U.S. FOOD & DRUG ADMINISTRATION
OFFICE OF REGULATORY AFFAIRS

Rapid Detection of Americium-241 in Food by Inductively-Coupled Plasma Mass Spectrometry

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➢ Motivations

- Americium-241 (^{241}Am) is a radionuclide of great concern for food safety due to:
  - ✓ its long physical half-life
  - ✓ harmful ionizing radiation, and
  - ✓ potential carcinogenicity
- ID and quantification of ^{241}Am in food are required by FDA food safety compliance and emergency response programs
- No rapid/sensitive method for detecting ^{241}Am in food at FDA intervention level of 2 Bq/kg since current radiometric methods are limited by ^{241}Am's slow α decay and low γ emission
- Need a simple and definitive method that can quickly assess level and extent of ^{241}Am contamination of foods to:
  - ✓ assist radiological risk assessment
  - ✓ provide prompt protective action after a nuclear or radiological emergency

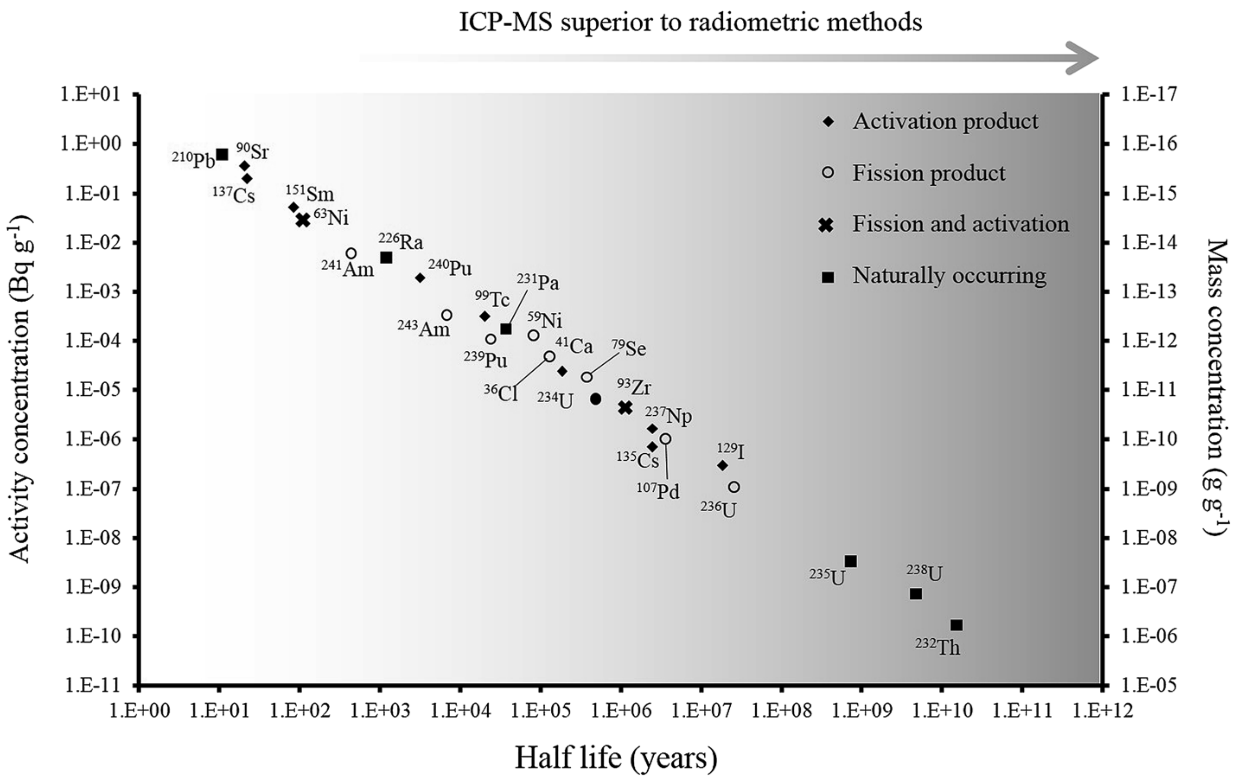
➢ Objectives

- Adapt FDA's traditional radiometric-counting methods to faster and more advantageous atom-counting method
- Develop a simple, rapid radiochemical procedure to effectively remove matrix, isobaric, and polyatomic interferences
- Develop a sensitive and robust quadrupole-based ICPMS method able to identify and quantify ^{241}Am in a wide variety of foods
- Provide sufficient sample throughput for response to radiological emergencies involving ^{241}Am

