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Study on Determination of Th in Biological Sample by INAA and RNAA

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Abstract

For Th determination (ppb or sub-ppb level) in environmental and biological sample, RNAA is known as a effective method. As a preliminary study for applying this method to real sample analysis, we determined radiochemical yield through overall separation procedure for the standard solution and NIST SRM samples. The chemical yield of standard solution and SRM are 85.9% and 87.4%, respectively and standard deviation is less than 5%. It is turned out that background effect is remarkingly decreased from camparison of interfering activity between INAA and RNAA

1. Introduction

It is known that three decay series of alpha radioactive nuclide are naturally present in the earth's crust. Th-232 which is one of the primordial radioactive elements has about 4075 Bq/g of specific activity and is a potential source of nuclear fuel(U-233). According to Taylor's crustal concentration [1], the conentration of Th is known as 9.6 ppm. In the aspect of health physics, even though usually present at low concentration in soil, Th is a toxic element that incurs internal exposure by inhalation of alpha activity associated with airborne dust, by intake of daily diet and by industrial activity. Therefore, carring out metabolism research of Th in human body, it is necessary to establish accurate analytical method for Th of ppb or sub-ppb level concentration in environmental or biological sample.

For this purpose, NAA(Neutron Activation Analysis) [2] which has advantage of high sensitivity can be used as a relevant method. Table. 1 shows the data for the comparison of detection limit of different analytical techniques for the determination of Th and good sensitivity of NAA method. In this table, detection limit of Th determination by INAA and RNAA are 2.0 ng and 0.025 ng, respectively.

In case of applying non-destructive INAA(Instrumental Neutron Activation Analysis) to analyze Th in biological sample, Uncertainty of analytical data is dependent on high background count rate due to interfering elements such as Na-24, Br-82, Fe-59, Co-60, Zn-65 etc. For this reason, to improve analytical precision and accuracy,

RNAA(Radiochemical Neutron Activation Analysis) [3] can be effectively applied to reduce background growth by radiation interaction such as compton scattering, pair production and photoelectric effect. For instance, H.S. Dang, etal. [4] determined the concentration of Th in urine(geometric mean : 2.7 ng/L) and human serum(geometric mean : 7.9 ng/L) using well established RNAA technique. G.S. Hewson, etal [5] also determined the concetration of Th in urine(geometric mean : 31 ng/L) and human serum(geometric mean : 480 ng/L) of mineral sand workers.

In this study, radiochemical yield was firstly determined through the overall separation procedure, after the direct analysis of Th soultion of different concentration made by dilution of Th standard solution certified by NIST, and also background lowering effect was examined by comparison between INAA and RNAA for Th in NIST SRM(Pine Needle and Oyster Tissue). In addition, it was found out that how effectively Pa-233 can be separated from sample through overall procedure and these results were considered quantitativly.

2. Experimental

2.1 Sample Preparation

To prepare Th solutions which have different concentration, stock solution of about 11.7 μg/ml was made by dilution of NIST standard solution. Since exact concentration is not important to decide radiochemical yield by activity produced, we made Th solution of approximately 0.1μg, 1.67μg, 2.34μg, 4.01μg and 6.35μg per ml for irradiation. Two SRM samples (NIST SRM 1566a Oyster Tissue and NIST SRM 1575 Pine Needle) were dried for 2 hrs at 80°C in oven in accordance with recommend procedure of NIST certificate and then prepared in polyethylene capsule washed by 1N HNO_3.

2.2 Sample Irradiation

Prepared solution samples were irradiated under the thermal flux of 1.7 X 10^{13} $n/cm^2 \cdot sec$ for 20 minutes or shorter using PTS(Pneumatic Transfer System) of HANARO research reactor. NIST SRM samples were also irradiated in the same condition for 5 hrs or longer. These samples were allowed to cool for more than 10 days to allow the decay of short-lived interfering activities(Na-24, Br-82 etc).

