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The Yield Study of Chemical Separation for the Thorium and Uranium Isotopes from Sea Sediments

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Summary

Chemical separation methods of thorium and uranium isotopes from Ocean sediment samples have been studied in this work intensively. Following the separation of thorium isotopes by cation exchange resin from 3 N-HCl solution, the uranium isotopes were extracted into mesityl oxide from 1 N-HNO₃ solution saturated with LiNO₃ as a salting-out reagent. The uranium isotopes were then stripped into distilled water and extracted again with TTA-benzen solution (0.2 M TTA) adjusting the pH of the aqueous phase to 3.2 and by adding EDTA as a masking reagent.

To study the chemical yield for entire separation techniques, the Th-234 and U-232 isotopes as tracers were added to the sample solution. The uranium isotopes were recovered from the samples by 56.7% on the average, ranging from 32% to 79% for six samples, and the thorium isotopes were recovered by 86.7% with which agrees well for Th-separations in the works reported by other investigators.

The isotopes separated were determined by the ordinarily alphaspectrometric method with the use of 200 channel pulse height analyzer and silicon surface barrier detector.

I. Introduction

Mesityl oxide has widely been used for the separation of thorium isotopes from ocean bottom sediments¹⁾ and other thorium contained samples²⁾. Mesityl oxide, however, is also found to be a good extract for uranium separation in the same behavior for thorium extraction³⁾. In the point of uranium recovery and chemicals available in the laboratory, the chemistry in the separation of uranium isotopes by mesityl oxide extraction technique has mainly been studied and modified in this work. The separation techniques for yield study were then applied on the silty-clay sea sediment samples collected from Senkaku-shore area.

The separation of thorium isotopes was followed by cation exchange technique described by Y. Miyake⁴⁾ and others⁵⁾. The recoveries for thorium and uranium isotopes were determined by the introduction of Th-234 and U-232 tracers to the sample solutions, respectively. The isotopes isolated in the analysis were electrodeposited onto a stainless

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steel disk by constant voltage technique described by Goldberg, Dooley et al.^{1),6)} and M. Skanoue⁷⁾. The isotopes were determined by the introduction of alpha-spectrometric method using a silicon surface barrier detector coupled to a 200 channel pulse height analyzer.

II. Experimental

1. Sample Preparation

The silty-clay samples were air dried first, then dried up in a oven at 110°C for 24 hours and 60 meshes were collected.

2. Sample Decomposition

About 20 grams of sample powder were dissolved in 150 ml of conc. HCl in a 300 ml teflon beaker. The tracer solution of Th-234 and U-232 were spiked to the sample solution to study the chemical yields in the separation and purification procedures. The solution was then heated under an infra-red lamp and left for several days to attain the isotopic exchange equilibrium between tracer and the isotopes in a sample. The liquid phase was separated from residual solid phase by centrifugation in a 50 ml polyethylene centrifuge tube. Leaching was repeated and the residue was washed several times with conc. HCl. The supernatant was added to the original solution and the remaining residue was discarded.

3. Co-precipitation of Radioactive Elements with Hydroxide

Sample solution was transferred to the conical beaker and iron hydroxide was precipitated by passing ammonia gas into the solution. The hydroxide precipitate was dissolved in a small amount of 8 N-HCl and evaporated nearly to dryness with an addition of few drops of conc. HClO₄ and conc. HNO₃. The residue was dissolved in 150 ml of 1 N-HCl and was reprecipitated by the procedures described above.

4. Initial Separation of Thorium and Uranium Isotopes by Cation exchange Method

The residue obtained by the evaporation was dissolved in about 40 ml of 3 N-HCl and pass the solution through a cation exchange column (12 mm x 120 mm, packed with Dowex 50 x 8, 100-200 mesh resin), previously washed with 3N-HCl solution. The thorium isotopes have a strong tendency to adsorb selectively on cation exchanger and other impurities pass through the column. The thorium isotopes were eluted from the column with 45 ml of 0.5M H₂C₂O₄ solution. The flow rate of solution was nearly 0.6 ml/min. The Th-234 solution used as a radioactive tracer was separated from uranyl nitrate by the method modified by Goldberg and Koide¹⁾.

5. Electrodeposition of Thorium Isotopes.

Adding 1 ml of conc. HClO₄ and conc. HNO₃ to the thorium eluate, the solution

was taken to dryness to decompose the oxalic acid. The residue was dissolved in 15 ml of 2 M ammonium chloride to make up the electrolytic solution^{1),5)}, instead of the method developed by Komura and Sakanoue⁷⁾. The solution thus prepared was placed in an electroplating unit.

