



ELSEVIER

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Determination of plutonium isotopes in bilberry using liquid scintillation spectrometry and alpha-particle spectrometry

Meryem Seferinoğlu*, Nazife Aslan, Aylin Kurt, Pınar Esra Erden, Hülya Mert

Turkish Atomic Energy Authority, Sarayköy Nuclear Research and Training Center, 06983 Kazan, Ankara, Turkey

HIGHLIGHTS

- Sample preparation methods for Pu using LSS and alpha spectrometry developed.
- Complete separation of plutonium from interfering radionuclides.
- Commercial bilberry was spiked with NPL 2011 (AH-B11144) proficiency test sample.
- Results were checked using ζ test, z-test, rel. bias and rel. uncert. outlier tests.
- Recommended procedures successfully applied to bilberry samples.

ARTICLE INFO

Available online 1 December 2013

Keywords:

Plutonium

Activity concentration

Liquid scintillation spectrometry

 α -Particle spectrometry

ABSTRACT

This paper presents α -particle spectrometry and liquid scintillation spectrometry methods to determine plutonium isotopes in bilberry. The analytical procedure involves sample preparation steps for ashing, digestion of bilberry samples, radiochemical separation of plutonium radioisotopes and their measurement. The validity of the method was checked for coherence using the ζ test, z-test, relative bias and relative uncertainty outlier tests. The results indicated that the recommended procedures for both measurement systems could be successfully applied for the accurate determination of plutonium activities in bilberry samples.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

A number of radionuclides have been released into the environment through various sources, as a result of nuclear weapon testing, nuclear facilities and nuclear power plant accidents (Varga et al., 2007; Yamamoto et al., 1966). Among these radionuclides, the actinides, particularly plutonium isotopes such as ^{238}Pu , ^{239}Pu , ^{240}Pu and ^{241}Pu are the most important radionuclides from the viewpoint of their, for a part, extremely long half-lives (^{238}Pu , $t_{1/2}=87.74$ years; ^{239}Pu , $t_{1/2}=24110$ years; ^{240}Pu , $t_{1/2}=6561$ years and ^{241}Pu , $t_{1/2}=14.33$ years—recommended data (LNHB, 2013)) and their radiological toxicities (Muramatsu et al., 1999). The plutonium on earth is an anthropogenic element being created within the past seven decades by human activities involving fissionable materials. Therefore, the determination of their concentrations in the environment is of high importance (Pereygin and Chuburkov, 1997).

Recently, radioactivity found in wild food products is of great interest for the assessment of total exposure of the population as a whole (Wätjen et al., 2012). Bilberry is one of the economically

most important wild foods in many countries (Miina et al., 2009). It is also a widespread plant in many regions such as the Marmara and Black Sea in Turkey and widely collected for both house consumption and sale. It is well-known for its ability to accumulate man-made pollutants including radioactive ones. Such features make it an ideal material for studying the concentrations and behaviour of artificial radioactive isotopes such as $^{238,239+240}\text{Pu}$, ^{137}Cs , and ^{90}Sr (Gaca et al., 2006; Švadlenková et al., 1996; Fawaris and Johanson, 1994; Mietelski and Vajda, 1997).

The main purpose of this study is to develop reliable measurement techniques, including suitable radiochemical separation procedures for the isolation of plutonium from bilberry to determine the activity concentration of plutonium with a high level of accuracy.

2. Experimental

2.1. Instrumentation and calibration

Activity concentrations of $^{238, 239+240}\text{Pu}$ isotopes were determined by using α -particle spectrometry and liquid scintillation spectrometry (LSS) methods. Alpha-emitting sources were counted by a Passivated Implanted Planar Silicon (PIPS) detector with an active surface area of 450 mm². The energy calibration was performed by

* Corresponding author. Tel.: +90 3128101613; fax: +90 3128154307.