➢ Decay-Counting vs Atom-Counting

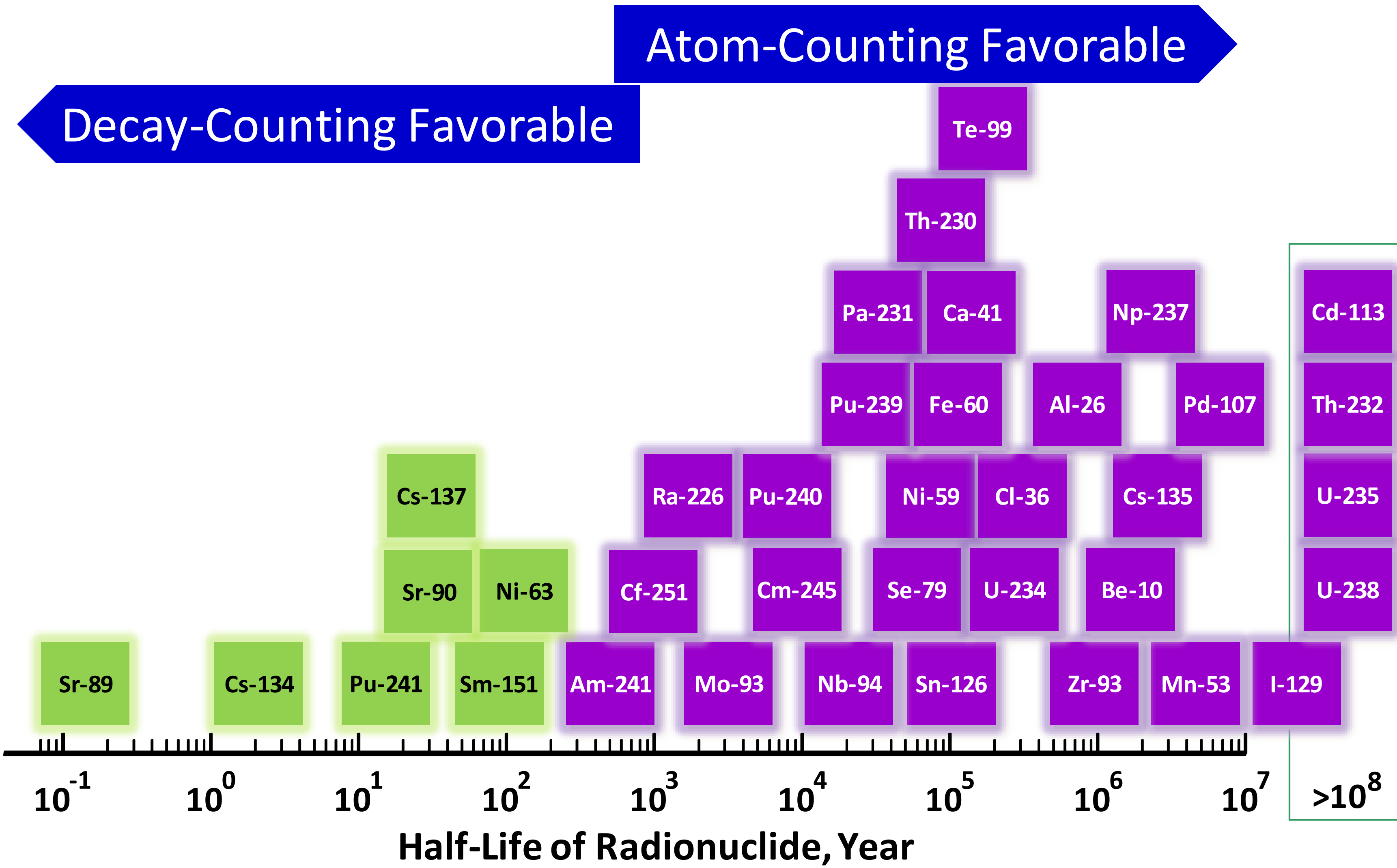
For the same amount radioactivity, the number of atoms increases with increasing half-life ($T_{1/2}$) of radionuclide, which makes atom-counting favorable over decay-counting techniques for longer lived radionuclides

$$Number\ of\ atoms = \frac{Activity}{0.693} \times T_{1/2}$$



Reference: B. C. Russell, I. W. Croudace, P. E. Warwick and J. A. Milton, Anal. Chem., 2014, 86, 8719–8726

