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A Study on Determination of Fallout Pu in the Environment

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Abstract

Using an ammonium oxalate-ammonium sulfate electrolyte, a simple, quantitative, and fast technique for preparing sources for analytical alpha spectrometry was developed. To determine the optimum conditions for plating plutonium, parameters such as current density and pH of electrolyte affecting the electrodeposition of the plutonium have been investigated. An optimized electrodeposition step for the determination of plutonium has been validated with a result of application to IAEA-Reference Soils. The new method of fallout Pu determination has been applied to environmental samples such as soil, sediment and moss samples in Korea.

1. INTRODUCTION

Sources for alpha spectrometric measurements have usually been prepared by vacuum sublimation, direct evaporation, electrodeposition, and micro-coprecipitation. Among source preparations, electrodeposition is a commonly used method in the preparation of sources for alpha spectrometry, because the technique is simple and gives a very thin deposit, which is essential for a high resolution of the peak. The most widespread method for electrodepositing actinides is that described by Talvitie[1]. This method is lengthy and needs a precise pH adjustment. The local concentration of ammonium hydroxide can occur and cause polymerization of plutonium. Also,

hydrolysis of Pu(IV) can occur in the immediate vicinity of each drop of concentrated NH_4OH used in the initial pH adjustment.

In this studies, a simple, quantitative, and fast technique of electrodeposition step for the determination of fallout plutonium was modified on the base of the Talvitie method. Also, an optimized method of fallout plutonium have been validated with a result of application to IAEA-Reference Soils. The optimized procedure of fallout Pu has been applied to environmental samples such as soil, sediment and moss samples in Korea.

2. METHODS

2.1 Preparation of electrodeposition solution and electrodeposition cell

The ^{242}Pu tracer of high alpha purity was obtained from Isotope Products Laboratories, USA. Radioisotope dilution was made by weight. Electrolyte modified in this study was prepared as following; 30 g ammonium oxalate, 50 g ammonium sulfate, 18 g hydroxylammonium sulfate and 2 g diethyl triamino pentaacetic acid are dissolved in one liter H_2O and then exactly adjusted to pH 1.8 with H_2SO_4.

The cell used for these experiments was made of teflon. The effective area of electrodeposition was 3.14 cm^2. The anode was a polished platinum spiral wire (diam. 1.5 cm). The upper lid not only prevented releasing of the electrolyte outward but also checked amount of the electrolyte during the electrodeposition step.

2.2 Alpha spectrometry system

The alpha spectrometer (EG&G ORTEC, Model 676A) was composed of an ion-implanted silicon detector (ORTEC, size : 450 mm^2, alpha resolution : 25 keV FWHM at 5.486 MeV of ^{241}Am) in a vacuum chamber (Edwards Model E2M8), a detector bias supplier, a preamplifier, a linear amplifier and a multichannel pulse-height analyzer. The chamber was kept in a vacuum below 10^{-2} Torr during the measurement with a vacuum pump.

2.3 Radiochemical analyses of $^{239,240}Pu$ and ^{238}Pu in the environmental samples

The keys to an accurate measurement of $^{239,240}Pu$ and ^{238}Pu by alpha-particle spectrometry are to obtain plutonium fraction free from major matrix components such as silica, iron, aluminum, etc. and other alpha-emitters and to prepare source for alpha spectrometry. The TOPO (trioctyl phosphineoxide) and anion exchange method can completely separate plutonium fraction from other hindered ions. Therefore, the determination of $^{239,240}Pu$ and ^{238}Pu was carried out an aliquots of 100 g of soil and 30 g of moss according to TOPO extraction method[2]. The chemical yields attained with this analytical procedure were in the range of 70 to 80 %.

3. RESULTS AND DISCUSSIONS

3.1 Modification of electrodeposition step

A chelating agent such as NTA (Nitrilo triacetic acid), EDTA (Ethylene diamine tetraacetic acid) and DTPA (Diethyl triamino pentaacetic acid) has good acid solubility at an acid condition and prevents polymerization and hydrolysis during the electrodeposition. Puphal and Olsen[3] used DTPA to improve the yield of several nuclides on the electrodeposition. In this study 0.005 M DTPA chelating agent was added to ammonium oxalate-ammonium sulfate electrolyte. To determine the optimum conditions for plating plutonium, it is necessary to determine the effects of such parameters as current density and pH of electrolyte on the electrodeposition for plutonium. The maximum yields were obtained with current densities of 950 mA. In this study pH was controlled with 0.1 M H_2SO_4 and NH_4OH. The results of this study was shown that the optimum pH was 1.8.

The distance between the electrodes is not critical as long as the current density is maintained at 950 mA. Darkening of the cathode occurred at a spacing of 2 mm, and excessive voltage was required at a spacing of about 8 mm resulting in boiling and electrolyte loss. A distance of about 5 mm gave the best plate.

