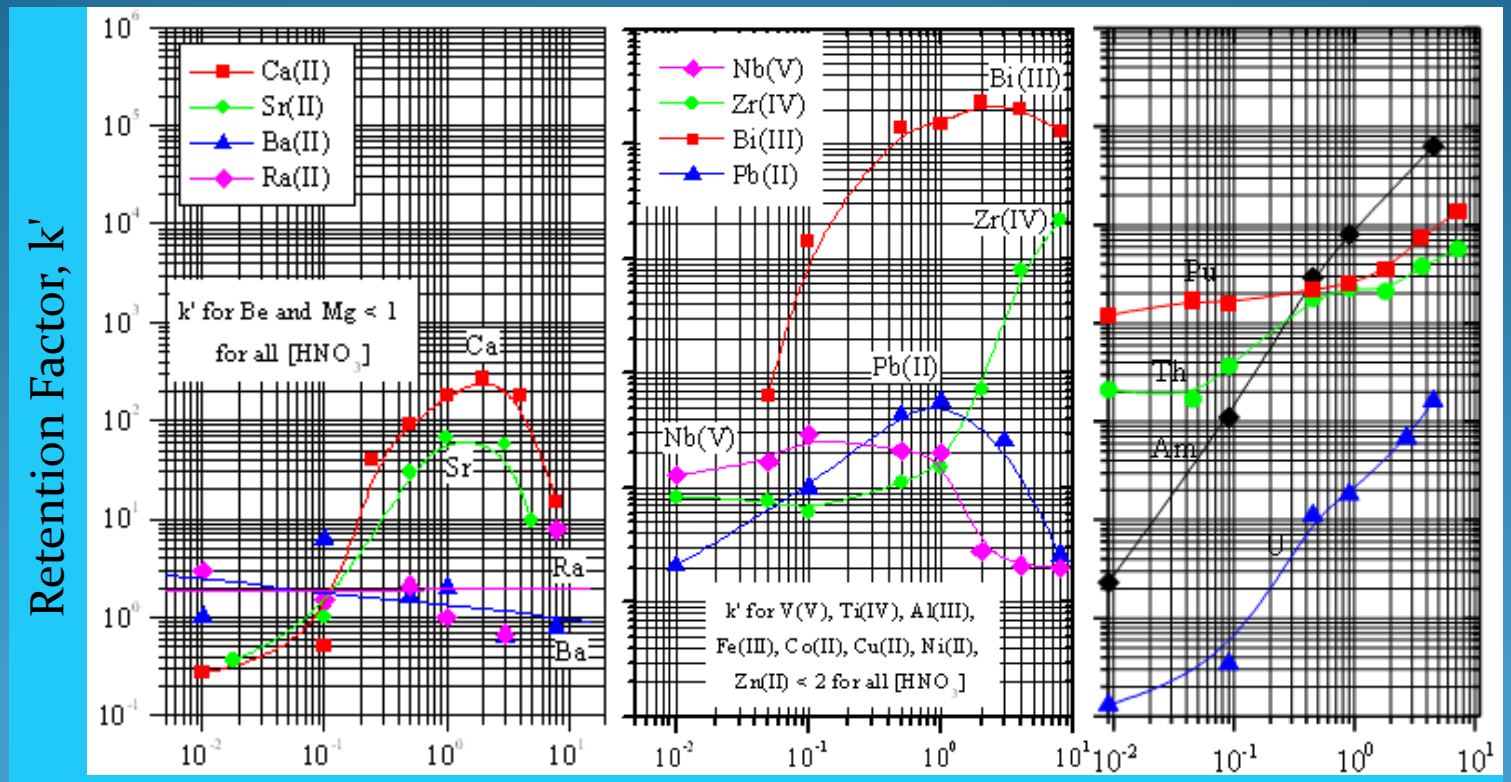
- The benchmark level FDA uses to evaluate food safety is 2 Bq/kg, i.e. for $^{241}Am+^{238}Pu+^{239}Pu$. This is equivalent to ~0.9 ppt of ^{239}Pu or ~0.2 ppt of ^{240}Pu
- With a preference for detecting Pu at 1/3 of the benchmark level, an screening method would ideally be capable of detecting ~0.3 ppt of ^{239}Pu or ~0.1 ppt of ^{240}Pu
- For confirmatory analysis, the method accuracy and precision should be better than ±10% and 20%, respectively
- The method needs be robust enough for analysis of Pu in complex food matrices

Sample Preparation



Justification of using DGA resin:
It has a high affinity toward actinides including Pu(IV), and the uptake increases with increasing acid concentration.

