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Evaluation of Daily Intake of ^{238}U and ^{232}Th in a Korean Mixed Diet Sample Using RNAA

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Abstract

To estimate the degree of intake of ^{238}U and ^{232}Th through daily diet, a Korean mixed diet sample was prepared after the investigation of the amount of consumption of the daily diet which corresponds to the age of 20 to 60 years. For the analysis of U and Th, the RNAA method was applied. Two standard reference materials were used for quality control and assurance and the analytical results were compared with a certified value. The determination of U and Th in the Korean mixed diet sample was carried out under the same analytical conditions and procedures with SRM. It is found that the concentration of U and Th in a Korean mixed diet was about 35.4 ppb and 3.4 ppb. From these results, the daily intake of ^{238}U and ^{232}Th by diet is evaluated to be 6.98 and 0.67 μg per day, respectively. Radioactivities related to the intake of ^{238}U and ^{232}Th were estimated to be about 86 mBq and 2.7 mBq per person per day and the annual dose equivalents from ^{238}U and ^{232}Th revealed as 3.18 μSv and 0.29 μSv per person, respectively.

Key Words : uranium, thorium, RNAA, daily intake, annual dose equivalent

1. Introduction

^{238}U and ^{232}Th are radioactive nuclides which incur internal doses by inhalation of airborne particulate matter and the intake of daily diet and industrial activities. Therfore, prior to metabolism research of Uranium(U) and Thorium(Th), it is necessary to apply an accurate and precise analytical method for U and Th, and it is also important to assess radiation doses from this natural source for human health. In this viewpoint, many studies have been reported.[1-6]

Even though there are several sensitive analytical techniques for U and Th such as isotope-dilution

mass spectrometry, neutron-induced track counting or induced coupled plasma-mass spectrometry, it was known that Radiochemical Neutron Activation Analysis(RNAA) possesses the considerable advantage of being blank-free [7]. The aim of this study is to apply RNAA for the determination of U and Th in the Korean mixed diet sample based on the food daily data for 77 Korean adults of 20 to 60 years and to evaluate the daily intake level of ^{238}U and ^{232}Th. The average amount of daily food consumption of Koreans can be estimated from the diet data.

In this study, it was intended to estimate the daily intake level of ^{238}U and ^{232}Th and to assess the annual dose equivalent from the concentrations of U and Th in a Korean mixed diet sample.

2. Experimental

2.1. Sample Collection

The criteria for the collection of a Korean mixed diet sample based on ICRP(International Commission on Radiation Protection) recommendations are defined as follows : i) Adults more than 100 persons which corresponds to the age of 20 to 60 years living in Korea, ii) Report of the whole diet which a person intakes on the food chart, iii) Reject insufficient reports from statistical data. Based on the above criteria, food consumption reports of 120 persons including personal cards and check lists of food intake were collected from April to October 1996. 77 reports were then selected and statistically treated, and 71 species of food were then purchased in a market of Seoul, pretreated and stored in polyethylene containers.

2.2. Preparation and Irradiation of the Sample

To prepare the Korean mixed diet for the analysis of U and Th, the diet samples were pretreated with the following procedures : the diet samples were mixed with a blender for homogenization and freeze dried for 30 hours at -80℃. After freeze-drying, the weight of total diet sample reduced from 1120.0 g to 130.2 g. The freeze dried sample was finely ground with an agate mortar. The diet sample was put in a polyethylene capsule washed with 1N HNO_3 for neutron irradiation. Standard reference materials(NIST SRM 1575 Pine Needle, 1566a Oyster Tissue) for quality control were prepared with the same methods after drying for 2 hrs at 80 ℃ in accordance with the recommended procedures of the NIST certificate.

The prepared diet sample was irradiated for 4 hours using the pneumatic transfer system of the HANARO research reactor($\phi_{th} = 1.7 \times 10^{13}$ n/cm^2 sec). Standard reference materials were also irradiated in the same condition.