The thorium isotopes were plated onto a 2.5 cm diameter stainless steel disk for 60 minutes at a voltage of 7 volts and current of 0.35-0.55 A. Before the current is turned off, the electrolyte is made basic by the addition of 2 ml of concentrated ammonium hydroxide solution. If this step is omitted, the collapse of the cathode basic layer when the current is turned off causes the deposited hydroxide to redissolve immediately in the solution. After an electrodeposition, stainless steel cathode was rinsed sufficiently with distilled water, then dried under an infra-red lamp. The electrodeposited plate was counted under 1-inch end-window type G.M counter to determine the chemical yield of thorium isotopes. The overall chemical yield varied from 33 to 100 per cent.

6. Purification and electrodeposition of Uranium Isotopes

The uranium fraction was taken nearly to dryness with the addition of conc. HClO_4 and conc. HNO_3 . The residue was dissolved in 30 ml of 1 N- HNO_3 solution and 24 g of LiNO_3 was dissolved by heating. The uranium isotopes were extracted with 25 ml of mesityl oxide. The extraction was repeated with another 10 ml of mesityl oxide and the organic phase was washed several times with 1 N- HNO_3 solution saturated with LiNO_3 . Then, the uranium isotopes were stripped into aqueous phase with 20 ml of distilled water.

For masking the metallic ions (i. e. Ag, Cu, Fe, Zr, e.t.c.) , EDTA solution was added to the aqueous phase and the pH of the solution was adjusted to 3.2 by NaOH solution. The uranium isotopes were then extracted again with 0.2M TTA-benzen solvent. The extraction was repeated. The organic phase was washed two times with HNO_3 solution which was adjusted the pH to 3, and the uranium isotopes were back extracted into 10 ml of 2 N- HNO_3 solution (x2). The solution was evaporated to dryness with an addition of few drops of conc. HClO_4 and conc. HNO_3 to decompose any organic matter. The purified uranium isotopes were taken up with 2 ml of 2 N- HClO_4 , while beaker was still hot. Then 2.5 ml of 2 M HCOONH_4 solution and 10 ml of distilled water were added to make up the electrolytic solution.

The uranium contained electrolytic solution was transferred into electrodeposition cell and the uranium isotopes were electroplated on a stainless steel (3.2 cm in diameter) for two and a half hours at a constant voltage of 8.4 volts. The schematic diagrams for all the separation and purification procedures described above are shown in Fig. 1.