Decay-Counting vs Atom-Counting



➢ Method Challenges

- The FDA's DIL for ^{241}Am alone is 2 Bq/kg or 15.8 pg/kg
- For detecting ^{241}Am at 1/3 of its FDA's DIL, limit of detection for the proposed ICPMS method must be <~5.3 pg/kg or ~5.3 fg/g
- The detection efficiency for our Aridus II desolvating nebulizer and Q-ICP-MS is ~0.01% tandem system
- At 1/3 of FDA's DIL, a 50 g of food sample will contain ~0.3 pg or ~$7x10^8$ atoms of ^{241}Am

➢ Method Challenges

Isobaric and Polyatomic Interferences in Analysis of ^{241}Am by ID-ICPMS

Interferences to ^{241}Am (Analyte)

Element	Species	Abundance, %
Pu	^{241}Pu	-
	$^{240}Pu^{1}H$	-
Bi	$^{209}Bi^{32}S$	100
	$^{209}Bi^{16}O_2$	100
Pb	$^{204}Pb^{37}Cl$	1.4
	$^{204}Pb^{37}Cl$	1.4
	$^{206}Pb^{35}Cl$	24.1
	$^{207}Pb^{34}S$	22.1
	$^{208}Pb^{33}S$	52.4
	$^{208}Pb^{16}O_2{}^{1}H$	52.4
Tl	$^{203}Tl^{38}Ar$	29.52
	$^{205}Tl^{36}Ar$	70.48
	$^{205}Tl^{36}S$	70.48
Hg	$^{201}Hg^{40}Ar$	13.18
	$^{204}Hg^{37}Cl$	6.87
Hf	$^{178}Hf^{14}N^{16}O_3{}^{1}H$	27.28
	$^{179}Hf^{14}N^{16}O_3$	13.62
Pt	$^{194}Pt^{14}N^{16}O_2{}^{1}H$	32.86
	$^{195}Pt^{14}N^{16}O_2$	33.78

Interferences to ^{243}Am (Tracer)

Element	Species	Abundance, %
Bi	$^{209}Bi^{34}S$	100
Pb	$^{206}Pb^{37}Cl$	24.1
	$^{207}Pb^{36}Ar$	22.1
	$^{208}Pb^{35}Cl$	52.4
Tl	$^{203}Tl^{40}Ar$	29.52
	$^{205}Tl^{38}Ar$	70.48

References:

Zhongtang Wang et al., J Radioanal Nucl Chem (2017) 312:151–160
Suresh Kumar Aggarwal, Mass Spectrometry Reviews. 2016 May 6

➢ Experimental Approach

To analyze trace level of ^{241}Am in foods, the MDVP project was conducted with the followings in mind:

