

Estimation of the Microgramme Amount of Thorium in the Lake Biwa Water

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This is the fourth in a series of the papers dealing with the estimation of microgramme amount of thorium in natural substances.

The thorium content in the Lake Biwa water was estimated to be 5.83×10^{-2} microgrammes per liter on analysing the flock which was obtained at Keage Jo'suijo (Department of Water-supply Office of Kyoto).

The process for the determination of the thorium content consists of three steps ; the first is a sampling of the flock and the determination of an accumulation factor of the thorium using titanium as an internal indicator, the second a colorimetric measurement of thorium which is extracted from the flock by using cyclohexanone, and the third a calculation of the thorium content in the Lake Biwa water.

INTRODUCTION

In the present paper the thorium content of the water of Lake Biwa was determined by a method of colorimetric analysis.

The process for the determination of thorium in the lake water consisted of three steps ; the first was a co-precipitation of thorium with aluminium hydroxide from the lake water, the second a colorimetric analysis of thorium which was extracted by the use of cyclohexanone, and the third a calculation of the thorium content of the lake water. As the methods used for each of the above steps have already been reported in detail⁽¹⁾⁽²⁾⁽³⁾, they are, in this report, summarized briefly.

1.1. Aluminium Hydroxide Co-precipitation Method. After passing through the Lake Biwa drainage, water from the Lake Biwa flows through a cleaning bed at Keage Jo'suijo (Department of Water-supply Office of Kyoto City), where it is cleansed by installation as schematically shown in Fig 1.

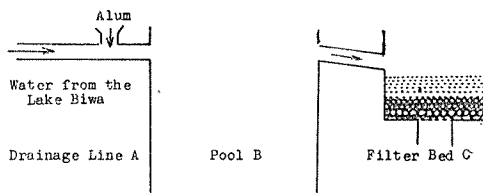


Fig. 1. The cleaning installation at Keage Jo'suijo

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At the entrance of the pool B, the water is added the alum (aluminium potassium sulfate) solution at the ratio of about 8 mg. of alum to 1 liter (of lake water). Aluminium ion is soon hydrolysed and set down to the bottom of the pool B together with colloidal particles, planctons, and some other cations which are contained in the water. The Aluminium hydroxide deposit in the pool B will be referred to as the flock in this report. The supernatant water in the pool B is then led into the filter bed C.

It should be noted that the aluminium hydroxide co-precipitation method which is employed at the water-supply office for cleaning the water of the Lake Biwa is identical in principle with that which is generally used in the laboratory for the extraction of minute amounts of elements in natural water. According to the results of the authors' studies⁽⁴⁾⁽⁵⁾ on the aluminium hydroxide co-precipitation method, thorium, titanium and iron ions can be precipitated completely with aluminium ions by this method. Therefore, thorium, if it be present in the Lake Biwa water, should be deposited with the aluminium hydroxide in the pool B.

1.2. Accumulation Factor. For the calculation of the thorium content of the lake water an accumulation factor, F , which is defined by the equation (1), was determined.

$$F = \frac{\text{the amount of titanium in unit gram of the flock}}{\text{the amount of titanium in unit volume of the lake water}} \quad (1)$$

If one assume that both titanium and thorium show the same behaviour during this precipitation in the pool B, the amount of thorium in the lake water can be obtained by the following equation.

The amount of thorium in unit volume of lake water

$$= \frac{\text{the amount of thorium in unit gram of flock}}{F} \quad (2)$$

1.3. Sampling of the Flock. The deposit in the pool B was sucked up with water and dried in the air. Typical changes in weight of one of the flocks during heating are listed in Table 1.

Table 1. Weight changes of the flock. *

Dried in the air	10.0235 g
Heated in an electric oven (100°—105°C)	8.8135 g
Ignited at 800°C	6.5542 g
Insoluble matter on wet ashing	3.1647 g

* Sampled on Nov. 16, 1956.

PROCEDURE

2.1. Wet Ashing of the Flock. Ten grams of the flock which was collected from the bottom of the pool B and dried in air was placed on a 250 ml. Kjeldahl digestion flask, and was added 100 ml. of conc. nitric acid and 20 ml. of conc. perchloric acid. The mixture was heated, with occasional stirring,

untill the organic matter was destroyed. After the organic matter was destroyed, the solution was added about 100 ml. of distilled water and was transferred through No. 5 C filter paper (Tokyo-Roshi) into a 1 liter volumetric flask. The insoluble material on the filter paper was washed several times with distilled water, and the washings were combined with the filtrate and then made to 1 liter with distilled water. The solution was used for the determination of thorium and titanium.

2.2. Determination of Thorium. A 250 ml. of aliquot of this solution was transferred to a 500 ml. beaker and was neutralised with sodium hydroxide solution. The precipitated aluminium hydroxide was filtered and washed with distilled water. The hydroxide precipitate was then transferred to a 100 ml. of 6-N sodium hydroxide solution, and was heated for about 5 minutes with stirring.

