Comparative Study of the Determination of Natural Radionuclides(^{238}U, ^{232}Th) in Living Processed Products Using ED-XRF and ICP-MS

Hyeon-Woo Lee [a,b], Ji-Young Park [a], Jong-Myoung Lim [a], Mee Jang [a], Hoon Lee [c], and Jin-Hong Lee [b*]
[a]*Nuclear Emergency and Environmental Protection Division, Korea Atomic Energy Research Institute, Daejeon, 34057, Korea*
[b]*Department of Environmental Engineering, ChungNam National University, Daejeon 305-764, Korea*
[c]*Radiation Safety Division, Korea Foundation Of Nuclear Safety, 13493, Gyeonggi-do*
*Corresponding author: jinlee@cnu.ac.kr

1. Introduction

NORM(Naturally Occurring Radioactive Materials) exists throughout environment and It is important that the systematic management of natural radionuclides is required as the "Act on protective action guidelines against radiation in the natural environment" was implemented in 2012.[1-3] Today, a number of eco-friendly and functional health products are produced including advertising effects such as negative ions and far infrared rays. Natural materials such as tourmaline, bentonite and germanium are used that emit anions and far infrared rays, but materials with high radioactivity concentrations that are naturally present such as monazite and zircon are mixed on the manufacturing process. Therefore, in order to ensure the safety of consumers, it is necessary to control the raw materials and manage the products using a rapid and accurate method. In this study, the concentrations of natural radionuclides(^{238}U, ^{232}Th) in living processed products were compared between ED-XRF for the purpose of rapid screening and ICP-MS for the precise analysis.[4,5]

2. Materials and Methods

2.1 Sample selection and pretreatment

In this study, certified reference material (CRM) were used for evaluating the validity for both analytical methods. A total of 49 living processed products including health products, textile products, and minerals were used. All of the samples were ashed at 550 ℃ for 5 hours.

2.2 Experimental method

For the ED-XRF determination, then, the dried sample was transferred to the cylindrical plastic sample cup (Φ 32 mm) with mylar film attached in a clean hood. Three duplicated samples were measured using ED-XRF (Xepos HE, SPECTRO, Germany) in the presence of He gas for about 30 minutes. Then, the same samples were measured by ICP-MS (iCAP-RQ, Thermo fisher scientific) after Alkali-fusion and pretreatment.[6] Fig. 1 shows the pretreatment conditions and analysis process. For alkali-fusion, an automatic fusion device(K2 prime, Katanax^{TM}, Canada) was used and after fusion, the complex medium was simplified using the Fe (Ⅲ) hydroxide co-precipitation method. Finally, the sample was diluted 100 to 1,000 times with 2 % HNO_3 and spiked with ^{187}Re as internal standard.

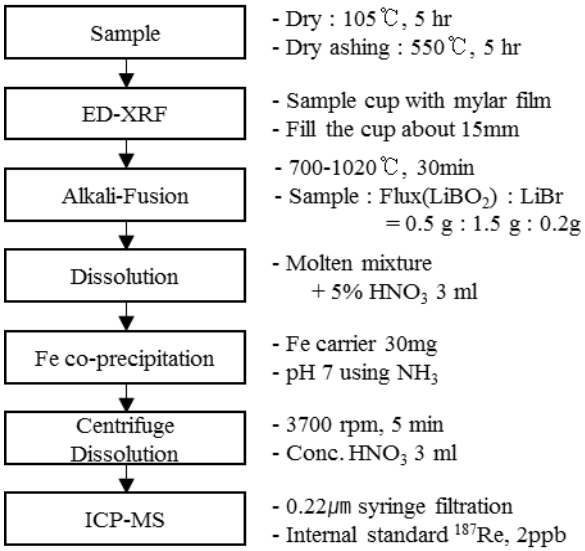

Fig. 1. Schematic analysis method of NORM samples

3. Results

3.1. Method validation of ED-XRF and ICP-MS

Table 1 shows the certified concentration (^{238}U, ^{232}Th) of the CRMs and the analysis result of ED-XRF and ICP-MS concentration. The α-spectrometer values were added as the control group. U-test can be used as a statistical index to evaluate analytical results, and there is no systematic bias of analysis values when U-score is less than 1.64. U-score except for SRM 1633c and 694 were less than 1.64, so it can be judged that the results are statistically reliable. Also, ED-XRF and ICP-MS values maintained a relatively linear relationship. Thus, one may conclude that ED-XRF is suitable for application of rapid screening purpose.

Table 1 : Accuracy and precision of ED-XRF, ICP-MS and α-spectrometer measurement with various certified reference materials