2.3. Measurement of Radioactivity

2.3.1. Analysis of Uranium

Irradiated mixed diet samples and standard reference material(NIST SRM 1566a, Oyster Tissue) were allowed to cool for more than 3 days. The isotopic sample(0.5 ml of ^{237}Np solution [0.1μ Ci/50ml, Isotope Products Laboratories]) was irradiated for 15 min. to produce appropriate activity of ^{238}Np ($T_{1/2}$ = 50.8 hr, E_γ = 984 keV). The absolute activity of ^{238}Np is not required, because the chemical yield measurement is based on the relative measurements of ^{238}Np in an unprocessed aliquot(as standard) and the sample fraction separated according to the RNAA procedure. Uranium was determined by using the nuclear reaction of

$$^{238}U\ (n,\gamma)\ ^{239}U \xrightarrow{\beta^-} {}^{239}Np$$
$$(T_{1/2} = 2.36\ day,\ E_\gamma = 277.6\ keV)$$

All samples were analyzed by estimating the activity of ^{239}Np. For the γ-ray measurement of ^{239}Np, ^{238}Np and other nuclides, HP-Ge semiconductor detector(EG & G ORTEC, GEM-25185, 1.85 keV resolution at 1332 keV of ^{60}Co, Peak to Compton ratio 45 : 1) and 8K multichannel analyzer(MCB 919, EG & G ORTEC) were used.

2.3.2. Analysis of Thorium

The irradiated mixed diet sample and standard reference material(NIST SRM 1575, Pine Needle) were allowed to cool for more than 10 days to reduce the interfering activities of medium-lived nuclides(^{24}Na, ^{82}Br etc). Thorium was determined by using the nuclear reaction of

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

All samples were analyzed by estimating the activity of ^{233}Pa under the same detecting system.

2.5. Radiochemical Separation of U and Th

The integrated RNAA method using an anion exchange resin (Dowex 1×8, Cl^- form 100-200 mesh) precipitation method were applied for the analysis of Uranium.[5] The stepwise separation procedures of U(^{239}Np) are as follows : before sample digestion, an aliqout of $^{237+238}Np$ solution was added and then the samples were digested in concentrated HNO_3. This digested solution was almost evaporated to dryness and 25 ml of 9M HCl was added. 0.5 g of hydroxyl amine hydrochloride was added and the sample was warmed gently for 10 minutes to convert Np to Np^{4+}. The ion exchange column was then prepared, the digested solution of sample was loaded, and Np was eluted from the column with 60 ml of 1M HCl. The volume of 60 ml was evaporated to about 5 ml. 7 ml of H_2SO_4 and about 100 mg of K_2SO_4 were added. After the solution was warmed gently, 40 mg of Ba carrier was added dropwise and this formed a $BaSO_4$ precipitate. This precipitate was filtered using a filterpaper(whatman 542) and gamma-ray activity of ^{239}Np was finally measured.

For analysis of Thorium, the well established RNAA method was applied.[4] The separation procedure of Th(^{233}Pa) is as follows : the samples were digested in concentrated HNO_3. 40 mg of Mn carrier was added and the solution was heated to dryness. 25ml of 4M HNO_3 was added and the sample was warmed gently. The MnO_2 precipitate was then centrifuged and the supernatant was discarded. After this precipitate was dissolved by the addition of a few drops of H_2O_2, 7 ml of H_2SO_4 was added and also about 100 mg of K_2SO_4 was added. And then the soultion was warmed gently, 40 mg of Ba carrier($BaCl_2$) was added dropwise and obtained a $BaSO_4$ precipitate. The $BaSO_4$ precipitate was dissolved again. This solution was cooled and then 40-50 ml of water was added with constant stirring to obtain the $BaSO_4$ precipitate again. This precipitate was filtered using a filterpaper(whatman 542) and counted for a 312 keV γ-ray peak of ^{233}Pa.