DGA Resin, Normal
(N,N,N',N'-tetra-n-octyldiglycolamide)



(Courtesy of Eichrom Technologies)

Instrument Optimization

Instrument Parameters for Pu Isotopic Analysis:

The purified Pu was analyzed by Agilent 7700x quadrupole ICPMS for ^{239}Pu, ^{240}Pu, and $^{239}Pu/^{240}Pu$. Pu isotopes were identified and separated according to their mass-to-charge ratio (M/Z). ^{239}Pu and ^{240}Pu were quantified using isotope-dilution technique. The instrument was optimized for isotopic analysis of Pu.

Plasma Condition
RF Power = 1550 W
RF Matching = 1.5 V
Sampling Depth = 8 mm
Carrier Gas = 1.17 L/mim
Concentric Nebulizer = Self-aspirating
Spray Chamber Temperature = 2 ^{o}C

Ion Lenses
Extract Lens 1 = 0 V
Extract Lens 2 = -200 V
Omega Bias = -100 V
Omega Lens = 13 V
Cell Entrance = -30 V
Cell Exit = -50 V
Deflect = 16.4 V
Plate Bias = -40 V

Octopole Parameters
Octopole RF = 200 V
Octopole Bias = -8 V

Q-Pole Parameters
AMU Gain = 136
AMU Offset = 120
Axis Gain = 1.0015
Axis Offset = 0.1
QP Bias = -3 V

Detector Parameters
Discriminator = 4.5 mV
Analog HV = 1713 V
Pulse HV = 955 V

Data Collection
Point Per Peak = 3
Dwell Time Per Point = 0. 3 sec
Number of Replicates = 20

Results and Discussion

Deficiency discovered in the initial study:

The following biased results were observed when the purified Pu fractions were analyzed without sufficient resin rinsing and post-separation H_2O_2 treatment.

Results of ^{239}Pu (Bq/kg)

Food Description	Known	Measured	Bias, %
Whole Wheat Bread	0.21309	0.3441	61.48
Peas	0.21309	0.2374	11.41
Vanilla Ice Cream	0.21309	0.2545	19.43
Taco w/Beef & Cheese	0.21309	0.2787	30.79
Bean & Bacon Soup	0.21309	0.2646	24.17

Results of ^{240}Pu (Bq/kg)

Food Discription	Known	Measured	Bias, %
Whole Wheat Bread	0.51573	0.5177	0.38
Peas	0.51573	0.6459	25.24
Vanilla Ice Cream	0.51573	0.5480	6.26
Taco w/Beef & Cheese	0.51573	0.5249	1.78
Bean & Bacon Soup	0.51573	0.5164	0.13

Interference from uranium hydride (UH^+) formation

Source of U in sample:

Incomplete removal of U naturally presented in food
(^{234}U=0.006%, ^{235}U=0.71%, ^{238}U =99.28%)

Source of H in sample:

Incomplete removal of organic substances in purified Pu sample
(resin wash off, 5% HNO_3 solution, residual carbon from food matrix)

Ion mass of UH^+ = $^{238}U + {}^{1}H^+ = {}^{239}(UH)^+$ = 239 amu

Ion mass of $^{239}Pu^+$ = 239 amu

Ion signals of $^{239}Pu^+$ and $^{239}(UH)^+$ are unresolvable by ICPMS. Therefore, it leads to polyatomic ion interference.

Elimination of UH^+

- Use of desolvating nebulizer to remove sample water content before introducing sample into plasma
- Improve removal of sample U content
- Total destruction of residual carbon

Improvement observed with modified procedure:

The following results were obtained by increasing resin rinsing and adding H_2O_2 treatment

Results of ^{239}Pu (Bq/kg)

Food Description	Known ^{239}Pu	Measured	Bias, %
Whole wheat bread	0.21309	0.2351	10.33
Peas	0.21309	0.2177	2.16
Vanilla ice cream	0.21309	0.2213	3.85
Taco w/beef & cheese	0.21309	0.2611	22.53
Bean & bacon soup	0.21309	0.2613	22.62

Results of ^{240}Pu (Bq/kg)

Food Description	Known ^{240}Pu	Measured	Bias, %
Whole wheat bread	0.51573	0.5229	1.39
Peas	0.51573	0.5167	0.19
Vanilla ice cream	0.51573	0.5131	-0.51
Taco w/beef & cheese	0.51573	0.5105	-1.01
Bean & bacon soup	0.51573	0.5174	0.32

