

Establishment of a Special Nuclear Materials Analysis Center in ROK for National Safeguards Regulation

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Abstract

Special nuclear material (SNM) is defined as material subjected to International Atomic Energy Agency (IAEA) safeguards. The ROK is obligated to control domestic SNMs based on the state's system of accounting for and control nuclear material (SSAC). In addition, the demand for the independent nuclear material analysis and verification capabilities of regulatory expert organizations is increasing, due to the demand for strong safeguards for nuclear facilities enhanced State-Level Approach (SLA).

The determination of uranium (U) isotopic analysis is of particular significance in connection with environmental monitoring and verification of nuclear activities in facilities for specific safeguards-related applications. Declared information on SNMs from bulk handling facilities (BHF) shall be verified in accordance with the Nuclear Safety Act. Since 2018, the Korea Institute of Nuclear Nonproliferation and Control (KINAC) has been conducting a precision analysis to verify the quantity and composition of SNMs.

The composition of SNMs can be verified using destructive analysis methods:

- 1) U isotope analysis using Thermal Ionization Mass Spectrometry (TIMS)
- 2) U/O analysis using Thermal Gravimetric Analysis (TGA)
- 3) U concentration analysis using (Laser Ablation)-Inductively Coupled Plasma-Mass Spectrometry ((LA)-ICP-MS)

Based on the regulatory expert organization's independent ability to nuclear material analysis, regular verification of the analysis results of the collected samples from BHF and information on SNMs reported by the operator is performed.

Currently, it is not being carried out in ROK due to the absence of regulatory and legal binding force for SNMs analysis and evaluation. Therefore, we intend to push ahead the regulation of technical standard guidelines related to nuclear material accounting and control analysis and evaluation through the establishment of a precision analysis system.

Introduction

The International Atomic Energy Agency (IAEA) is calling for the expansion of the capabilities of the State's System of Accounting and Control (SSAC) of nuclear material, in accordance with the recent strengthening of the State-Level Approach (SLA). In addition, verification of the

amount and composition of Special Nuclear Material (SNM) is legally required following the revision of the regulation concerning nuclear material accounting and control (NMAC) in 2014. Accordingly, the Korea Institute of Nuclear Nonproliferation and Control (KINAC) is verifying the declared values of SNM of each nuclear license-holder, using precision destructive analysis.

KINAC has established a precision analysis system to ensure the ability to verify regulators' independent SNM values. To verify the declared values, the U quantity and composition in SNM from nuclear facilities is measured using Thermal Gravimetric Analysis (TGA), Thermal Ionization Mass Spectrometry (TIMS) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) equipment.

This study aims to examine the precise analysis results obtained by the SNM analysis center at KINAC as a regulatory agency in ROK, in accordance with the national safeguards regulation. In addition, in order to expand the utilization of the analysis results of the collected samples from the facilities, we suggest as a future direction for Korea's progress, the revision of regulations related to safeguards, to establish an SNM analysis system.

Materials and Methods

In South Korea, the KEPCO Nuclear Fuel Co. (KNF), a fuel fabrication plant, is a representative bulk handling facility (BHF). KNF has been supplying nuclear fuels to nuclear power plants (NPP) in Korea, both pressurized water reactors (PWRs) and pressurized heavy water reactors (PHWRs).

Currently, KINAC is conducting sample collection and destructive analysis (DA) in a BHF to verify the composition of SNM (UO₂ pellet and powder) in accordance with the Nuclear Safety Act. The results of the analysis of the collected samples are being used to verify the SNM values reported by facility operators.

Table 1 shows the information reported by the facility for the samples collected from KNF.

Table 1. Declared values of the collected samples from KNF

Sample	Physical Form	Declared Value (wt %)	
		U Concentration	Enrichment
1	Pellet	88.145	0.71
2	Powder	84.790	0.71
3	Powder	87.350	0.71
4	Powder	87.277	0.71
5	Pellet	82.510	2.02
6	Pellet	80.800	2.00
7	Pellet	88.148	3.50
8	Powder	87.800	3.63
9	Powder	87.881	4.10
10	Pellet	88.142	4.65

In order to verify the declared values provided by the facility, a precise analysis of SNM (Table 1) was performed using the following analysis equipment [1].

The U/O ratio was investigated by TGA (SETSYS Evolution, SETARAM).



The stoichiometry of the collected SNMs was close to UO_2 . When UO_2 is oxidized, as shown in equation (1), it all becomes U_3O_8 [2]. The O/U ratio in UO_2 is determined by measuring the difference in weight before and after oxidation, using TGA. The U concentration (amount) in UO_2 is a key factor used to calculate the total amount of U in the SNM in the facility. The oxidation curves were obtained under isothermal conditions using TGA. Approximately 1.50 g of sample was prepared in a platinum pan and heated from 25 °C to 900 °C under pure 99.999% argon as a protective gas, and a mixed gas (20% oxygen/80% helium) as a reactive gas atmosphere. The TGA analysis was performed at least twice per sample.