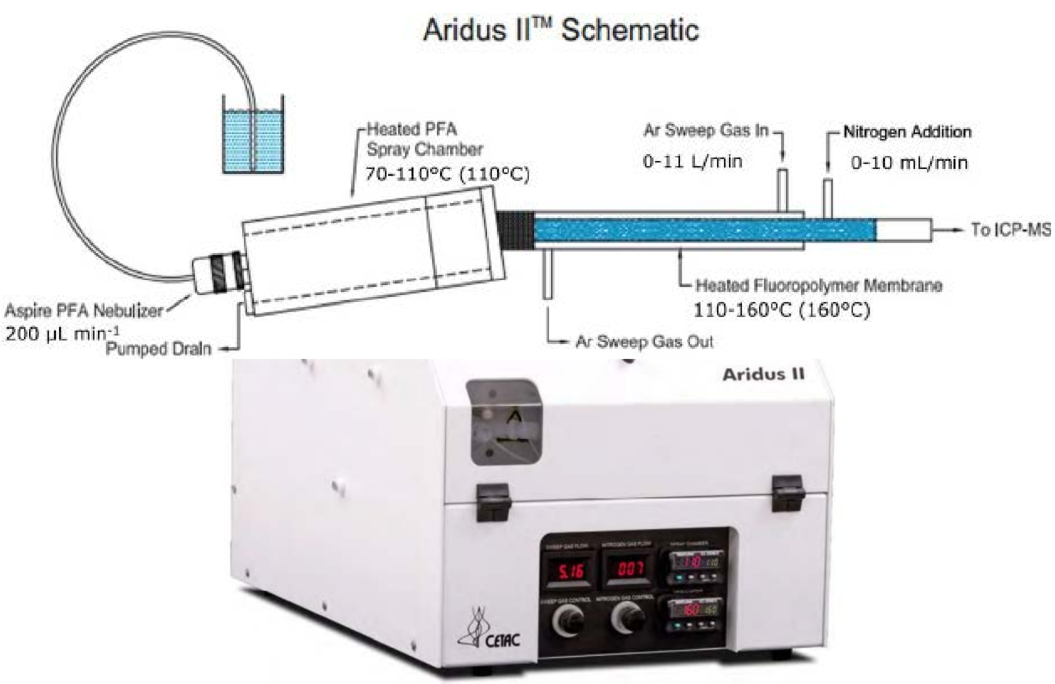
- Apply expedited dry/wet ashing to convert Am in food into soluble ionic forms
- Use DGA resin to separate Am from matrix and interferences
- Broaden method applicability by including a wide variety of foods in the study
- Maximize ^{241}Am and ^{243}Am signal intensities by using small sample volumes (~0.5 mL) in ICPMS analysis
- Utilizing a desolvating nebulizer to increase analyte transport and ionization efficiency

➢ Experimental Approach

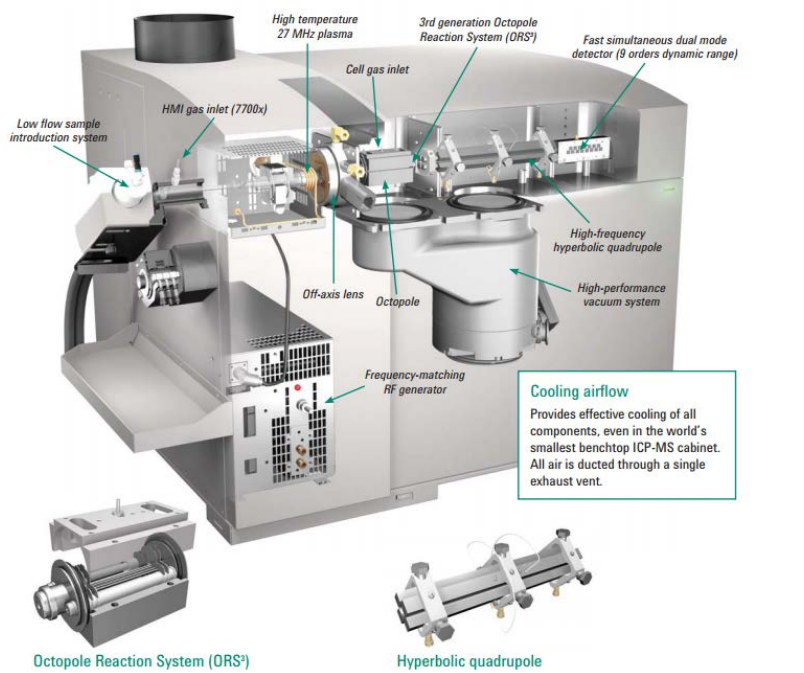
Instrument Setup

- Concentrate ^{241}Am in small sample volume (~0.5 mL) for ICPMS analysis
- Maximize ^{241}Am ionization efficiency
- Increase ^{241}Am detection sensitivity
- Reduce oxide interferences
- Reduce hydride interferences