E-mail addresses: meryem.seferinoglu@taek.gov.tr, mseferinoglu@hotmail.com (M. Seferinoğlu).

using an electroplated mixed α standard source containing ^{238}U , 1.67 Bq ($\pm 5.2\%$); ^{234}U , 1.63 Bq ($\pm 4.9\%$); ^{239}Pu , 1.91 Bq ($\pm 5.5\%$) and ^{241}Am , 1.81 Bq ($\pm 5.5\%$) supplied from Eckert & Ziegler Isotope Products.

Count rates were measured using a Wallac1220 Quantulus ultra low-level liquid scintillation counter with a pulse shape discrimination device (pulse shape analyzer, PSA) and an external standard of ^{152}Eu which allows to measure the external spectral quench parameter (SQP[E]). Analytical results were determined using WinQ and Easy View software for the instrument and process control. Twenty milliliter low diffusion polyethylene vials (Perkin Elmer) and UltimaGold LLT scintillation cocktail (Perkin Elmer) were used.

2.2. Sample description

Spiked bilberry was prepared by using commercial bilberry and the "Alpha High" proficiency test exercise sample (AH-B11144) of the NPL-2011 proficiency test. Commercial bilberry was dried in an oven at 80 °C for 24 h and then homogenized by grinding. Before spiking by AH-B11144 solution, the bilberry was measured by alpha spectrometry to assess the activities of α -emitting radionuclides, especially plutonium isotopes. For this purpose, the activity concentrations of uranium, radium, americium and plutonium in the commercial bilberry sample were investigated. The analyses of ^{238}U , ^{234}U , ^{241}Am and $^{239+240}\text{Pu}$ radioisotopes were performed by using the modified Eichrom Method ACW03 VBS (Eichrom, 2005). The ^{226}Ra analysis was carried out by using the BaSO_4 co-precipitation method as described in our previous studies (Erden et al., 2013; Dirican et al., 2012). Any activities of these radionuclides were not detected in 20.0 g of sample. The detection limits of alpha-particle spectrometry for interesting radionuclides were calculated using the formulae reported by Currie (1968). The detection limits were found to be 0.060 Bq kg^{-1} for ^{238}U , 0.060 Bq kg^{-1} for ^{234}U , 0.100 Bq kg^{-1} for ^{226}Ra , 0.070 Bq kg^{-1} for ^{241}Am and 0.015 Bq kg^{-1} for $^{239+240}\text{Pu}$. The bilberry was spiked with the AH-B11144 proficiency test sample containing 6.138 ± 0.026 ($k=2$) (0.42%) Bq g^{-1} of ^{239}Pu activity concentration (Gilligan and Harms, 2011).

The developed method was applied to the international comparison bilberry sample (CCR(II)-S8 supplementary comparison "bilberries") prepared by the Institute for Reference Materials and Measurements (EC-JRC-IRMM). The samples were collected in the summer of 2005 in a region close to the Chernobyl reactor site, but outside the exclusion area. The sample preparation was described elsewhere by Wätjen et al. (2012).

2.3. Reagents and tracer

All reagents used in this analysis were of analytical grade and supplied from Merck. The UTEVA (100–150 μm particle size) and TRU (100–150 μm particle size) extraction chromatographic resins were supplied by Eichrom Technologies, Inc. (Darien, Illinois, USA). The ^{242}Pu tracer solution with an activity concentration of 26.77 ± 0.18 Bq g^{-1} ($k=2$) used only for alpha spectrometry was obtained from the National Institute of Standards and Technology (NIST), SRM 43341. The tracer solution was diluted in 0.1 M HCl to reduce the activity concentration to 0.1044 Bq g^{-1} .

High capacity cocktail UltimaGold LLT and high purity double-deionized water were used throughout for the liquid scintillation spectrometry method. The standard ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ solutions were purchased from Eckert & Ziegler Isotope Products.