Unlike TGA analysis, which can be used to analyze solid samples (UO_2 pellet and powder) without pre-treatment, a pre-treatment process that involves the dissolution of solid samples is required for ICP-MS and TIMS analysis. The method of dissolving the UO_2 pellet and powder sample is as follows [3]. In consideration of the U content in the sample, aliquot 0.002 g ~ 0.004 g of the sample were placed into a Teflon container with 10 mL of 8 M nitric acid solution. The lid is closed and the container is put on a 180 °C hot plate until the sample dissolves completely. The dissolved samples are prepared for ICP-MS and TIMS analyses to fit within the analysis equipment's acceptable concentration range by diluting with 2 % HNO_3 . All procedures were conducted with highly purified water ($> 18.2 \text{ M}\Omega/\text{cm}$) and ultrapure 60 % nitric acid (Merck).

The U isotope was investigated by TIMS (TRITON Plus, Thermo Fisher Scientific Inc.) [4]. All analyses were performed using rhenium (Re) double filaments. Before use, the filaments were degassed under vacuum conditions ($\sim 2.0 \times 10^{-7}$ mbar) using a degassing instrument following the set procedure and methods. To load the sample, a filament was stored for at least 24 hours after degassing was completed. The 1 μL sample was loaded on the Re filament and all samples were dried. The filament current was then slowly increased until the filament glowed red and the current (2 A) was maintained for 2~3 sec before being slowly being reduced to zero. The analysis was performed using a sequence in which the main isotope (for ^{235}U , ^{238}U) was placed in the faraday cup and the minor isotope (for ^{234}U , ^{236}U) was placed in the ion counter to adjust the detector position so that it could be measured at the same time.

The U enrichment was calculated by ICP-MS (iCAP RQ, Thermo Fisher Scientific Inc.) [5]. The samples dissolved through the pretreatment process were prepared by further dilution using 2 % nitric acid(v/v) so that the U concentration in the final analysis sample did not exceed 25 $\mu\text{g/L}$. To measure the concentration of U-235 and U-238 with ICP-MS, standard solutions of U-235 (IRMM-054) and U-238 (1000 mg/L single stock solution, Sigma Aldrich) were used to determine the calibration curve. Analysis of the SNM samples was performed when the calibration curve results for U-235 and U-238 elements satisfied $R^2 > 0.995$ and $\text{RSD} < 5 \%$.

Results and Discussion

The results obtained through TGA analysis were used to calculate the U/O ratio using the following equation.

$$U/O = \frac{(1-w_u-w_I) \times A_u}{w_u \times A_o}, \text{ (where, } w_u = F_s \left(\frac{m_f - m_i w_f}{m_i} \right) \text{)} \quad (2)$$

where,

m_i = mass of the sample before oxidation

m_f = mass of the sample after oxidation (= $m_{f,measured} - m_{buoyancy}$)

w_u = mass ratio of the sample before oxidation

w_I = mass ratio of impurity before oxidation (nominal value = 0.0002)

w_f = mass ratio of impurity after oxidation (nominal value = 0.000076)

F_s = mass ratio of uranium after oxidation ($F_s = \frac{3A_u}{3A_u + 8A_o}$)

A_o = atomic weight of oxygen (molar mass)

A_u = atomic weight of uranium (molar mass)

If the enrichment is presented as,

$$\text{Isotopic ratio: } A_u = 1 / \sum \frac{w_{U-N}}{A_{U-N}}, \quad \text{Mass ratio (wt\%): } A_u = \sum_N (w_{U-N} \cdot A_{U-N})$$

See table 2 for each U isotope's molar mass (A_{U-N}). U-234 and U-236 are negligible for enriched U samples, so A_U was calculated from isotopes U-235 and U-238.

Table 2. The molar mass of each U isotope

U isotope	U-234	U-235	U-236	U-238
A_{U-N}	234.0409	235.0439	236.0456	238.0508

The U concentration value was calculated by substituting the values obtained from TGA into the above equation, as shown in Table 3 and Figure 1. The measurement results showed an error of up to 0.05% for pellet samples, and 0.2% to 0.8% for powder samples. The relative measurement uncertainty at the 95% confidence level for all measurement results was 0.01%.

In the case of the pellets, it was confirmed that the difference between the analysis result and the declared value remained within the error range results of analysis uncertainty, but for the powder, the error tended to be out of the error range. This is thought to be due to additional oxidation that occurred during the powder storage process, and weight reduction caused by the loss of air in the pores when the powder was sintered during the TGA analysis. However, since the IAEA also showed the same tendency, it will be necessary to determine the cause of error for the UO₂ powder samples.