2.3 Radiochemical Separation Procedure

Except for solution samples, powdered samples were digested in concentrated HNO_3 and added a few drops of H_2O_2 to accelerate and to complete digestion until clear solution was obtained. RNAA method of reference [4] was applied to subsequent procedure. As shown in Figure. 1, subsequent separation procedures are as follows ;

- Add Mn carrier (40mg) and heat the solution to dryness
- Add 25ml of 4M HNO_3 and warm gently (50 - 60°C)

- Add 250 - 300 mg of $KBrO_3$ and keep warm gently
- Black MnO_2 precipitaion appear and keep aside that to coagulate precipitation
- The MnO_2 precipitate are then centrifuged and supernatant discarded
- The MnO_2 precipitate is redissolved in HNO_3/H_2O_2
- The redissolved solution is transfered back to the beaker
- To this solution, add 7ml of H_2SO_4 and 100mg of K_2SO_4
- The solution is warmed gently and 25mg of Ba carrier is added dropwise
- $BaSO_4$ precipitation occur and this precipitate is allowed to settle for 2 - 3 hrs
- Filter the precipitate
- counting

2.4 Radioactivity Measurement

Thorium was determined by both of INAA and RNAA using the nuclear reaction of

$$^{232}Th\ (n,\gamma)\ ^{233}Th \xrightarrow{\beta^-} {}^{233}Pa\ (\ T_{1/2} = 27d,\ E_\gamma = 312\ keV)$$

All samples were analyzed by relative method based on estimating the ratio of ^{233}Pa -activity between sample and standard. For the determination of Th and other gamma ray emitting nuclide, HP Ge semiconductor(EG & G ORTEC, GEM20180, 1.8keV resolution at 1332keV of Co-60, Peak to Compton ratio 45 : 1) and 8K MCA(MCB 919, EG & G ORTEC) were used for counting samples.

3. Results and Discussion

3.1 Radiochemical Yield of Th-solution

Table 2 shows the radiochemical yields of Th obtained from this work.. Average yield was about 85.9% and standard deviation was less than 5% indicating good reproducibility. It can be assumed that low recovery of 10% or more is mainly resulted from absorption of beaker wall, or loss in MnO_2 centrifugation and $BaSO_4$ filtering procedure.

3.2 Th Analysis of Standard Reference Materials

Table 3 shows Th concentration to compare separation effect between INAA and RNAA. Th concentration of SRM (Pine Needle and Oyster Tissue) certified by NIST is 0.037ppm and 0.04ppm, respectively. Average yield of Th was 87.4% and standard deviation was 4.3%. In comparison with 90.4% of reported yield of [4], our result is reasonable.

It was found out that count rate of elements such as Fe, Zn, Co which induce background increasing by radiation interaction was remarkably reduced. Table 4 shows reduction percentage of concentration for Fe, Zn, Co, etc after radiochemical separation. The reduction percentage of Fe, Zn and Co are 93.7, 81.2 and 99.8%. In addition, Figure

2 shows Gamma-ray spectrum of INAA and RNAA. It was detected that background was decreased and signal to noise ratio of Pa-233 was three times as high as through RNAA procedure under the same counting condition.

4. Conclusion

It can be concluded that Th determination using RNAA is more sensitive than INAA. From these results, This RNAA method will be able to be applied effectively for determining Th in real biological sample which has ppb or sub-ppb concentration.

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Reference

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Table. 1 Comparison of detection limit of different analytical techniques for the determination of Thorium

Analytical Technique	Detection Limit (ng)	Remarks
RNAA	0.025*	Only Th can be analysed
INAA	2.00*	Th is analysed with other nuclide
Fluorometry	10.00(1)	Total Th is analysed
Spectrometry	46.00(2)	Isotopic analysis of all emitting isotope can be done simultaneously
Spectrophotometry	100.0(3)	Total Th is analysed
Mass spectrometry	0.01(4)	Isotopic analysis can be done

* Neutron Flux : $\sim 10^{13} n/cm^2 \cdot sec$, Irradiation time : 2days, Counting time : ~ 16hours
(1) Sill and Willis 1962 (2) Wrenn etal. 1981 (3) Petro etal 1967
(4) Tilton and Aldrich 1954

Table 2. Radiochemical yield of Th standard solution by RNAA

Sanmple number	Th Concentration (μg/ml)	measured Th (μg/ml)	Yield (%)
1(n=3)	0.1	0.0873 ± 0.006	87.3 ± 6
2	1.67	1.42	85
3	2.34	1.90	81
4	4.01	3.25	81
5	6.35	5.84	92
6	1000	860	86
Average yield ± standard deviation = 85.9 ± 4.8(%)			

