研究論文**214. Determination of Thorium in Various Aqueous Samples by Anion Exchange, (II)*****Analytical method of urine, tap water and sea water***

陰イオン交換法による各種水溶液試料中のトリウムの定量, (II)

尿, 水道水および海水中のトリウムの分析法

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An analytical method for thorium in various aqueous samples such as urine, tap water and sea water is described.

The method proposed is as follows: thorium is co-precipitated with the basic phosphate precipitates of calcium and magnesium in a sample of a large volume. The precipitate is dissolved with 1N nitric acid and then the solution is made 40 v/o 1N nitric acid-60 v/o ethanol mixed solution by adding ethanol. The resultant solution is passed through the Dowex 1-X8 resin column ($0.7\text{cm}^2 \times 2.8\text{cm}$), and the column is washed with 20 v/o 1N nitric acid-80 v/o ethanol mixed solution and then water. The elution is carried out with 8N hydrochloric acid. The amount of thorium is determined by a photoelectric spectrometer, using neo-thorin.

The sensitivity is $0.5 \sim 1.0 \mu\text{g Th}$, and recovery for μg amount of thorium is 99% for 400~600 ml of human urine, 97% or 96% for 1,000 ml of tap water or sea water, respectively.

I. INTRODUCTION

The workers who are treating thorium or its compounds are to be monitored for thorium content in urine for the radiation control. The determination procedure should be simple and rapid. The present study was carried out to find a suitable method for thorium in urine as a routine method.

The method consists of (1) concentration from the sample by the co-precipitation, (2) purification of thorium from many other ions by an anion exchange in nitric acid-ethanol mixed solution medium, and (3) spectrophotometric determination with neo-thorin.

The co-precipitation of thorium with basic phosphate precipitate is adopted in order to avoid laborious ashing procedure⁽¹⁾⁽²⁾ of the sample.

II. EXPERIMENTAL**Reagents and resin**

Standard thorium solution: Thorium chloride, reagent grade, dissolved in 0.2N hydrochloric acid was standardized by an usual oxalate method.

Carrier-free ^{234}Th tracer was prepared by an anion exchange method⁽³⁾ and kept as 0.2N nitric acid solution.

Synthetic urine: The chemical composition is given in Table 1.

Basic phosphate was prepared from synthetic urine by a procedure described in the preceding paper⁽⁴⁾.

Dowex 1-X8 (100~200 mesh) column of $0.7\text{cm}^2 \times 2.8\text{cm}$ was pretreated with 40 v/o

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Table 1 Chemical composition of synthetic urine

Constituent	Amount (g)	Constituent	Amount (g)
Cl	7.1	NH ₃	0.70
Na	4.0	Ca	0.20
K	2.0	Mg	0.15
P	1.16	Urea	30.0
S	1.10	Water	1200

1N nitric acid-60 v/o ethanol mixed solution.

Neo-thorin, *o*-(4,5-dihydroxy-2,7-disulfo-3-naphthylazo)-benzen arsonic acid, was obtained from the Wako Pure Chemical Industries, Ltd., 0.1% aqueous solution.

All other reagents were of an analytical grade and used without further purification.

Counter: G.M. counter with an end window of 1.5mg mica/cm² thick.

Photometer: Hitachi photoelectric spectrometer, type EPU-2A, with 1 cm cells at 580 mμ.

Procedure

(1) Co-precipitation

To urine sample of 400~600ml, 6N sodium hydroxide is added till pH value of the solution reaches about 9. After standing for about 30 min, the supernatant solution is discarded. The precipitate formed is centrifuged at 3200 r.p.m. for a few min, and dissolved with a few ml of 7.5N nitric acid. The solution is diluted to about 200 ml with demineralized water. The precipitation is repeated by adding 2 ml of 6N phosphoric acid and 2 ml of 6N sodium hydroxide. The final precipitate is separated again, and is dissolved with a few ml of 7.5N nitric acid. The resultant solution is evaporated to complete dryness on a hot plate and all organic substances are destroyed. The residue is taken up with 4.0 ml of 1N nitric acid, then 6.0 ml of 99.5 v/o ethanol is added.

(2) Anion exchange

The solution is passed through the anion resin column at a flow rate of about 0.6 ml/min. In order to eliminate calcium, magnesium, and phosphate, the column is washed with about 35 ml of 20 v/o 1N nitric acid-80 v/o ethanol mixed solution (flow rate 1.4~1.7 ml/min), and then with 20 ml of demineralized water (flow rate~1.7 ml/min).

Thorium is eluted with about 20 ml of 8N hydrochloric acid at the flow rate of about 0.7 ml/min, and the eluate is taken into a 20 ml measuring flask.

(3) Spectrophotometric determination

The eluate is evaporated on a water bath, and is transferred quantitatively into a 10 ml measuring flask with 2.5 ml of 0.2N hydrochloric acid and small amount of water. After 2.5 ml of 0.2M potassium chloride solution and 1.00 ml of neo-thorin are added, the solution is made up to 10 ml. The absorbancy is measured against a reference solution.

III. RESULT AND DISCUSSION

1. Co-precipitation of thorium

The relationship between co-precipitation ratio of thorium and pH value of the solution is studied using ²³⁴Th as a tracer and the synthetic urine as a sample by the method mentioned in II-(1). The results given in Fig. 1 shows thorium is completely carried down with the phosphate precipitate at the pH range over 8.

Fig. 1 Co-precipitation of thorium

Thorium accumulated in a human body, might possibly be excreted as organo-compound which do not co-precipitated with basic phosphate precipitates. However, according to the carrying down tests, it is proved that thorium in ²³⁴Th exposed rabbit's urine is

also completely co-precipitated. Therefore, it is concluded thorium in urine sample, can be collected by the above co-precipitation method.