3. Results and Discussion

From the results of the food chart, the average amount of daily food consumption in Korean was estimated to be ~1700 g per day. Table 1 shows the average consumption frequency of different food items for a day. Among 77 species of food as

Table 1. Average Consumption Frequency of Different Food Items for a One Day Representative Mixed Diet of Adult Koreans and the Weight of Each Item to Prepare One Day of a Korean's Representative Total Diet

	50's	40's	30's	20's	overall
boiled rice	2.33	2.48	2.14	1.76	2.18 X 210g = 457.8g
kimch'i	2.20	2.64	2.40	1.81	2.26 X 60g = 135.7g
soybean paste stew	0.26	0.68	0.60	0.27	0.45 X 180g = 81g
kimch'i stew	0.36	0.30	0.31	0.23	0.30 X 180g = 54g
fish stew	0.17	0.27	0.17	0.20	0.20 X 180g = 36g
seaweed soupl	0.21	0.07	0.10	0.12	0.13 X 350g = 45.5g
broth (meat juice)	0.24	0.32	0.29	0.31	0.29 X 350g = 101.5g
bean-sprout soup	0.10	0.20	0.13	0.07	0.13 X 350g = 45.5g
bean curd stew	0.02	0.09	0.08	0.03	0.06 X 180g = 10.8g
lamyeon	0.10	0.11	0.14	0.24	0.15 X 120g = 18g
noodles with bean sauce	0.02	0.05	0.04	0.07	0.05 X 520g = 26g
wheat noodles	0.00	0.02	0.00	0.04	0.02 X 750g = 15g
noodles	0.06	0.07	0.17	0.03	0.08 X 90g = 7.2g
Chinese-style hotchpotch	0.00	0.04	0.01	0.02	0.02 X 790g = 15.8g
meat and Chinese noodles	0.14	0.02	0.01	0.05	0.06 X 200g = 12g
pizza	0.02	0.00	0.00	0.05	0.02 X 200g = 4g
hamburger, sandwiches	0.02	0.00	0.01	0.09	0.03 X 200g = 6g
cake	0.06	0.04	0.02	0.01	0.03 X 100g = 3g
pie	0.00	0.02	0.00	0.02	0.01 X 100g = 1g
doughnut	0.04	0.02	0.01	0.01	0.02 X 100g = 2g
table bread	0.00	0.09	0.05	0.09	0.06 X 100g = 6g
cabbage	0.00	0.02	0.01	0.12	0.04 X 70g = 2.8g
radish	0.18	0.09	0.24	0.20	0.18 X 70g = 12.6g
Welsh onion	0.04	0.05	0.10	0.05	0.06 X 20g = 1.2g
mushroom	0.06	0.07	0.01	0.09	0.06 X 70g = 4.2g
bean sprouts	0.08	0.09	0.14	0.13	0.11 X 70g = 7.7g
lettuce	0.04	0.07	0.14	0.09	0.09 X 40g = 3.6g
garlic	0.04	0.04	0.04	0.04	0.04 X 10g = 0.4g
red pepper	0.02	0.09	0.08	0.06	0.06 X 20g = 1.2g
cucumber	0.04	0.09	0.06	0.16	0.09 X 70g = 6.3g
sesame leaf	0.12	0.00	0.07	0.06	0.06 X 20g = 1.2g
spinach	0.10	0.21	0.13	0.09	0.13 X 70g = 9.1g
carrot	0.10	0.00	0.01	0.07	0.05 X 70g = 3.5g
onion	0.02	0.00	0.01	0.07	0.03 X 40g = 1.2g
pumpkin	0.02	0.04	0.01	0.02	0.02 X 70g = 1.4g
broad bellflower	0.16	0.00	0.02	0.05	0.06 X 70g = 4.2g

(Continued)

Table 1. Average Consumption Frequency of Different Food Items for a One Day Representative Mixed Diet of Adult Koreans and the Weight of Each Item to Prepare One Day of a Korean' s Representative Total Diet