Table 3. The TGA results of the KNF samples

Sample #	U concentration (wt%)		Relative Uncertainty ($k=2$)
	Declared value	Measured Value	
1	88.145	88.145	0.0113
2	84.790	84.744	0.0118
3	87.350	86.684	0.0115
4	87.277	86.572	0.0127
5	82.510	82.516	0.0194
6	80.800	80.811	0.0136
7	88.148	88.141	0.0125
8	87.800	87.541	0.0126
9	87.881	87.665	0.0125
10	88.142	88.138	0.0125

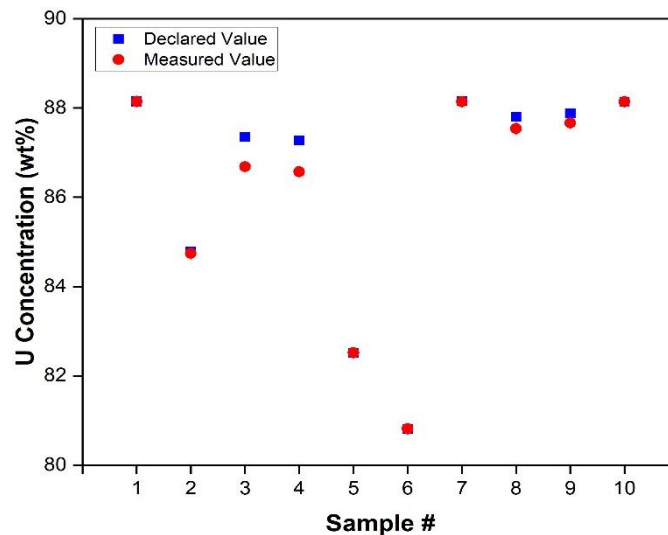


Figure 1. The TGA results of KNF samples

The results of U enrichment obtained using TIMS are shown in Table 4 and Figure 2. As a result of the TIMS analysis, the natural uranium (NU) samples showed a value of 0.71 %, and the low enriched uranium (LEU) samples showed a value of 2.01 % to 4.65 %. The analysis results' relative standard deviation (RSD) was 7.2E-03 % ~ 1.7E-01 %. The TIMS analysis results were similar to the facility's declared value. However, sample # 6 showed a significant difference, as the declared value was 2.0 %, while the TIMS analysis showed that the U enrichment value was 2.6 %.

Since the error range of the $^{235}\text{U}/^{238}\text{U}$ value was managed to within 0.2 % by analyzing the U standard sample (U005A) before analyzing the sample through TIMS, the reason for the difference between the declared value and the analysis result value is considered to be not related to equipment operation. The same sample was cross-analyzed at an institution that operates the TIMS instrument, and they confirmed the results of U enrichment were similar to the values measured by KINAC. These analysis results were reported to the KNF facility and IAEA manager at the

discussion meeting. Using cross-analysis with related institutions operating TIMS in Korea, we intend to continuously conduct verification of U enrichment analysis results.

Table 4. The TIMS results of the KNF samples

Sample #	U enrichment (wt%)		Standard Deviation	Relative Error (%)	Relative Standard Deviation (%)
	Declared value	Measured Value			
1	0.71	0.71	0.0002	0.23	0.024
2	0.71	0.71	0.0006	0.29	0.085
3	0.71	0.71	0.0004	0.35	0.052
4	0.71	0.71	0.0004	0.36	0.057
5	2.02	2.01	0.0025	0.67	0.123
6	2.00	2.60	0.0039	30.16	0.151
7	3.5	3.52	0.0013	0.45	0.038
8	3.63	3.63	0.0027	0.05	0.076
9	4.10	4.10	0.0035	0.16	0.084
10	4.65	4.65	0.0022	0.05	0.048

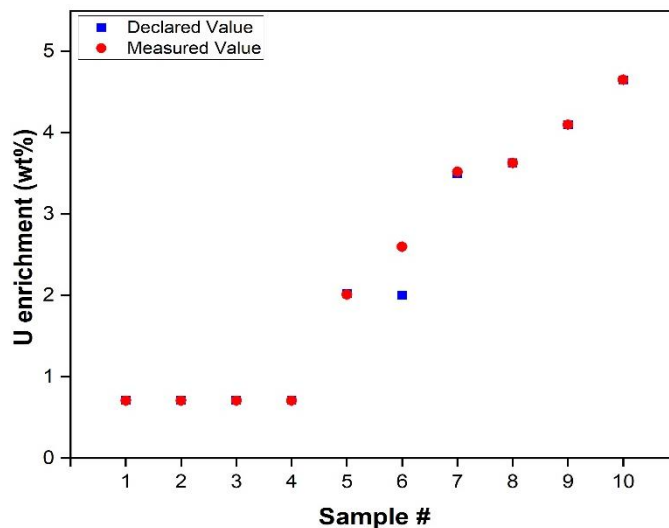


Figure 2. The TIMS results of KNF samples

The U enrichment of the analysis sample was calculated based on the U concentration measured by ICP-MS, and the results are shown in Table 5 and Figure 3. The calibration curve results for U isotopes conducted before the SNM analysis showed that U-235 and U-238 had R^2 values close to 1, and RSD values of 4.628 % and 2.258 %, respectively. It was shown that the conditions for