CRM	Element	Certified value(mg/kg)	Experimental result(mg/kg)					
			ED-XRF		ICP-MS		α-spectrometer	
		Mean ± unc.[a]	Mean ± SD (1s)	U-score	Mean ± SD (1s)	U-score	Mean ± SD (1s)	U-score
SRM 2709a	Th[b]	10.9 ± 0.2	10.67 ± 0.31	0.4	11.08 ± 0.68	0.1	10.01 ± 0.49	0.9
San Joaquin Soil	U[b]	3.15 ± 0.05	3.53 ± 0.21	0.9	3.38 ± 0.14	0.8	3.35 ± 0.29	0.4
SRM 1646a	Th[b]	5.8	5.53 ± 0.31	-	5.68 ± 0.12	-	5.14 ± 0.34	-
Estuarine Sediment	U[b]	2.0	1.60 ± 0.10	-	2.05 ± 0.03	-	1.93 ± 0.09	-
SRM 1633c	Th	23.0 ± 0.4	19.97 ± 0.06	7.3	23.64 ± 0.29	0.9	21.25 ± 1.47	0.6
Trace Elements in Coal Fly Ash	U	9.25 ± 0.45	11.47 ± 0.91	1.2	8.73 ± 0.31	0.7	10.62 ± 0.51	1.2
SRM 694	-							
Western Phosphate Rock	U	141.4 ± 0.6	119.93 ± 1.67	6.3	154.28 ± 1.81	3.5	143.96 ± 6.56	0.2
SRM 600	Th[c]	120.9 ± 4.4	126.83 ± 0.78	1.3	124.90 ± 1.27	0.8	113.21 ± 12.27	0.3
Bauxite (Austrrailian-Darling Range)	U[c]	10.0 ± 0.3	9.40 ± 0.26	1.1	9.60 ± 0.23	0.8	10.67 ± 0.82	0.4
BCS 388	Th	158.6 ± 20.0	151.00 ± 1.04	0.4	188.64 ± 1.78	1.5	149.89 ± 17.04	0.2
Zircon	U	288.3 ± 40.0	266.13 ± 1.54	0.6	298.98 ± 22.84	0.2	239.94 ± 43.07	0.5

a Expanded uncertainty with the coverage factor of 2(approximately 95% confidence)
b Reference/information value
c ICP-MS result in our work

3.2 Analytical results for living processed products

Fig. 2 shows the distribution of radioactivity concentration in the living processed products, and the linear relationship close to 1.0 was observed except for 2 of the 49 samples used ED-XRF and ICP-MS. However, it was observed that the concentrations using ICP-MS were 2.5 times higher than those using ED-XRF results in two samples (e.g., mineral bracelet and necklace). It was suspected that the matrix effect for the ED-XRF measurement could affect analytical accuracy. And these mineral bracelet and necklace samples also showed very high radio-activity (e.g., 14 $Bq \cdot g^{-1}$ for ^{232}Th, 1.8 $Bq \cdot g^{-1}$for ^{238}U) and this values are about 10 times higher than the criteria values defined in the Act on protective action guidelines against radiation in the natural environment.

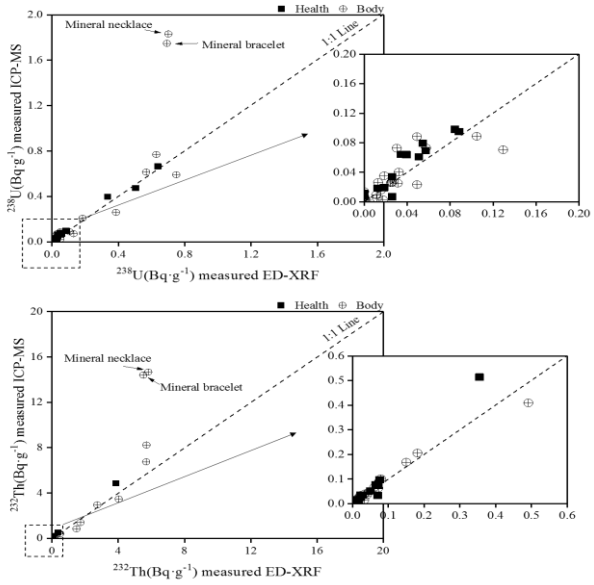

Fig. 2. Analytical results of ^{238}U, ^{232}Th in living processed products using ED-XRF and ICP-MS

4. Conclusions

In this study, the concentrations of natural radio-nuclides (e.g., ^{238}U and ^{232}Th) in living processed products were analyzed using ED-XRF for the purpose of rapid screening and ICP-MS for precise analysis. To validate of both analytical methods, six CRMs such as soil, rock, ash, phosphate ore, bauxite, and zircon were analyzed. Based on CRM analysis, 49 kinds of living processed products were analyzed. When analyzing ED-XRF and ICP-MS, a good linear relationship was observed excluding 2 out of 49 samples. Thus one may conclude that the application of ED-XRF for the rapid screening is possible with accurate determination using ICP-MS.

REFERENCES

[1] International Commission on Radiological Protection. 'The 2007 Recommendations of the International Commission on Radiological Protection', ICRP Publication 103, 2007.
[2] International Atomic Energy Agency, 'Extent of Environmental Contamination by naturally occurring radioactive material (NORM) and technological options for mitigation', Tech report 419, 2003.
[3] A. S. Paschoa, "Potential environmental and regulatory implications of naturally occurring radioactive materials (NORM)", Applied Radiation and Isotopes, 1998 March; 49(3):189-196.
[4] F.S. Al-Saleh and G.A. Al-Harshan, "Measurements of radiation level in petroleum products and wastes in Riyadh City Refinery", Journal of Environmetal Radioactivity, 2008 July; 99:1026-1031.
[5] N. M. Hassan, T. Ishikawa, M. Hosoda, A. Sorimachi, S. Tokonami, Ma. Fukushi and S. K. Sahoo, "Assessment of the natural radioactivity using two

techniques for the measurement of radionuclide concentration in building materials used in Japan", Journal of Radioanalytical and Nuclear Chemistry, 2009 June; 283:15-21.
[6] J. Mantero, M. Lehritane, S. Hurtado and R. Garcı´a-Tenorio, "Radioanalytical determination of actinoids in refractory matrices by alkali fusion", Journal of Radioanalytical and Nuclear Chemistry, 2010 November; 286(2):557-563.