3.2 Validation of optimization

An optimized electrodeposition step for the determination of plutonium is validated

by its application to several IAEA-Reference Soils. As shown in Table 1, the concentrations of plutonium using the optimized electrodeposition step are so consistent with reference values reported by IAEA that this method can be applied to different soils with reliable results.

The chemical yield obtained in the environmental samples were compared between the Talvitie method and the modified one. The chemical yield of the optimized method of electrodeposition step was about 7 % higher than a Talvitie method. Also the time consumed from leaching until the final result is a little shorter than the processing times of conventional methods, because this method does not need pH adjustment. Hence, the new method is quantitative and reliable. The entire analytical procedure of $^{239,240}Pu$ and ^{238}Pu is completed in about three days, excluding counting time for the one batch (4 samples).

3.3 Application to environmental samples

The new method of fallout Pu determination described above has been applied to environmental samples such as soil, sediment and moss samples in this study. The activity concentrations of $^{239,240}Pu$ and ^{238}Pu in the environmental samples are in good agreement with those reported by UNSCEAR (1982) for the north temperate zone (40-30°)[4]. Also, the activity ratios of $^{238}Pu/^{239,240}Pu$ in the environmental samples were found to be in the range of 0.027 to 0.077, with a mean value of 0.043. The mean activity ratio of $^{238}Pu/^{239,240}Pu$ is not much different from the typical value of world-wide fallout[5]. Fig. 1 shows the typical α-particle spectrum of plutonium fraction isolated from the GONGJU soil using the method described above. The alpha peaks of ^{242}Pu, $^{239,240}Pu$ and ^{238}Pu are well resolved and the spectrum is free from contributions due to various thorium and uranium isotopes.

4. REFERCECES

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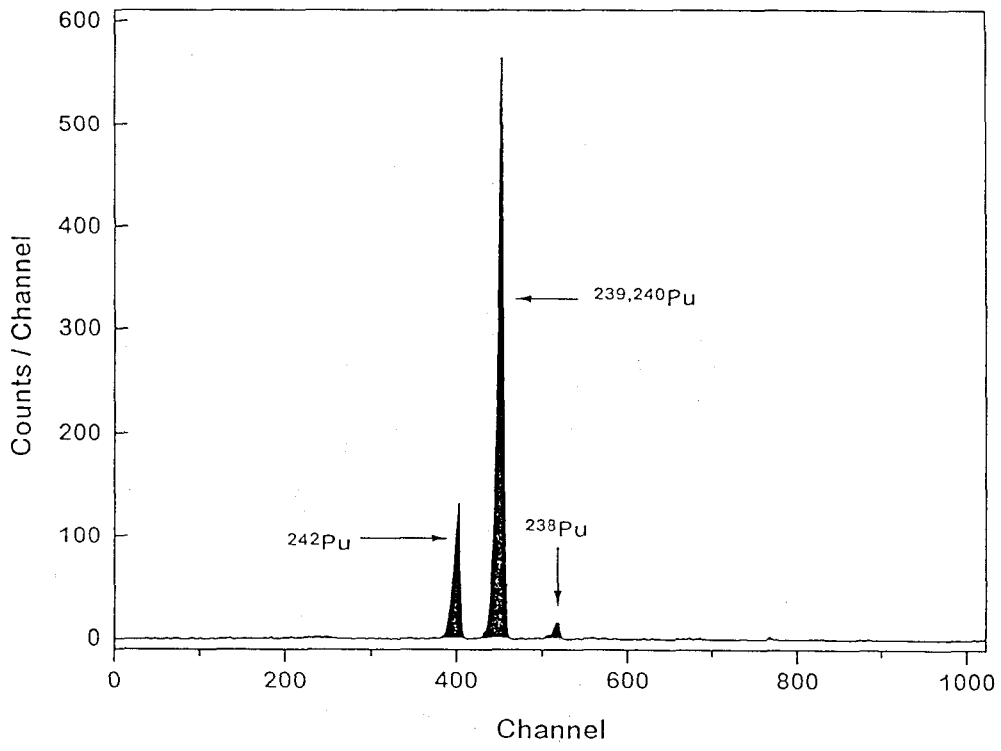

Fig. 1. Alpha spectra of fallout Pu in the GONGJU Soil

Table 1. Plutonium results for soil reference samples obtained by the 'optimized method'

Sample	Concentration of $^{239,240}Pu$ (Bq kg^{-1})		Concentration of ^{238}Pu (Bq kg^{-1})	
	Ref. Value	This method*	Ref. Value	This method
IAEA-326 Soil	0.495 ± 0.025	0.484 ± 0.031**	0.019 ± 0.002	0.022 ± 0.003
IAEA-327 Soil	0.584 ± 0.018	0.587 ± 0.012	0.020 ± 0.005	0.023 ± 0.006

* Number of aliquots analyzed is 3

** Error is 1σ