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

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Presentation to 25th Annual CIRMS Conference
National Institute of Standards and Technology
Gaithersburg, Maryland 2017
Outline

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Motivations

- Americium-241 (\(^{241}\text{Am}\)) 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 \(^{241}\text{Am}\) in food are required by FDA food safety compliance and emergency response programs

- No rapid/sensitive method for detecting \(^{241}\text{Am}\) in food at FDA intervention level of 2 Bq/kg since current radiometric methods are limited by \(^{241}\text{Am}\)’s slow \(\alpha\) decay and low \(\gamma\) emission

- Need a simple and definitive method that can quickly assess level and extent of \(^{241}\text{Am}\) 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.

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

ICP-MS superior to radiometric methods

Decay-Counting vs Atom-Counting

Atom-Counting Favorable

Decay-Counting Favorable

Half-Life of Radionuclide, Year

10^{-1}  10^{0}  10^{1}  10^{2}  10^{3}  10^{4}  10^{5}  10^{6}  10^{7}  >10^{8}
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 $<\sim 5.3$ pg/kg or $\sim 5.3$ fg/g

- The detection efficiency for our Aridus II desolvating nebulizer and Q-ICP-MS is $\sim 0.01\%$ tandem system

- At 1/3 of FDA’s DIL, a 50 g of food sample will contain $\sim 0.3$ pg or $\sim 7x10^8$ atoms of $^{241}$Am
### Method Challenges

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

#### Interferences to $^{241}$Am (Analyte)

<table>
<thead>
<tr>
<th>Element</th>
<th>Species</th>
<th>Abundance, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu</td>
<td>$^{241}$Pu</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$^{240}$Pu$^1$H</td>
<td>-</td>
</tr>
<tr>
<td>Bi</td>
<td>$^{209}$Bi$^{32}$S</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>$^{209}$Bi$^{16}$O$_2$</td>
<td>100</td>
</tr>
<tr>
<td>Pb</td>
<td>$^{204}$Pb$^{37}$Cl</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>$^{204}$Pb$^{37}$Cl</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>$^{206}$Pb$^{35}$Cl</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>$^{207}$Pb$^{34}$S</td>
<td>22.1</td>
</tr>
<tr>
<td></td>
<td>$^{208}$Pb$^{33}$S</td>
<td>52.4</td>
</tr>
<tr>
<td></td>
<td>$^{208}$Pb$^{16}$O$_2$$^1$H</td>
<td>52.4</td>
</tr>
<tr>
<td>Tl</td>
<td>$^{203}$Tl$^{38}$Ar</td>
<td>29.52</td>
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<tr>
<td></td>
<td>$^{205}$Tl$^{36}$Ar</td>
<td>70.48</td>
</tr>
<tr>
<td></td>
<td>$^{205}$Tl$^{36}$S</td>
<td>70.48</td>
</tr>
<tr>
<td>Hg</td>
<td>$^{201}$Hg$^{40}$Ar</td>
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<td></td>
<td>$^{204}$Hg$^{37}$Cl</td>
<td>6.87</td>
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<tr>
<td>Hf</td>
<td>$^{178}$Hf$^{14}$N$_6$O$_3$$^1$H</td>
<td>27.28</td>
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<tr>
<td></td>
<td>$^{179}$Hf$^{14}$N$_6$O$_3$</td>
<td>13.62</td>
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<tr>
<td>Pt</td>
<td>$^{194}$Pt$^{14}$N$_6$O$_2$$^1$H</td>
<td>32.86</td>
</tr>
<tr>
<td></td>
<td>$^{195}$Pt$^{14}$N$_6$O$_2$</td>
<td>33.78</td>
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</tbody>
</table>

#### Interferences to $^{243}$Am (Tracer)

<table>
<thead>
<tr>
<th>Element</th>
<th>Species</th>
<th>Abundance, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>$^{209}$Bi$^{34}$S</td>
<td>100</td>
</tr>
<tr>
<td>Pb</td>
<td>$^{206}$Pb$^{37}$Cl</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>$^{207}$Pb$^{36}$Ar</td>
<td>22.1</td>
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<td></td>
<td>$^{208}$Pb$^{35}$Cl</td>
<td>52.4</td>
</tr>
<tr>
<td>Tl</td>
<td>$^{203}$Tl$^{40}$Ar</td>
<td>29.52</td>
</tr>
<tr>
<td></td>
<td>$^{205}$Tl$^{38}$Ar</td>
<td>70.48</td>
</tr>
</tbody>
</table>

**References:**

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

CETAC Aridus II Desolvating Nebulizer System

![Aridus II Schematic](image)

Agilent 7700x Q-ICP-MS

![Agilent 7700x Q-ICP-MS](image)
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
- 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

Bi & Pu are retained by resin

D (Am) Evaporated to dryness then dissolved in 0.5 mL of 5% HNO$_3$ before Q-ICP-MS analysis
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 $^{241}\text{Am}/^{243}\text{Am}$ 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 $^{241}\text{Am}/^{243}\text{Am}$ 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

<table>
<thead>
<tr>
<th>Samples Per batch</th>
<th>Ashing hr</th>
<th>Digestion hr</th>
<th>Separation hr</th>
<th>ICPMS Analysis hr</th>
<th>Total hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>24</td>
<td>1.0</td>
<td>4.0</td>
<td>0.3</td>
<td>29.3</td>
</tr>
<tr>
<td>8</td>
<td>24</td>
<td>1.3</td>
<td>4.5</td>
<td>0.5</td>
<td>30.3</td>
</tr>
<tr>
<td>12</td>
<td>24</td>
<td>1.7</td>
<td>5.0</td>
<td>0.7</td>
<td>31.4</td>
</tr>
<tr>
<td>16</td>
<td>24</td>
<td>2.0</td>
<td>5.5</td>
<td>1.0</td>
<td>32.5</td>
</tr>
</tbody>
</table>

Based on ~50 g of food for each sample

Results and recovery observed with the proposed method procedure

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

Uncertainty is estimated at 95% confidence level
Results and Discussions

Comparison of limit of detections

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

$$\text{LOD}_{\text{Am}} = 3S_{y/x} + b$$

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 $\sim 2.1$ pg/kg or $0.27$ Bq/kg, which is $\sim 7$ times below its FDA’s derived intervention level.
- Analysis of a batch of 16 samples can be completed in $\sim 32$ 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

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Thank you!

Any questions?