

Alpha Spectrometry for Determination of ^{238}U , ^{235}U , ^{234}U , ^{232}Th and ^{230}Th in Soil Sample

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1. Introduction

Nuclear power plant releases radiation substances into its peripheral environment when it is on normal operation or accident [1]. Therefore, monitoring of radioactivity in soil around the nuclear power plant is important. In this study, the radioactivity of uranium and thorium isotopes in soil (NIST SRM 2709a) is analyzed by alpha spectrometry. Alpha spectrometry is a powerful analytical tool for the identification and assay of the alpha-emitting sources primarily due to its high counting efficiency, high sensitivity and low price [2]. Another aim of this study is to present the extent of disequilibrium of $^{238}\text{U}/^{234}\text{U}$ and $^{238}\text{U}/^{230}\text{Th}$. The soil sample was decomposed by a fusion technique, and the source for the alpha spectrometry was prepared by electrodeposition of an alpha-emitting nuclides onto a metallic substrate.

2. Materials and Methods

2.1 Sample Preparation

All reagents and solvents were of AR grade and used without further purification unless otherwise noted. HNO_3 , HCl , HF and NH_4OH were purchased from Merck. NH_4SCN , Na_2SO_4 , and NaHSO_4 were bought from Aldrich. *L*-ascorbic acid and ammonium oxalate monohydrate are purchased from Showa Chemical (Japan) and Kanto Chemical (Japan), respectively. KOH , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and oxalic acid dehydrate were bought from Junsei Chemical (Japan). Ethanol was purchased from Samchun Chemicals (Korea). Deionized water (DI water) was obtained using a Milli-Q Direct 8 water system (18.2 $\text{M}\Omega \cdot \text{cm}$). The soil sample (SRM 2709a, San Joaquin Soil) was purchased from National Institute of Standards & Technology.

After the sample was put (ca. 20 g) into a porcelain dish and ashed in a muffle furnace with a gradual heating program up to 550 °C for 5 h to eliminate organic matter, a known amount of sample (ca. 0.5 g) was decomposed by fusion technique with 0.5 g of LiBO_2 and 0.25 g of LiBr . And then ^{232}U (0.1596 Bq/g, ca. 1g) and ^{229}Th (0.3973 Bq/g, ca. 1g) tracer solutions were added into the fused sample.

0.5 ml of FeCl_3 aqueous solution (50 mg/g) was added into the fused sample and then pH was adjusted to 7 by slowly adding a concentrated ammonia solution in order to co-precipitate uranium and thorium with iron ($\text{Fe}(\text{OH})_3$). The pH was controlled using pH test strips. The precipitate was then centrifuged for 6 min at 3800 rpm and the supernatant was discarded. The precipitate was

then re-dissolved using 50 ml of 8 M HCl . To remove LiBO_2 , lanthanum and hydroxide co-precipitations were done with 5 mg of La nitrate hexa-dehydrate and 30 mg of Ca nitrate dehydrate solution dissolved in 2% HNO_3 . And then 20 ml of 3.2 M $(\text{NH}_4)_2\text{HPO}_4$, 5 ml of 10% TiCl_3 and 20 ml of HF were added into the solution with stirring, in that order. The solution was then centrifuged for 6 min at 3800 rpm and the supernatant was discarded. The precipitate was then re-dissolved using 10 ml of mixed solution (8 M HCl + 0.5 M H_3BO_3 + 0.5 M $\text{Al}(\text{NO}_3)_3$).

2.2 Separation of Uranium and Thorium Isotopes

Two chromatographic columns were prepared, containing approximately 3.8 ml of Eichrom UTEVA and TEVA resin (100 ~ 150 μm) respectively. The columns were pre-conditioned with 10 ml of 8 M HNO_3 . The pre-concentrated sample was passed through the TEVA column using the gravity flow rate, followed by passing the solution through the UTEVA column. And then 10 ml of 5 M HCl and 10 ml of 2 M HNO_3 were added to the UTEVA column, in that order. Uranium was eluted with 20 ml of 0.1 M ammonium bi-oxalate solution and evaporated to dryness. Thorium was eluted with 10 ml of 2 M HNO_3 and 10 ml of 0.01 M ammonium bi-oxalate solution from the TEVA column and evaporated to dryness.

2.3 Electrodeposition and Quantitative Analysis using Alpha Spectrometry

The dry residue was dissolved in 2.5 ml of 5 wt% NaHSO_4 , 5 ml of deionized water, and 5 ml of 15 wt% Na_2SO_4 . The solution was transferred to an electrodeposition cell. 1 ml of 0.02 wt% ammonium oxalate was added into a cell as an electrolyte solution. The uranium isotopes were electrodeposited on a stainless steel disc for 2 h at 880 – 890 mA. One minute prior to the end of this stage, 2 ml of 25 wt% KOH was added into the cell before switching off the current to prevent a re-dissolution of the electrodeposited uranium layer into the electrolyte solution. The cell was disassembled and the disc was then rinsed with 3×2 ml of 5 wt% NH_4OH solution and ethanol. In addition, the back of the disc was heated with a gas torch to bind the deposit to the disc surface and remove any organic impurities.