CETAC Aridus II Desolvating Nebulizer System



Agilent 7700x Q-ICP-MS

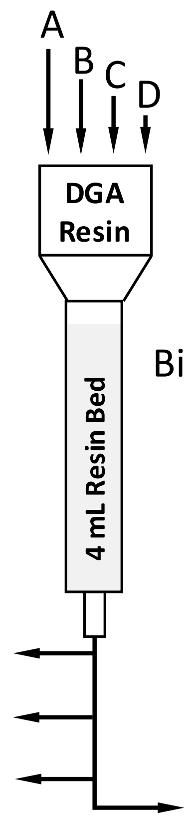


➢ Sample Preparation

Sample Digestion

1. Ash ~50 g of food up to 550 °C
2. Transfer ash to a glass beaker
3. Add known amount of ^{243}Am tracer
4. Boil ash in 20 mL of conc. HNO_3 for 40 min
5. Filter sample digest
6. Evaporate filtrate down to ~10 mL

Am Separation



Bi & Pu are retained by resin

(Matrix) A

(Pb, Tl, Pt, Hg) B

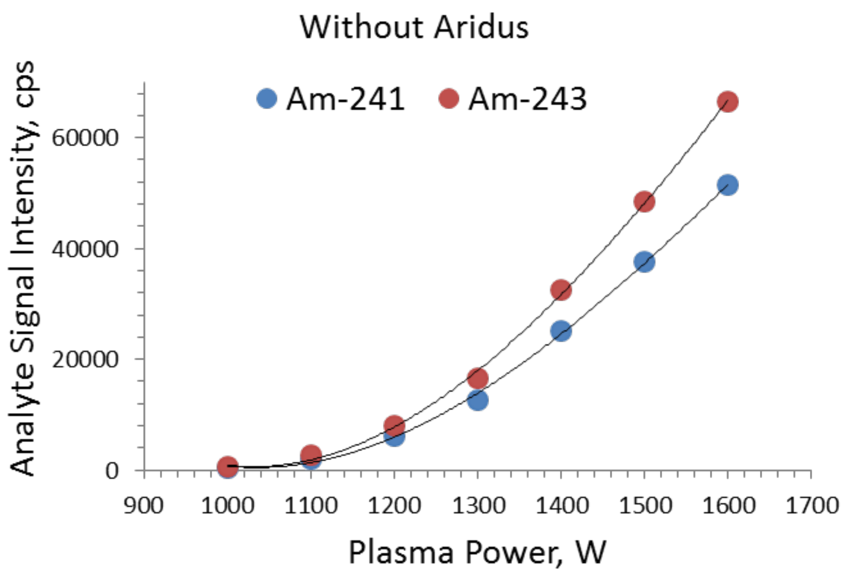
(Hf) C

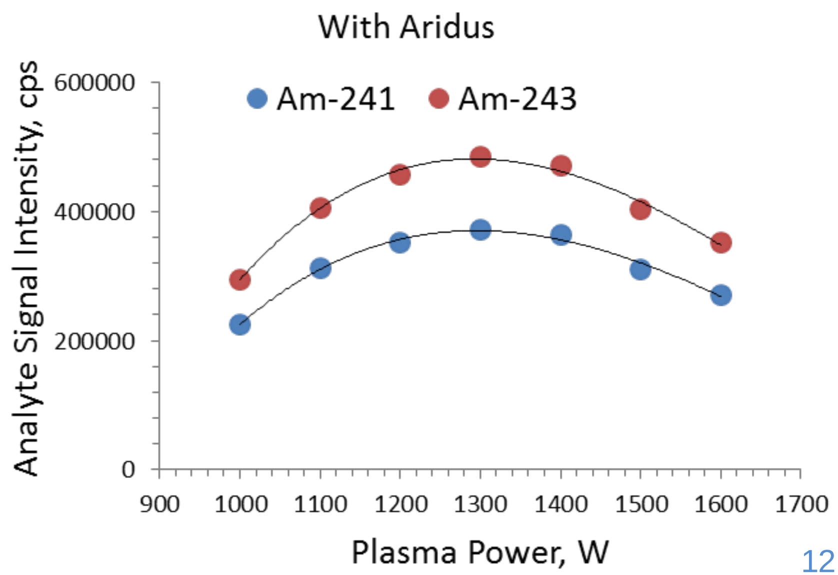
D (Am) Evaporated to dryness then dissolved in 0.5 mL of 5% HNO_3 before Q-ICP-MS analysis