	50' s	40' s	30' s	20' s	overall
bean curd	0.31	0.86	0.46	0.37	0.50 X 80g = 40g
beef	0.43	0.52	0.19	0.11	0.31 X 60g = 18.6g
pork	0.20	0.38	0.44	0.37	0.35 X 60g = 21g
chicken	0.04	0.11	0.19	0.08	0.13 X 60g = 7.8g
* egg	0.30	0.38	0.71	0.49	0.47 X 50g = 23.5g
tuna	0.06	0.00	0.07	0.04	0.04 X 70g = 2.8g
mackerel	0.18	0.30	0.18	0.07	0.18 X 70g = 12.6g
anchovy	0.18	0.27	0.12	0.06	0.16 X 13g = 2.1g
cuttlefish	0.04	0.02	0.06	0.16	0.07 X 70g = 4.9g
walleye pollack	0.08	0.00	0.04	0.08	0.05 X 70g = 3.5g
mackerel pike	0.00	0.04	0.00	0.01	0.01 X 70g = 0.7g
shellfish	0.04	0.07	0.00	0.02	0.03 X 30g = 0.9g
fish ball	0.00	0.02	0.12	0.05	0.05 X 50g = 2.5g
laver	0.71	0.95	0.74	0.42	0.71 X 3g = 2.1g
brown seaweed	0.06	0.20	0.08	0.05	0.10 X 70g = 7g
green layer	0.02	0.04	0.00	0.04	0.03 X 70g = 2.1g
** milk	48.98	140.18	20.24	96.19	76.40
icecream	0.00	0.00	0.04	0.09	0.03 X 100g = 3g
yogurt	0.33	0.34	0.15	0.26	0.27 X 180g = 48.6g
apple	0.71	0.59	0.58	0.23	0.53 X 100g = 53g
persimmon	0.51	0.30	0.10	0.09	0.25 X 100g = 25g
orange	0.06	0.39	0.29	0.20	0.24 X 100g = 24g
pear	0.06	0.05	0.10	0.05	0.07 X 100g = 7g
** beer	3.06	2.68	89.29	82.16	44.30
** distilled spirits	21.43	13.39	63.93	31.49	32.56
** raw rice wine	0.00	0.00	0.00	4.86	1.22
** refined rice wine	6.12	0.00	4.76	0.86	2.94
** coffee	29	50	48	77	51
** coke	6	10.5	16.5	39	18
** soft drink	3	3	3	7.5	4.5
** sweat rice drink	6	3	0	1.5	3
** orange juice	0	10.5	22.5	10.5	10.5
** adlay tea	2	0	0	2	1
** green tea	4	4	8	3	5
** tea	0	0	1	3	1

* Number

** Volume in ml

Table 2. Analytical Results of U and Th in Standard Reference Material and the Mixed Diet Sample by RNAA

	Sample	SRM Oyster Tissue (Certified value : 132 ± 12 ppb)			Mixed Diet Sample		
	Run No.	1	2	3	1	2	3
U	Analytical value (ppb)	114	113	112	39.1	37.8	29.2
	Counting error (%)	8.7	13.3	2.0	9.0	10	4.4
	Mean ± SD	113 ± 1 ppb			35.4 ± 4.4 ppb		
	Sample	SRM Pine Needle (Certified Value : 37 ± 8 ppb)			Mixed Diet Sample		
	Run No.	1	2		1	2	
Th	Analytical Value(ppb)	33	37		3.2	3.6	
	Counting error (%)	1.5	1.8		3.1	2.8	
	Mean ± SD	35 ± 3 ppb			3.4 ± 0.2 ppb		

shown in Table 1, the major food items in the Korean diet are boiled rice(27%), kimchi(8%), soybean paste stew, fish stew, bean curd etc.