Alpha spectrometry measurement was conducted using a Canberra Alpha Analyst system with a passivated implanted planar silicon (PIPS) detector (450 mm^2 active

area, Canberra) and the data were analyzed using Canberra Genie 2000 software. The count time was 90000 s.

3. Results and Discussion

3.1 Activity Concentrations of Uranium and Thorium

In our experimental procedure, uninteresting nuclides were clearly separated and only interesting uranium and thorium isotopes (^{238}U , ^{235}U , ^{234}U , ^{232}U , ^{232}Th , ^{230}Th and ^{229}Th) appeared in the alpha spectra (Fig. 1 and 2). ^{232}U and ^{229}Th were added to the soil sample as tracers to calculate the radioactivity concentration.

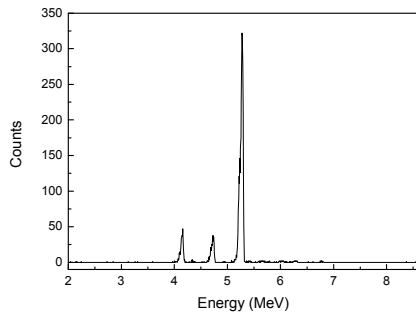


Fig. 1. Alpha spectrum of uranium isotopes separated from soil (NIST SRM 2709a) with UTEVA resin.

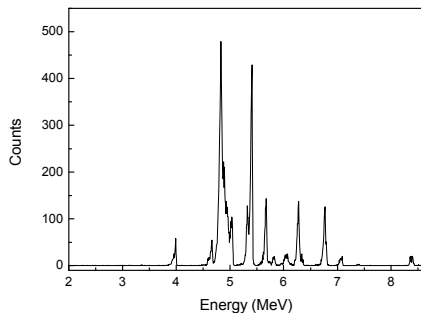


Fig. 2. Alpha spectrum of thorium isotopes separated from soil (NIST SRM 2709a) with TEVA resin.

The peak area determination in the alpha spectra for the uranium/thorium-electrodeposited disc showed that the chemical yields (tracer recovery) for isotopes were 87 ~ 100 %, and the radioactivity concentrations of ^{238}U , ^{235}U , ^{234}U , ^{232}Th and ^{230}Th were 38.64 ± 1.94 , 1.84 ± 0.10 , 36.88 ± 3.37 , 40.38 ± 3.01 and 41.38 ± 2.86 Bq/kg, respectively.

3.2 Activity Concentration Ratios

The ratios of $^{238}\text{U}/^{230}\text{Th}$, $^{234}\text{U}/^{230}\text{Th}$, $^{238}\text{U}/^{234}\text{U}$ and $^{238}\text{U}/^{232}\text{Th}$ were 0.93, 0.85, 1.05 and 0.96, respectively. The interpretation of U-Th data relies on a time evolution law of the U-series nuclides, which is the classical law used to account the variations of the radioactivity disequilibria during weathering, namely a loss and gain model [3]:

$$\frac{\partial^{238}\text{U}}{\partial t} = f_{238}^{238}\text{U}_0 - k_{238}^{238}\text{U} - \lambda_{238}^{238}\text{U} \quad (1)$$

$$\frac{\partial^{234}\text{U}}{\partial t} = f_{234}^{234}\text{U}_0 - k_{234}^{234}\text{U} - \lambda_{234}^{234}\text{U} + \lambda_{238}^{238}\text{U} \quad (2)$$

$$\frac{\partial^{230}\text{Th}}{\partial t} = f_{230}^{230}\text{Th}_0 - k_{230}^{230}\text{Th} - \lambda_{230}^{230}\text{Th} + \lambda_{234}^{234}\text{U} \quad (3)$$

$$\frac{\partial^{232}\text{Th}}{\partial t} = f_{232}^{232}\text{Th}_0 - k_{232}^{232}\text{Th} - \lambda_{232}^{232}\text{Th} \quad (4)$$

λ_i is the decay constant (in y^{-1}) of nuclide i , k_i is the first-order rate constant (in y^{-1}) for leaching of nuclide i and f_i is the input flux (in y^{-1}) of nuclide i gained by the sample.

The concentration of ^{238}U and ^{232}Th in soil depends on the formation and minerals in the soil itself. In many cases, the ratio of $^{238}\text{U}/^{232}\text{Th}$ is ca. 1 for the soil if it is not affected by peripheral plants or organisms [4].

4. Conclusions

In this work, uranium and thorium isotopes were chemically separated from a soil sample (NIST SRM 2709a) using chromatographic columns, and electrodeposited on a stainless steel disc to measure the radioactivity concentration of the isotopes with an alpha spectrometer. The ratio of $^{238}\text{U}/^{234}\text{U}$ for the soil sample was ca. 1 which is considered to be in secular equilibrium. However, ratios of $^{238}\text{U}/^{230}\text{Th}$ and $^{234}\text{U}/^{230}\text{Th}$ were slightly lower than 1, which indicates ^{230}Th accumulation in the soil. The ratio of $^{238}\text{U}/^{232}\text{Th}$ was ca. 1. This indicates that various mineral are uniformly included in the soil sample.

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