A. 10 mL of sample digest
B. 10 mL of conc. HNO_3
C. 10 mL of conc. HNO_3+0.2M HF
D. 15 mL of 0.5M HCl

Instrument Optimization

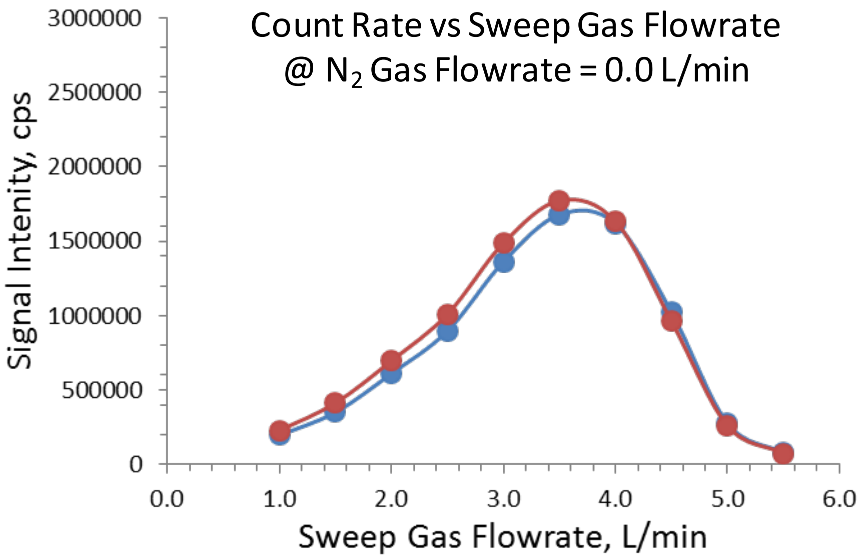
- Found maximum analyte signal intensity at plasma power = ~1300 W while using Aridus II desolvating nebulizer
- Observed ~7-fold increase in analyte signal intensity while using Aridus II desolvating nebulizer
- Found $^{241}Am/^{243}Am$ ratio was independent of plasma power
- Observed a similar degree of isotope fractionation with or without using Aridus II desolvating nebulizer

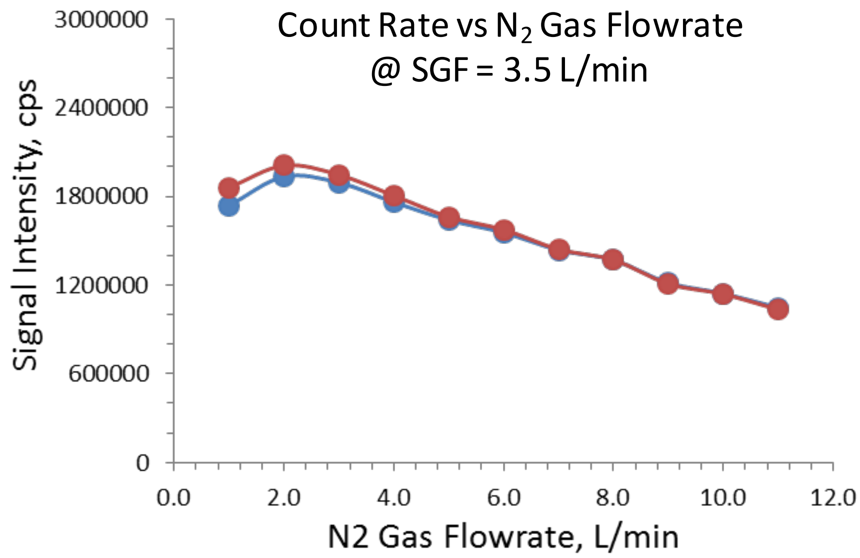




Instrument Optimization

- Found the optimum sweep gas flowrate at ~3.5 L/min for Aridus II desolvating nebulizer
- Found the optimum N2 gas flowrate at ~2 L/min for Aridus II desolvating nebulizer
- Found $^{241}Am/^{243}Am$ ratio was independent of plasma power
- Observed a similar degree of isotope fractionation with or without using Aridus II desolvating nebulizer