In this process, aluminium hydroxide was turned into aluminate ion and was separated from the co-precipitated hydroxide of iron, titanium and thorium by decantation and then by using a centrifuge.

2.3. Extraction of Thorium with Cyclohexanone. The hydroxide precipitates were transferred into a 100 ml. beaker and were dissolved with small amount of nitric acid. The solution was added 20 ml. of saturated solution of ammonium nitrate and adjusted, with the use of a pH meter, at 0.65 in pH value by adding ammonium hydroxide or nitric acid. The solution was poured into a 50 ml. separatory funnel and was added about 30 ml. of cyclohexanone. After shaking vigorously for about 30 seconds, the aqueous phase was drained off into the second separatory funnel. The extraction was made once more with 20 ml. of cyclohexanone. The cyclohexanone phases were combined in another separatory funnel and were stripped with about 15 ml. of distilled water. Thorium was accumulated in this water phase with the stripping procedure.

2.4. Spectrophotometric Determination of Thorium. The water phase was drained into a 50 ml. beaker. To this solution, 2 ml. of 1 % (by weight) hydroxylamine hydrochloride solution was added and heated. On heating, small amount of Fe (III), which was contaminated in the extraction process, was reduced to Fe (II), thus, the colorimetric interference of Fe (III) was eliminated. After cooling, the solution was transferred into a 20 ml. volumetric flask. To this solution, 1 ml. of 0.5 % *o*-arsonophenylazo-chromothropic acid solution was added as a colorimetric reagent and was made to the volume.

The absorbance was measured on a spectrophotometer at a wave length of 600 m μ .

2.5. Determination of Titanium. The determination of titanium in the flock was made colorimetrically with the hydrogen peroxide method.

A 20 ml. aliquot of wet ashed solution, which was obtained during the determination of thorium, was transferred into a 100 ml. beaker. The solution was evaporated almost to dryness on a hot plate. The residual solution was added 4 ml. of conc. sulfuric acid and heated for about ten minutes. After cooling, the solution was diluted with cold water and was transferred into a

50 ml. volumetric flask. To this solution, dilute phosphoric acid was added from a buret until the yellow color of ferric ion was destroyed. The color developed on adding 2 ml. of 3 % hydrogen peroxide solution. The absorbance was measured on a spectrophotometer at a wave length of 430 m μ .

The determination of titanium in the lake water was carried out as follows. To 5 liter of the lake water, 10 ml. of 1 M alum solution was added and was adjusted at 7 in pH valum by adding ammonium hydroxide solution. After standing one day, the precipitate of aluminium hydroxide was filtered and treated in the same way as in the case of the flock.

ERSULTS

Samples of the flock and the lake water, which were used in the present study, were obtained at Keage Jo'suijo. Table 2 lists the titanium and chloride ion content of the Lake Biwa water. Table 3 lists the thorium and titanium contents of the flock.

Table 2. Ti and Cl contents of the Lake Biwa water.

Ti (μ g/liter)	11.0	11.6	11.2	Av.	11.34
Cl (mg/liter)	5.2	5.5	5.2	Av.	5.3
Date of sampling					
Nov. 1956	6	11	16		

Table 3. Th and Ti contents of the flock dried in air.

Th (μ g/10g flock)	42.5	41.6	49.5
Ti (mg/10g flack)	8.86	8.17	9.71
Date of sampling			
Nov. 1956	7	12	16

3.1. Calculation. From the equations (1) and (2), one can obtain the following equation :

$$\frac{\text{Th in flock}}{\text{Ti in flock}} = \frac{\text{Th in lake water}}{\text{Ti in lake water}} \quad (3)$$

Taking the average content of titamiun of the Lake Biwa water to be 11.37 μ g/liter, the thorium contents were obtained as follows.

$$42.3 \div 8.86 \div 10^3 \times 11.37 = 5.90 \times 10^{-2}$$

$$41.6 \div 8.17 \div 10^3 \times 11.37 = 5.78 \times 10^{-2}$$

$$49.5 \div 9.71 \div 10^3 \times 11.37 = 5.79 \times 10^{-2}$$

$$\text{Average thorium content} = 5.83 \times 10^{-2} \quad (\mu\text{g/liter})$$

SUMMARY

The thorium content of the Lake Biwa water was estimated to be 5.83×10^{-2} μ g/liter on analysing the flock using titanium as an internal indicator.

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REFERENCES

- (1) M. Ishibashi and S. Higashi, *Japan Analyst*, **3**, 213 (1954).
- (2) M. Ishibashi and S. Higashi, *Japan Analyst*, **4**, 14 (1955).
- (3) M. Ishibashi and S. Higashi, *Japan Analyst*, **5**, 135 (1956).
- (4) M. Ishibashi and S. Higashi, "Commemoration Volume for the Silver Jubilee, Institute for Chemical Research, Kyoto Univ." p. 121 (1951).
- (5) M. Ishibashi and T. Shigematsu, *ibid.*, p. 122 (1956).