2. Separation of thorium from Fe (III)

by anion exchange

Thorium was quantitatively adsorbed on a small column of the anion exchange resin Dowex 1-X8 from 40 v/o 1 N nitric acid-60 v/o ethanol mixed solution in the presence of phosphate⁽⁴⁾. By this ion exchange procedure, many other ions such as calcium, magnesium, and phosphate were eliminated. The elution of thorium was readily attained with a small amount of over 2 N hydrochloric acid⁽⁴⁾.

In this ion exchange procedure, the behavior of Fe (III) in the presence of phosphate is unknown. The separation of thorium from Fe (III) was examined tracerchemically using ⁵⁵⁺⁵⁹Fe as a tracer, and the results are given in Table 2.

In Table 2, "Detected activity" indicates the activity detected in the thorium fraction of the column operation. The results shows Fe (III) was completely adsorbed on the resin

Table 2 Contamination ratio of Fe (III)

Elutriant	Added iron (μ g)	Added activity (cpm)	Detected activity (cpm)	Contamination ratio (%)
2 N HCl	350	10425 $\pm$ 52	9231 $\pm$ 68	88.5 $\pm$ 0.8 [†]
4 N HCl	350	10425 $\pm$ 52	2828 $\pm$ 27	27.2 $\pm$ 0.3
5 N HCl	350	10425 $\pm$ 52	723 $\pm$ 9	6.9 $\pm$ 0.1
8 N HCl	350	10425 $\pm$ 52	385 $\pm$ 6	3.7 $\pm$ 0.1

[†] Standard deviation based on the counting error.

column. When the elution was carried out with 6~8 N hydrochloric acid, only a few percent of Fe (III) was eluted. Therefore, Fe (III) is roughly separated from thorium by the elution with 6~8 N hydrochloric acid.

3. Recovery of thorium

The recovery of thorium from 400~600 ml of human urine were studied both in tracerchemical and spectrochemical method. The results given in Table 3 shows that the recovery of μ g amount of thorium in urine is quantitatively.

Table 3 Recovery of thorium in human urine, tap water and sea water

Sample	Sample volume (ml)	Added thorium		Detected thorium		Recovery	
		²³⁴ Th (cpm)	Th (μ g)	²³⁴ Th (cpm)	Th (μ g)	²³⁴ Th (%)	Th (%)
Human urine	400	4140 $\pm$ 16	55	4320 $\pm$ 20	57	104 $\pm$ 0.6 [†]	104
	600	2080 $\pm$ 11	34	2160 $\pm$ 14	32	104 $\pm$ 0.6	94
	(Mean)					104	99
Tap water ^{††}	1000	4140 $\pm$ 16	109	4040 $\pm$ 20	—	98 $\pm$ 0.6	—
	1000	2080 $\pm$ 11	34	2040 $\pm$ 14	33	98 $\pm$ 0.6	97
	(Mean)					98	97
Sea water ^{††}	1000	3900 $\pm$ 11	69	3940 $\pm$ 13	66	101 $\pm$ 0.5	96

[†] Standard deviation based on the counting error.

^{††} The content of natural thorium have been reported that less 1 μ g/l for tap water (Ref. 5), and 0.5 μ g/l (Ref. 6) or 0.7 μ g/l (Ref. 7) for sea water.

4. Spectrophotometric determination

It is reported that the presence of elements like Zr (IV), Ce (III), Ce (IV), UO₂⁺⁺, and Fe (III) interferes the spectrophotometric determination of thorium with neo-thorin⁽⁸⁾.

Therefore, the elimination of large amount of these interfering elements is required for the photometric determination of thorium.

The content of iron in human urine is roughly 40~70 μ g⁽⁹⁾ or 200~300 μ g⁽¹⁰⁾⁽¹¹⁾

per 1000 ml. Therefore, the separation of thorium from Fe(III) is required only when large amounts of urine is taken. The elimination of Fe(III) from thorium can be attained by the column operation mentioned already. Furthermore, the coloration of Fe(III) with neo-thorin can be avoided by reduction of Fe(III) to (II) with hydroxylamine⁽⁸⁾.

The content of zirconium in urine has not yet been reported, but it is believed that the content in urine is extremely small. Hence, it may be considered that the effect of the presence of zirconium is negligible small for an ordinary sample.

5. Sensitivity

The determination of thorium in urine requires very high sensitivity for the radiation control. Fujita and Iwamoto⁽¹²⁾ calculated that only 0.2 dpm* thorium is excreted in 24 hr urine from the body containing the maximum permissible amount of natural thorium.

The detection limit of thorium in this method is chiefly determined by the sensitivity of the color reaction. In the case of neo-thorin, the sensitivity is 0.5~1.0 μ g of thorium. Therefore, this method is available for the radiation control purpose.

6. Application to tap water and sea water

The method can be used for the determination of thorium in tap water** and sea water with slight modifications. For tap water, calcium chloride (50 mg Ca) and phosphoric acid (6 N, ~2 ml) are added to a 1000 ml of sample. For sea water, phosphoric acid (6 N, ~2 ml) is added to a 1000 ml of sample, the basic phosphate of calcium and magnesium is precipitated by slowly adding of 2 ml of 6 N sodium hydroxide with constant stirring. Further treatments are the same with those for urine.

The recovery of thorium in 1000 ml of tap water or sea water is quantitative as is given in Table 3.

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* Natural thorium is in radiochemical equilibrium between ²³²Th activity and that of ²²⁸Th, hence 0.2 dpm of natural thorium corresponds to about 0.5 μ g.

** The maximum permissible concentration of thorium in a drinking water is 10^{-5} μ c/cm³ or 45 μ g/l for a 168 hr week for the soluble form (Ref. 13).