Results and Discussions

Estimated sample completion time and throughput

Samples Per batch	Ashing hr	Digestion hr	Separation hr	ICPMS Analysis hr	Total hr
4	24	1.0	4.0	0.3	29.3
8	24	1.3	4.5	0.5	30.3
12	24	1.7	5.0	0.7	31.4
16	24	2.0	5.5	1.0	32.5

Based on ~50 g of food for each sample

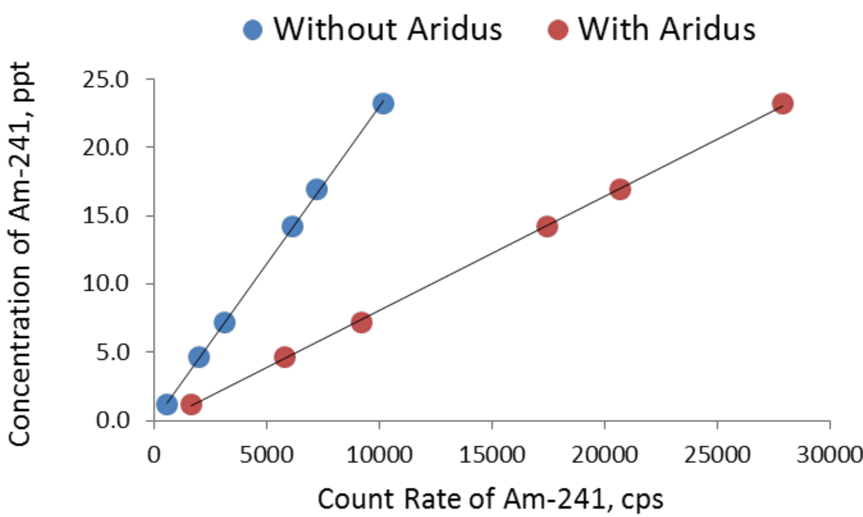
Results and recovery observed with the proposed method procedure

Food	Recovery of Am	Known, pg/g	Measured, pg/g	Diff., %
Corn bread	95%	16.22±0.04	15.8±1.1	-2.6
Ground beef	94%	16.22±0.04	16.1±1.2	-0.7
Chicken pot pie	92%	16.22±0.04	15.7±0.9	-3.2
American cheese	90%	16.22±0.04	16.7±1.3	3.0
Spinach	91%	16.22±0.04	17.2±1.2	6.0

Uncertainty is estimated at 95% confidence level

➢ Results and Discussions

Comparison of limit of detections



Limit of detection for ^{241}Am was estimated using linear regression analysis:

$$LOD_{Am} = 3S_{y/x} + b$$

Where,
$S_{y/x}$ = Standard error of the regression
b = Intercept

For analysis of ~50 grams of food:

LOD = 4.8 pg/kg without Aridus II
LOD = 2.1 pg/kg with Aridus II

The proposed method meets the detection limit requirement of 5.3 pg/kg

Conclusions

The preliminary study demonstrated:

- The proposed method provides sensitive and definitive detection of ^{241}Am in foods.
- The limit of detection for ^{241}Am was estimated to be ~2.1 pg/kg or 0.27 Bq/kg, which is ~7 times below its FDA's derived intervention level.
- Analysis of a batch of 16 samples can be completed in ~32 hours after sample receiving.
- The method accuracy was found to be better than ±10%.
- Despite that the method presented an alternative approach for analyzing ^{241}Am in foods, additional studies on the method performance characteristics are still needed before official use.

➢ Looking Ahead

- Evaluate method readability and reproducibility at target level
- Conduct a matrix extension study to demonstrate method applicability for a wide variety of foods
- Reduce sample preparation time by adapting wet ashing to mineralizing food samples
- Reduce Am separation time by using vacuum assisted chromatographic column
- Further improve method sensitivity, accuracy, and precision with high resolution ICPMS

Disclaimer

Reference to any commercial materials, equipment, or process does not, in any way, constitute approval, endorsement, or recommendation by the U.S. Food and Drug Administration.

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Thank you!

Any questions?

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