2.4. Digestion of the sample

Same sample preparation procedures such as weighing, ashing, dissolution of the residue and radiochemical separation steps were

applied for the LSS and alpha spectrometry methods. A subsample of 20.0 g of bilberry was weighed into a porcelain capsule on a microbalance calibrated with SI traceable weights (Benedik et al., 2008). A weighed aliquot of ^{242}Pu tracer was added only to the samples for alpha spectrometry; 0.1044 Bq was added in total. The tracer was added at the beginning of the procedure to quantify the radiochemical yield throughout the separation procedure.

The samples with tracer for alpha spectrometry and without for LSS were ashed in a microwave furnace used with a gradual heating programme up to 600 °C for 16 h to destroy organic matter. The ash was dissolved in 50 mL of 1.0 M HCl with heating and stirring for 1 h. The acidic solution was evaporated to incipient dryness. The residue was then treated with 10.0 mL of concentrated HNO_3 to completely dissolve the sample and evaporated to incipient dryness. Finally, the residue was re-dissolved with 10 mL of 3.0 M $\text{HNO}_3/1.0$ M $\text{Al}(\text{NO}_3)_3$ and transferred into a glass beaker. A 2 mL of freshly prepared 0.6 M ferrous sulphamate solution was added to reduce plutonium(IV) to plutonium(III), so that Pu was not retained on UTEVA resin. Since iron(III) can interfere with the uptake of americium on TRU resin, Fe(III) ions were reduced with ascorbic acid (Thakkar, 2002).

2.5. Radiochemical separation of plutonium isotopes

The Eichrom ACW03 VBS analytical procedure used for separation of americium, plutonium and uranium in water was modified for the analysis of plutonium isotopes in bilberry. The radiochemical separation is based on the isolation of plutonium radioisotopes from other radionuclides such as U, Am and Np in the sample using Eichrom resins prior to measurement by α -particle spectrometry and liquid scintillation spectrometry. The schematic diagram of the sequential separation is shown in Fig. 1.

The TRU and UTEVA columns were set up in tandem on the vacuum box system (Fig. 1). After conditioning of columns with 5 mL of 3.0 M HNO_3 , the sample solution (Section 2.4) was loaded on the columns. While uranium, neptunium and thorium in the sample are retained on UTEVA resin, the other actinides (Am and Pu) are passed through UTEVA resin and retained on TRU resin by this step. After rinsing the columns twice with 5 mL 3.0 M HNO_3 , UTEVA and TRU columns were separated. The TRU column was used for further analysis. Plutonium must be present as Pu^{4+} to be retained on the TRU resin. Plutonium(III) ions were oxidized to Pu^{4+} by addition of 6 mL of 2.0 M $\text{HNO}_3/0.1$ M NaNO_2 . The flow rate for the column should be adjusted to 1.0 mL min^{-1} for this step to be ensured that Pu^{3+} ions are completely converted to Pu^{4+} ions. The column was washed with 5 mL 0.5 M HNO_3 and then 0.5 M HNO_3 was used to lower the nitrate concentration prior to conversion to chloride. First, americium was removed from the column adding 3 mL of 9.0 M HCl to convert the column to chloride and 20 mL 4.0 M HCl. Traces of Th that may pass through the UTEVA resin were removed by adding 25 mL of 4.0 M HCl-0.1 M HF to the column. This solution selectively removes any residual thorium that may be present on the TRU column and leaves plutonium on the column. Finally, plutonium was eluted with 10 mL of 0.1 M ammonium bixalate ($\text{NH}_4\text{HC}_2\text{O}_4$) solution. The purified plutonium fraction was evaporated to incipient dryness. The thin sources for alpha spectrometry were prepared by electrodeposition using a sulfate system as described by the Eichrom ACW03 VBS analytical procedure (Eichrom, 2005) on stainless steel discs.

2.6. Source preparation for liquid scintillation spectrometry

The purified plutonium fraction was evaporated to dryness at about 150 °C to destroy any organic contaminants coming through

Download English Version:

<https://daneshyari.com/en/article/1878626>

Download Persian Version:

<https://daneshyari.com/article/1878626>

[Daneshyari.com](https://daneshyari.com)