ICP-MS analysis were satisfied. As a result of the analysis, NU was measured in the range of 0.66 % to 0.67 %, and 1.91 % to 4.71 % for LEU. Compared to the declared value, the results of the ICP-MS analysis conducted by KINAC tended to show a value of enrichment that was lower than the declared value.

In the pre-treatment process, tiny amounts of SNM solid samples are dissolved in acid, and this is expected to have caused an error when measuring the U concentration via ICP-MS, because the U concentration in the aliquot of the sample may not be homogeneous. The relative error in the declared value indicated an analysis accuracy within 8 %, and the RSD had a 1.01 % to 7.85 % value, excluding sample # 6. In the future, to satisfy the relative error and relative standard error, representing the accuracy and precision of the sample analysis at the level of precision analysis, we will conduct continuous analysis to ensure optimal ICP-MS analysis conditions, to achieve an error range within 5 %.

Table 5. The ICP-MS results of the KNF samples

Sample #	U enrichment (wt%)		Relative Error (%)	Relative Standard Deviation (rel. %)
	Declared value	Measured Value		
1	0.71	0.67	-5.77	6.58
2	0.71	0.66	-7.67	7.26
3	0.71	0.66	-6.66	3.47
4	0.71	0.67	-5.55	3.68
5	2.02	1.91	-5.60	1.01
6	2.00	2.41	20.58	5.74
7	3.5	3.45	-1.39	3.39
8	3.63	3.36	-7.37	7.85
9	4.10	3.93	-4.08	4.48
10	4.65	4.71	1.26	6.22

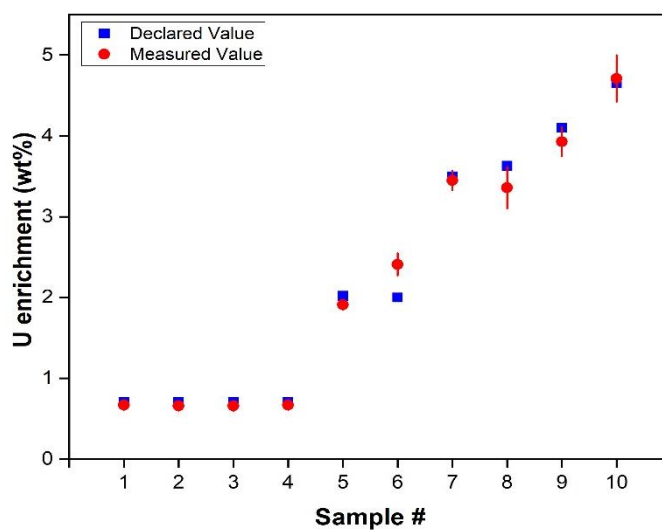


Figure 3. The ICP-MS results of KNF samples

Conclusions

In this study, U concentration and enrichment in SNM (UO₂ pellet and powder) from the KNF facility were analyzed using TGA, ICP-MS, and TIMS, and the results were compared with the declared values. In most cases, the confirmation measurements matched the declared values. In the case of the UO₂ powder, TGA U concentration results were partially different from the declared values. We confirmed that IAEA also observed the same tendency, so we would like to find the cause of the error in the future. The ICP-MS and TIMS results confirmed that the sample #6 result was significantly different from the declared value. A cross-analysis with other institutions confirmed that they were consistent with the results of KINAC. Based on these results, information about the difference between the declared value and the analysis results of the KNF sample were shared at the discussion meeting in which KINAC-KNF-IAEA participated.

Since there is no clear regulation in Korea, we do not require an additional clarification or correction by the facility for differences observed between the declared value and the analysis result; currently only the singularity of the analysis results is shared.

Therefore, we would like to revise the regulation to address discrepancies in the results of the DA of national inspection samples in the national inspection finding report list. Since this could involve a long time, depending on when DA analysis was performed after sampling, sufficient consultation with the KNF manager will be needed if the regulation is revised. But, this revision is expected to contribute to the spread of IAEA performance by expanding the usability of the analysis results conducted by KINAC.

References

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