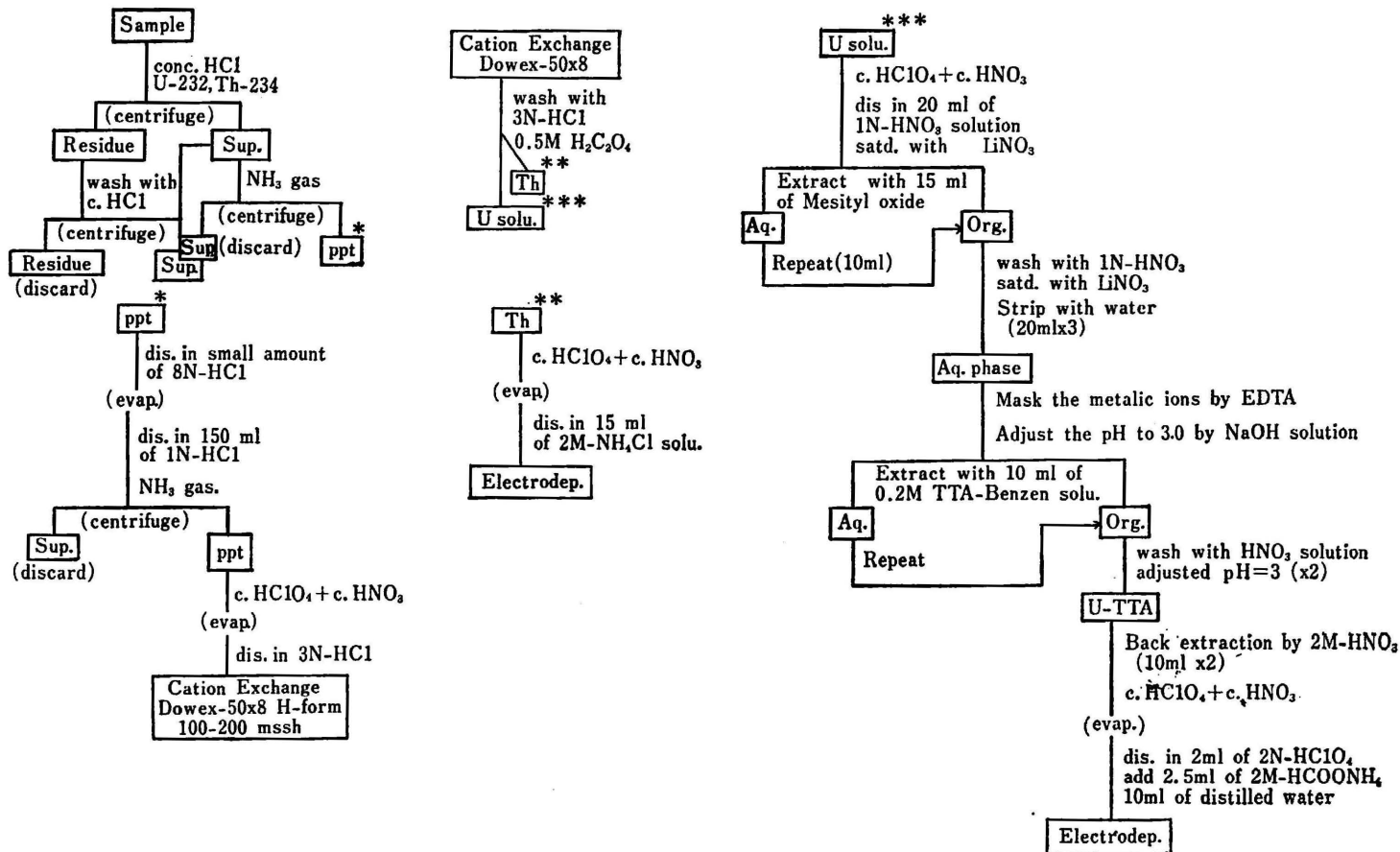


Fig. 1 Analytical Scheme for the Thorium and Uranium Separation

III. Results and Discussion

The intensities of the alpha particles from U-232 plated on the stainless steel disk were measured by the ordinary alpha spectrometric method with the use of a 200 multi-channel analyzer (Toshiba) and a silicon surface barrier detector (Hitachi-Horiba). The chemical yields for the uranium separation techniques were obtained as the activity ratios of counts of standard U-232 tracer to that of recovered from the entire separation process, rather than the measured areas under the respective peaks.

In precede with the uranium separation, the thorium isolation technique, by the use of cation exchanger, was also checked to assure the method. Chemical yields agree with the data reported by Miyake et. al⁴⁾.

Table 1 gives a comparison of the chemical yields of the thorium and the uranium isotopes. The spectra for U-232 recovered from the uranium separation process are shown in Fig. 3 and 4, in comparison with the standard U-232 spectrum in Fig. 2.

Table 1 Chemical Yield of Thorium and Uranium Isotopes

Sample	Uranium (%)	Thorium (%)
24	48.22	99
38	58.03	90
46	51.69	98
48	79.15	100
59	—	97
66	32.72	33
69	70.42	90
	Ave. 56.7	Ave. 86.7

The thorium isotopes have a strong tendency to adsorb selectively on the cation exchange resin in the hydrochloric acid media of high concentration, whereas uranium, iron and many other cations pass through it. The thorium isotopes adsorbed on the resin are subsequently eluted with 0.5M oxalic acid. It has been pointed out by other investigators⁴⁾ and author⁵⁾ that the thorium isotopes separated this way are not necessary to take the further purifications.

Mesityl oxide has well been used as an extractant for the thorium separation. It has been found out, however, that this solvent is also a good extractant for the uranium extraction³⁾ introducing the saturated LiNO₃ as a salting-out reagent. Since the thorium isotopes are also extracted completely in the same manner, they must have been isolated from the uranium in advance. Moreover, the small quantity of iron (10%) and zirconium (25%)³⁾ are also extracted in the process. EDTA solution may be added to mask any trace amount of iron and other preventive cations that make it difficult to prepare the final thin layer source for alpha counting.