The concentration of U in Oyster Tissue(NIST SRM 1633a) and the concentration of Th in Pine Nneedle(NIST SRM 1575) were respectively determined to check the accuracy and precision of the RNAA method. The mean value of U was 113 ± 1 ppb and the relative error was 15%. The mean value of Th was 35 ± 3 ppb and the relative error was 5%. The analytical results of standard reference materials and the mixed diet sample are presented in Table 2. If the uncertainty of the certified values and the counting error are taken into account, our analytical values are reasonable. Figure 1 shows the gamma-ray spectrum of ^{239}Np for U analysis in Oyster Tissue and the ^{238}Np standard solution for chemical yield calculation. Figure 2 shows the gamma-ray spectrum of ^{233}Pa for Th analysis in SRM Pine Needle.

The mean value of U and Th in the Korean mixed diet sample were 35.4 ± 4.4 and 3.4 ± 0.2 ppb, respectively. Figure 3 shows the gamma-ray spectra of ^{239}Np and ^{233}Pa for the analysis of U and Th in the Korean mixed diet sample. If the average amount of daily food consumption is 1700 g, the amount of ^{238}U and ^{232}Th intake by daily diet are estimated to be 6.98 and 0.67 μg per person per day, respectively. The amount of daily intake of ^{238}U for Korean was much higher than that of Japanese[8] and the amount of daily intake of ^{232}Th was not much different. K. Shiraishi and M. Yamamoto [9] was reported that fruits, vegetables, potatoes, beans, animal and fish products were the major contributor to dietary ^{238}U and ^{232}Th intakes for Japanese. Assuming that Korean have similiar diet habbits to the Japanese, the major contributor of ^{238}U and ^{232}Th intakes might be rice, vegetables and beans etc. More studies to obtain accurate information will be required for each food item.

Converting the intake amount of ^{238}U and ^{232}Th into radioactivity, these values are about 87 mBq per person per day for ^{238}U, and 2.7 mBq per person per day for ^{232}Th. Applying the dose

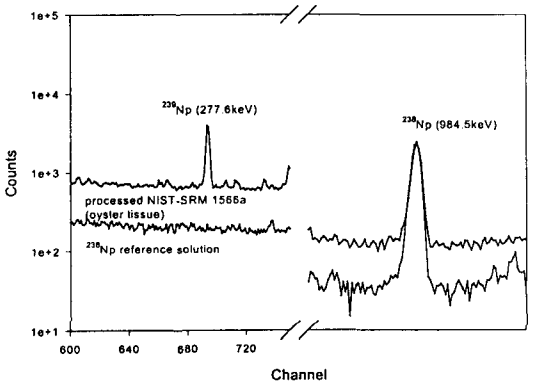

Fig. 1. Gamma-Ray Spectra of U Analysis in SRM Oyster Tissue and ^{238}Np Standard

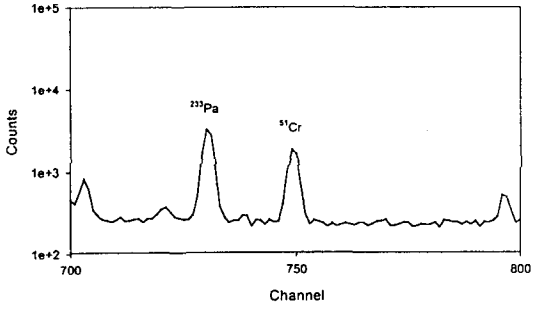

Fig. 2. Gamma-Ray Spectrum of Th Analysis in SRM Pine Needle

equivalent values of ICRP [10] which are 1.0×10^{-7} Sv/Bq for ^{238}U and 3.0×10^{-7} Sv/Bq for ^{232}Th, the annual dose equivalents by ^{238}U and ^{232}Th in daily diet are about 3.18 μSv and 0.29 μSv per person, respectively.