Table 3. Analytical Results of two NIST SRM samples by INAA and RNAA

SRM	Concentration of Th, ppm		
	INAA	RNAA	Certified value
Pine Needle	0.035 ± 0.003	0.030 ± 0.001	0.037 ± 0.003
Oyster Tissue	0.041 ± 0.001	0.039 ± 0.001	(0.04)

( ) value is recommand value

Table 4. Reduction percent of interfering elements before and after Radiochemical Separation

Element (ppm)	NIST SRM Pine Needle		NIST SRM Oyster Tissue		Reduction %
	before	after	before	after	
Ce	0.211	0.0923	0.350	0.096	64.4
Co	0.122	0.0314	0.537	0.0639	81.2
Cr	2.36	0.143	1.34	0.287	86.3
Fe	179	19	518	10	93.7
Hf	0.0259	0.0114	0.0356	0.0249	43.0
Sc	0.0371	0.0101	0.0549	0.0079	79.2
Zn	69.8	0.22	796	0.20	99.8

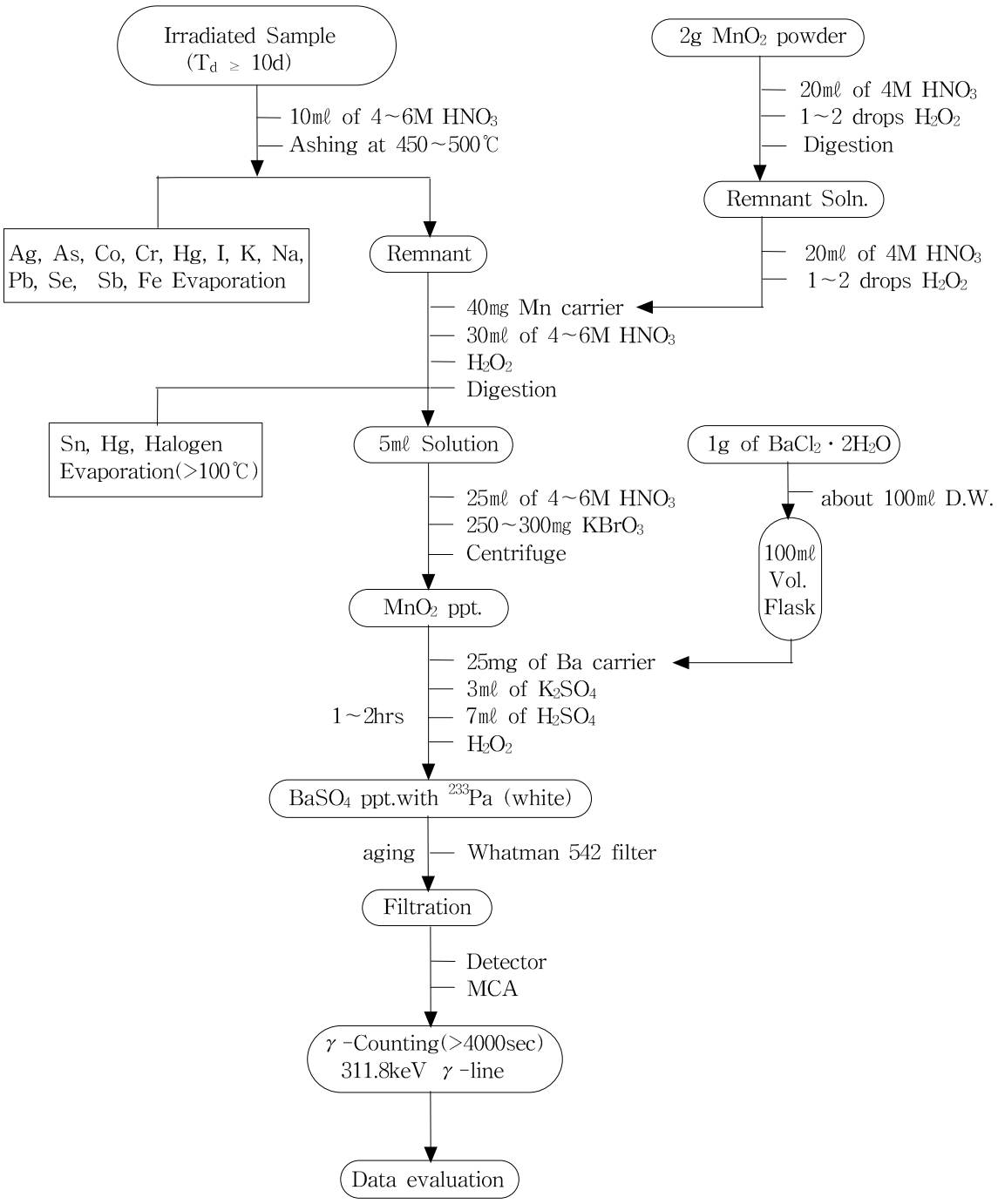

Figure 1. Radiochemical separation scheme for the determination of Th(^{233}Pa)

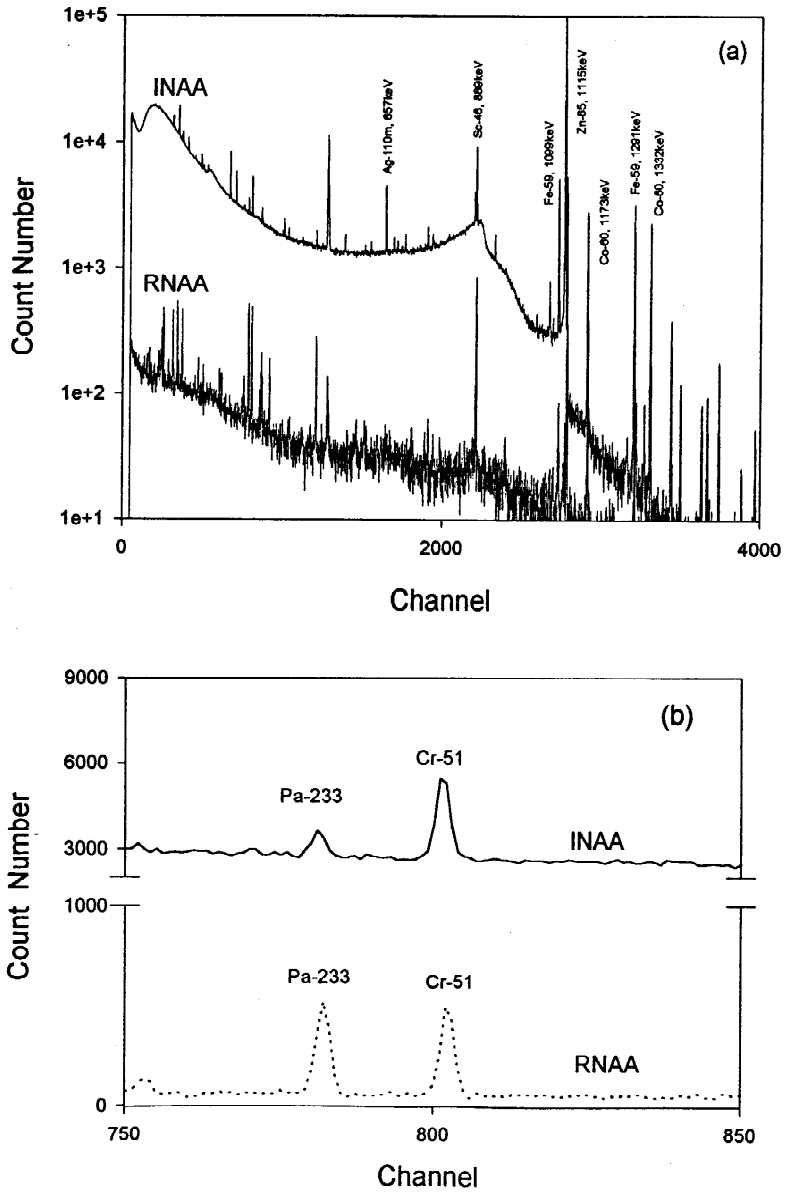

Figure 2. Gamma-ray spectrun of INAA and RNAA (a) 0 - 4000 channel (b) focused on Pa-233