Since the uranium isotopes are not extracted with TTA-benzen solution having

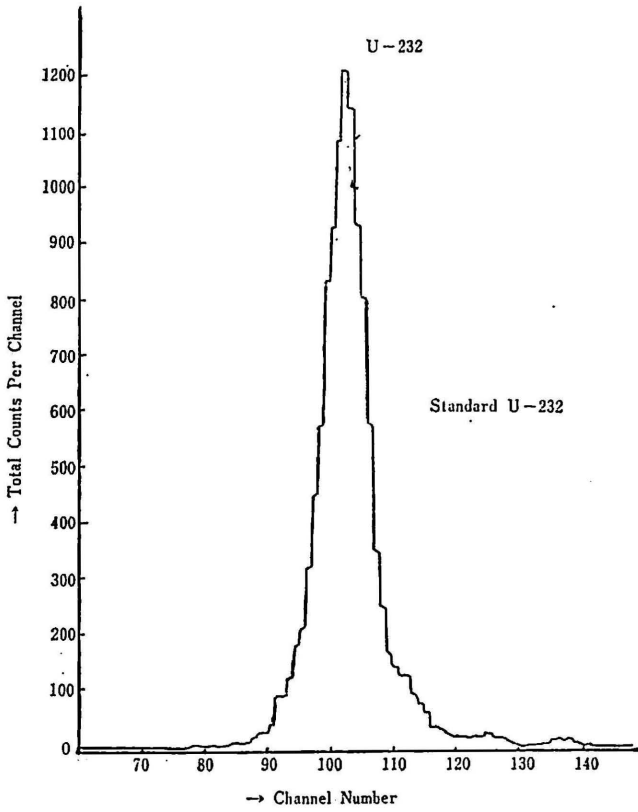


Fig. 2 The alpha-spectrum of standard U-232

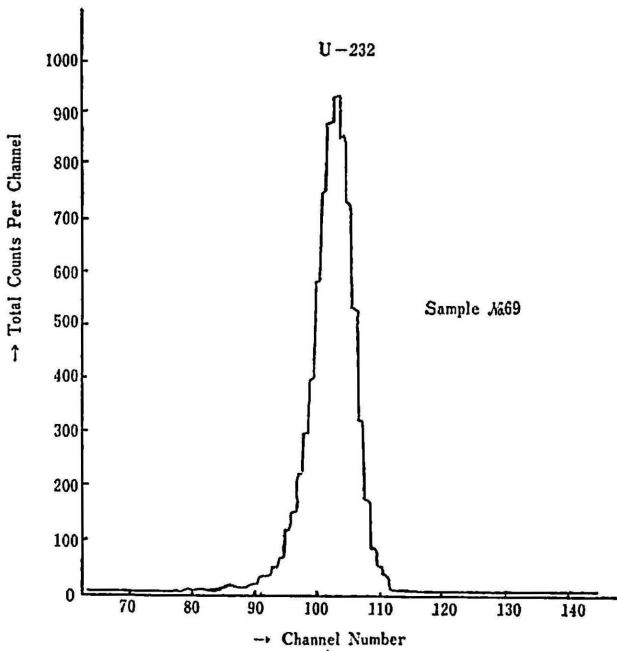


Fig. 3 The alpha-spectrum of U -232 recovered from silty-clay Sample

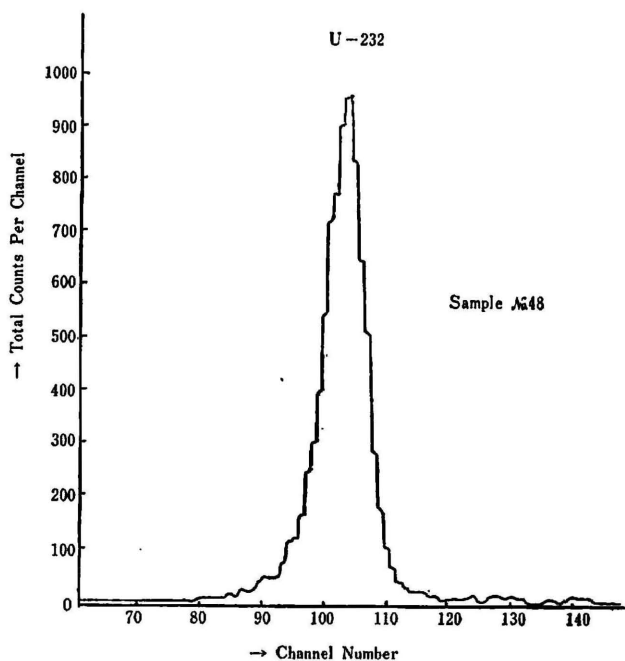


Fig. 4 The alpha-spectrum of U-232 recovered from silty-clay Sample

the pH less than 1, the pH of the aqueous phase must carefully be adjusted to 3.0. The procedures are then followed by the method for the thorium extraction process with which the uranium isotopes act the same chemically.

No apparent iron or other preventive radioactive species are found in the final purified uranium solution. The spectra obtained through the method give the clear separation of the uranium isotope and the technique may be applied for the isolation of the uranium isotopes in silty-clay ocean sediments.

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Bibliography

- 1) E. D. Goldberg and M. Koide, *Geochim. et Cosmo. Acta.*, 26, 417(1962)
- 2) C. V. Banks, R. E. Edwards, *Anal. Chem.*, 27, 947(1955)
- 3) J. S. Fritz, M.J. Richard and A. S. Bystroff, *Anal. Chem.*, 29, 577(1957)
- 4) Y. Miyake, *Science* 133, 1823(1961)
- 5) H. Taira, *Bull. of Sci. & Eng. Div., Univ. of the Ryukyus., Math. & Natural Sci.*, 12, 11(1969)
- 6) Dooley, J. R., Jr., Tatumoto, M., and Rosholt, J. N., *Econ. Geology*, vol. 59, pp 586-595 (1967)
- 7) M. Sakanoue and K. Komura, *The Science Reports of Kanazawa Univ.* vol. XII, No.1 June (1967)