A variety of foods, 30-100 g each, were spiked with ^{239}Pu and analyzed. (Bq/kg)

Food Group	Food Name	Known	Measured	Bias, %
Vegetable	Salad 1	3.54	3.52	-0.44
Vegetable	Salad 2	3.75	3.71	-1.02
Vegetable	Salad 3	3.64	3.64	-0.13
Fruit	Apple Sauce 1	7.78	7.76	-0.15
Fruit	Apple Sauce 2	7.58	7.52	-0.83
Fruit	Apple Sauce 3	7.11	7.05	-0.83
Meat	Fish 1	3.78	3.87	2.22
Meat	Fish 2	3.83	3.87	0.99
Meat	Fish 3	3.70	3.78	1.99
Meat	Fish 4	3.67	3.70	0.85
Meat	Beef 1	3.28	3.29	0.15
Meat	Beef 2	3.17	3.12	-1.48
Meat	Beef 3	3.06	3.07	0.32
Meat	Scallop 1	6.85	6.64	-3.05
Meat	Scallop 2	4.82	4.76	-1.40
Meat	Scallop 3	6.61	6.59	-0.34
Meat	Scallop 4	4.73	4.64	-1.97
Meat	Hamburger 1	4.21	4.17	-0.76
Meat	Hamburger 2	5.05	4.96	-1.69
Meat	Hamburger 3	5.05	5.10	0.93
Meat	Hamburger 4	5.07	5.05	-0.42
Grain	Rice Cracker 1	12.34	12.31	-0.28
Grain	Rice Cracker 2	11.78	11.71	-0.59
Grain	Rice Cracker 3	12.33	12.23	-0.85
Dairy	Dry Milk 1	2.15	2.10	-2.50
Dairy	Dry Milk 2	2.15	2.15	-0.11
Dairy	Dry Milk 3	2.24	2.23	-0.32
Dairy	Dry Milk 4	3.65	3.68	0.80

Results of isotopic ratio measurements

Ratios of $^{239}Pu/^{240}Pu$ standard were measured at different concentrations without applying mass bias correct ion. The concentrations of ^{239}Pu and ^{240}Pu for the isotopic ratio standard solutions were prepared to be near the levels that have regulatory significance

Conc. Level	Measured $^{239}Pu/^{242}Pu$ Ratio	Known $^{239}Pu/^{242}Pu$ Ratio	Difference, %
20 ppt	1.0025	0.9987	0.38
100 ppt	0.9987	0.9987	0
500 ppt	0.9999	0.9987	0.12

The $^{239}Pu/^{240}Pu$ ratios measured from the standard solutions indicated that the effect of mass bias was quite small in comparison with their measurement uncertainties. The Pu isotopic signature can be determined reasonably well at concentration of parts per trillion.

Recovery of Pu

The recovery of Pu was determined by analyzing how much added ^{242}Pu remained in each purified sample. A comparative ^{242}Pu measurements between each sample and tracer standard defines sample Pu recovery. The typical Pu recoveries observed for different food groups were found to be 76-92%.

Food Group	Pu Recovery, %
Vegetation	92
Meat	83
Grain	76
Dairy	91
Composite Meal	92

Conclusions

The preliminary study demonstrated that

- The proposed method provides sensitive detection of ^{239}Pu and ^{240}Pu in a variety of foods.
- The MDA and LOQ for ^{239}Pu were estimated to be ~0.1 Bq/kg and ~0.4 Bq/kg, which is ~20 times below its FDA's derived intervention level.
- The MDA and LOQ for ^{240}Pu are expected to be even lower when free of UH^{+} interference.
- The isotopic analysis of ^{239} and ^{240}Pu can be completed in 5 min enabling high sample throughput.
- The method has an ability to determine isotopic signature of Pu in food.
- The method sensitivity, accuracy, and precision can be further improved by coupling with a desolvating nebulizer.

Future Direction

- Enhance sample digestion procedure to solubilize refractory PuO_2
- Additional procedure modifications for eliminating UH^+ interference
- Add desolvating nebulizer unit to front end of ICPMS to increase sensitivity and remove H^+
- Further optimize ICPMS instrument parameters to improve sensitivity, accuracy, and precision of Pu isotopic ratio measurements.
- Couple ICPMS with a HPLC unit for rapid screening of Pu in food

Thank you!

Any questions?