4. Conclusions

For the trace analysis of U and Th in a Korean mixed diet sample, RNAA was applied and the analytical results were reliable. The daily intake level of ^{238}U and ^{232}Th was evaluated by measured concentrations of U and Th. The intake level of ^{238}U by daily diet was much higher than other reported values and ^{232}Th was not much different.

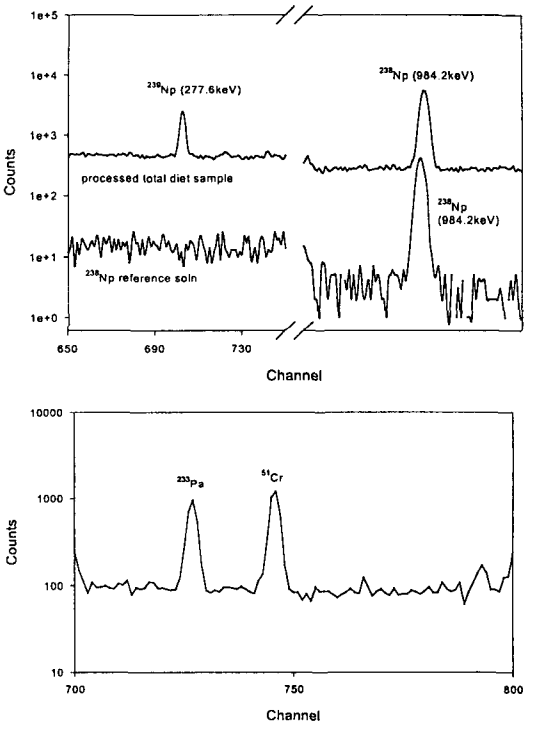

Fig. 3. Gamma-Ray Spectra of U and Th Analysis in a Korean Mixed Diet

It is necessary to carry out independent analysis for various food items to scrutinize the major contributor of U and Th.

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References

1. G. S. Hewson and J. J. Fardy "Thorium Metabolism and Bioassay of Mineral Sand Workers" Health Physics, Vol. 64(2), 147-156 (1993).
2. M. B. Gavini, F. G. Rocco, S. M. Kim "A New Radiochemical Procedure for Uranium Assay

in Environmental Samples" Jour. of Radioanalytical Chemistry, Vol. 67(2), 437-444 (1981).

3. L. Benedik, A. R. Byrne "Simultaneous Determination of Trace Uranium and Thorium by Radiochemical Neutron Activation Analysis" Jour. of Radioanalytical and Nuclear Chemistry, Articles, Vol. 189(2), 325-331 (1995).
4. H. S. Dang, D. D. Jaiswal, C. M. Sunta and S. D. Soman "A Sensitive Method for the Determination of Th in Body Fluids" Health Physics, Vol 57(3), 393-396 (1989).
5. A. R. Byrne and L. Benedik "Determination of Uranium at Trace Levels by Radiochemical Neutron Activation Analysis Employing Radioisotopic Yield Evaluation" Talanta, Vol. 35(3), 161-166 (1988).
6. Xiaolin Hou et al.,"A Study of Six elements daily Dietary Intake of Chinese People", Jour. of Radioanalytical and Nuclear Chemistry, Vol. 222(1-2), 165-170 (1997).
7. Zeev B. Alfassi, Activation Analysis Vol I, 62-91, CRC (1993).
8. Kunio Shiraishi, Yasuhito Igrashi, Yuichi Takaku et al. "Daily Intakes of ^{232}Th and ^{238}U in Japanese Males" Health Physics, Vol. 63(2), 187-191 (1992).
9. K. Shiraishi, M. Yamamoto. "Dietary ^{232}Th and ^{238}U Intakes for Japanese as Obtained in a Market Basket Study and contributions of Imported Foods to Internal Doses" Jour. of Radioanalytical and Nuclear Chemistry, Articles, Vol. 196(1), 89-96 (1995).
10. International Commission on Radiological Protection. ICRP Publication 61, Permagon Press, Oxford (1991).