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Isotopic analysis of plutonium in foods by inductively-coupled plasma mass spectrometry

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ABSTRACT

Pu isotopes in various foods were detected using a quadrupole ICPMS and Aridus II desolvation nebulizer. The method has ability to detect ^{239}Pu and ^{240}Pu at concentrations of ~52 pg/kg (0.12 Bq/kg) and ~9.5 pg/kg (0.08 Bq/kg) as well as ^{240}Pu/^{239}Pu ratio in < 8 h after receiving the samples. Foods were wet-ashed followed by DGA extraction for eliminating matrix, isobaric, and polyatomic interferences. A UH^+ formation rate $< 10^{-5}$ and a 5-fold enhanced sensitivity for Pu was achieved after system optimization.

1. Introduction

Globalization of the food production, trade, and distribution presents immense food safety challenges to authorities worldwide when local food contamination can rapidly become a national and global emergency. Concerns have increased regarding the possibility that a large number and variety of foods could become contaminated in the event of a large-scale nuclear or radiological accident/incident such as the Fukushima nuclear accident. To address growing food safety concerns, considerable efforts were put forth into developing rapid and sensitive radioanalytical methods for high-throughput sample analysis essential to emergency response and risk management (Maxwell et al., 2012; Evans et al., 2003). Among various radionuclides to be monitored, ^{239}Pu and ^{240}Pu in foods are of particular concern for the public health because of their known mutagenic and carcinogenic effects as documented by International Agency for Research on Cancer (2012). Given the high chemical and radiological toxicity of Pu, intervention levels as low as 1 Bq/kg (~436 pg/kg) for ^{239}Pu and 1 Bq/kg (~119 pg/kg) for ^{240}Pu are recommended by Codex (2016). The radioanalytical methods used for regulatory enforcement and compliance are required to make positive detection at one-fifth of the maximum contaminant level per the Code of Federal Regulations of the United States of America (2009). With a preference for detecting ^{239}Pu and ^{240}Pu at 1/5 of the guidance level with short turnaround time during emergency operation, a method needs to have minimum detection limits of ~87 pg/kg for ^{239}Pu and ~24 pg/kg for ^{240}Pu. Besides quantifying the Pu content in foods, it is also of importance to assess Pu source term (different sources often exhibit characteristic ^{240}Pu/^{239}Pu ratios) and its relative contribution for enabling objective decision-making essential to consequence management. As demonstrated by Zheng et al. (2013) and Ketterer et al. (2004), concentrations of Pu isotopes determined along with ^{240}Pu/^{239}Pu atom ratio can be used to fingerprint the origin of Pu and facilitate source apportionment of the Pu detected. Radiometric and mass spectrometric techniques namely alpha spectrometry and mass spectrometry were often applied to complement each other in isotopic analysis of radionuclides for avoiding their own limitations as described by Boulyga et al. (2001). Despite the fact that atom counting has clear advantages over decay counting in quantification of ^{239}Pu, ^{240}Pu, and ^{240}Pu/^{239}Pu ratio, certain types of mass spectrometers, such as thermal ionization mass spectrometer (TIMS) and high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS), remain inaccessible to most laboratories designated for emergency and routine operations due to high acquisition and maintenance costs. In contrast, generic quadrupole inductively-coupled plasma mass spectrometers (ICPMS) have become common laboratory instruments due to their versatility and affordability. In this context, an application of quadrupole ICPMS based method for rapid isotopic analysis of Pu in a wide variety of foods was studied. The method makes use of open-beaker wet digestion, simple one-step extraction, self-aspirating desolvation nebulizer, and rapid atom-counting procedure to achieve a sustainable high throughput sample analysis required for emergency operations. A detailed radiochemical procedure, instrument optimization, UH^+ correction, and measurement results from analyzing vegetable, grain, meat, dairy, and complex meal samples spiked with ^{239}Pu and ^{240}Pu are presented.

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2. Experimental

2.1. Standards and reagents

All chemicals used were ACS certified reagent grade (Fisher Scientific, Pittsburgh, PA, USA) except high purity ULTREX II HNO_3 (J.T. Baker, Phillipsburg, NJ, USA) and OPTIMA H_2O_2 (Fisher Scientific, Pittsburgh, PA, USA) used for final sample treatment after the Pu separation. Purified H_2O was obtained from a Milli-Q Integral water purification system. Primary ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{238}U, and $^{242}Pu/^{239}Pu$ isotopic ratio standards used for spike addition, UH^+ correction, and mass bias calibration were purchased from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) and New Brunswick Laboratory (NBL, Argonne, IL, USA), respectively. Diglycolamide (DGA) extractant resin (*N,N,N',N'*-tetra-*n*-octyldiglycolamide, Normal, 50–100 μm) was acquired from Eichrom Technologies, Inc. (Darien, IL, USA) and the resin was wetted in 3 M HNO_3 before use. A 7700x quadrupole ICPMS (Agilent, Santa Clara, CA, USA) coupled with an Aridus II desolvation nebulizer system equipped with 100 μL/min self-aspiration PFA nebulizer (CETAC, Omaha, NE, USA) was used for isotopic analysis of Pu. Test samples spiked with known amounts of either ^{239}Pu or ^{240}Pu or both were prepared from foods representing dairy, meat, vegetable, grain, and complex meal. The ^{239}Pu and ^{240}Pu standard solutions used for spiking the samples were prepared by gravimetric dilution of their primary standards with 3 M HNO_3. A reagent blank prepared with 5% HNO_3 was analyzed along with each batch of test samples. Certified vegetation reference materials used for method validation were supplied by Environmental Resource Associates (ERA, Golden, CO, USA).

2.2. Method procedure and instrument optimization

A radiochemical procedure shown in Fig. 1 was developed and applied for screening of Pu in a variety of foods. Each sample was predigested with concentrated HNO_3 in a glass beaker and then refluxed at boiling temperature for 60 min after dropwise addition of 30% H_2O_2. Sample digestion was started with low heat to avoid excessive foaming and the resulting digestate was chilled and then filtered. All Pu in oxidation states of Pu(III), Pu(V), and Pu(VI) was adjusted to Pu(IV) with $NaNO_2$ according to the study conducted by Lee et al. (2007) before batch extraction of Pu(IV) in form of $Pu(NO_3)_6^{2-}$ characterized by Marsh et al. (2000) under vigorous stirring. The DGA resin impregnated with Pu was retrieved by filtering the resin slurry through an empty column connected to a vacuum box system purchased from Eichrom for successive washing and elution. Diluted HNO_3 was used to wash off U from DGA resin before elution of Pu. The sample preparation for a batch of 8 samples took < 8 h. The ICPMS-Aridus II nebulizer system was first tuned using a solution containing ^{140}Ce, ^{205}Tl, and ^{238}U then optimized with $^{242}Pu/^{239}Pu$ isotopic ratio standard solution for maximizing Pu ion intensity and stability with the lowest possible mass bias. The ICPMS was tuned to operate in high mass mode (ion optics optimized for the transmission of high mass ions) with a reduced mass resolution of 0.75 amu at 50% peak height in exchange of higher ion transmission and smoother peak top. Aridus II was set to operate using a sweep gas flowrate of 2.6 L/min based on the response curves derived from the measured ^{239}Pu signal intensity and precision versus sweep gas flowrate. Natural U standard solutions of varying concentrations were analyzed to relate $^{238}UH^+$ and $^{238}U^+$ count rates under the same measurement conditions applied for sample analysis and the derived $^{238}UH^+/^{238}U^+$ ratio was used to quantify $^{238}UH^+$ contribution based on the ^{238}U observed in the given sample as described by Landstetter et al. (2015). For mass bias correction, a $^{242}Pu/^{239}Pu$ isotopic ratio standard solution was measured during sample analysis.

3. Results and discussions

Food matrices are complex with wide chemical and physical disparity. High contents of sugar, fat, protein, fiber, or starch in different foods posed distinct challenge during acid digestion. Carbohydrates were easily mineralized with concentrated HNO_3 but exothermic reaction needs be cautiously controlled to avoid sample spillage. Fat and protein were only partially digested due to insufficient oxidation potential produced by HNO_3/H_2O_2 at boiling temperature. To prevent fat from coating and coagulating DGA resin during the batch extraction, the undigested fat was solidified using an ice bath and then separated from sample solution. Dietary fiber and starch caused clogging when a fritted column was used to retrieve Pu impregnated

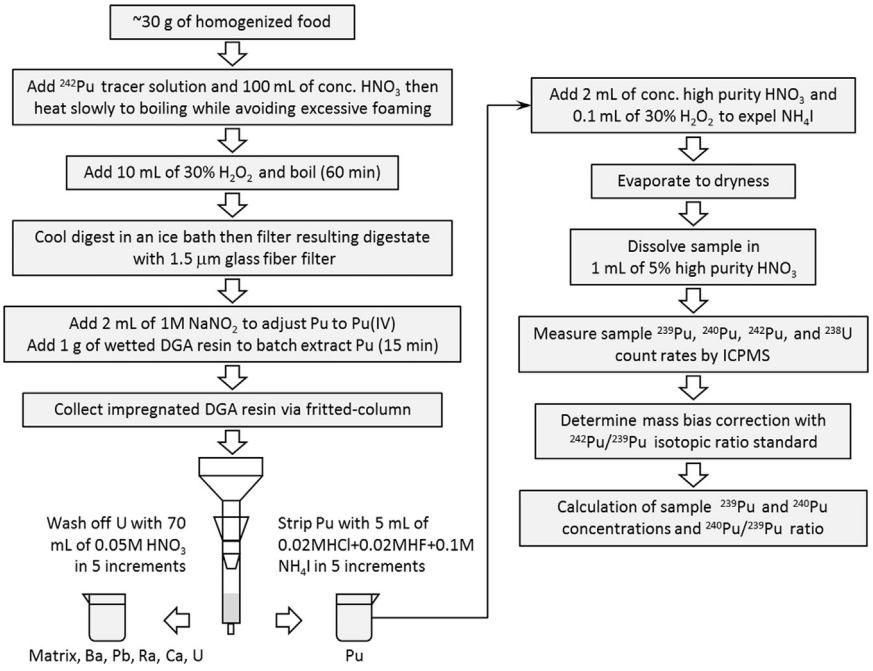

Fig. 1. Method procedure flowchart.

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