A Comparative Study on Age Determination of Uranium Oxides by Different Chemical Separation Methodologies Based on TEVA and UTEVA

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1. Introduction

Various radiochronology methods have been being developed in many laboratories by determining the disequilibrium in uranium series radionuclides to estimate the production date of uranium materials for nuclear forensic purposes. $^{230}Th/^{234}U$ is one of the most commonly used isotope pair due to the relatively rapid ingrowth of ^{230}Th and availability of tracer and spike.

The analytical procedures described here include both chemical procedures and mass spectrometry analyses for $^{230}Th/^{234}U$ age-determination of uranium oxide samples. In the chemical procedures, dissolution of uranium oxide samples, preparation of a stock solution, sample dilution, spiking of separate aliquots for IDMS of uranium and thorium, chemical separation of thorium isotopes with two different methods (TEVA and UTEVA resin) for MC-ICP-MS are compared. In mass spectrometry analysis, detailed uranium and thorium isotopic analyses based on MC-ICP-MS (Neptune Plus, Thermo Scientific, Germany), calculation, data analysis and evaluation are presented.

2. Experimental

2.1 Analytical Procedure

Overall analytical procedures are shown in Figure 1. The sample of uranium oxides was transferred to a PFA vial. 8 M nitric acid was added and the sample was heated on hot plate at 80 ℃ until it is completely dissolved. The sample solution was completely dried at 140 ℃ under reduced pressure. Approximately 500 ppm of uranium solution was prepared by adding 2 M nitric acid. For the IDMS of Th isotopes, portion (0.2 mL) of 500 ppm uranium solution was taken and spiked with ^{232}Th. Thorium isotopes were separated by TEVA or UTEVA. For chemical separation with TEVA resin, 0.8 mL of 0.02 M HF/0.02 M HNO_3 solution was used as an eluting solution for thorium isotopes and 0.2 mL of 5% nitric acid added to be 1 mL of final volume for mass spectrometry analysis. For the chemical separation with UTEVA resin, we used UTEVA resin (100-150 mesh, Eichrom) 1 mL and 5 M HCl as thorium eluent solution. One step was added for purification of thorium in separated samples. No chemical separation was applied for the IDMS of uranium isotopes. 500 ppm of uranium solution was diluted with Milli-Q water to make 100~150 ppt of sample solution and spiked with ^{233}U. The mass spectrometric analyses of thorium and uranium isotopes were then performed with simultaneous methods using MC-ICP-MS.

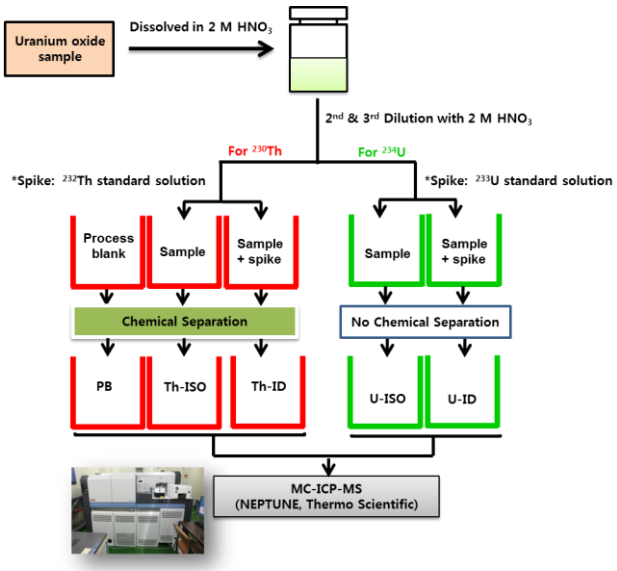

***Figure 1** Analytical procedure for uranium age-dating by determining $^{230}Th/^{234}U$ isotopic ratios*

2.2 Instrumentation

Isotopic measurements of uranium and thorium isotopes were performed using MC-ICP-MS (Neptune Plus, Thermo Scientific Inc., Germany). The multiple ion counter configurations used for measuring uranium and thorium isotopes in this study are shown in Table 1 and 2, respectively.

The typical operating conditions of MC-ICP-MS and a desolvation system (Aridus II, CETAC, USA) are summarized in Table 2.

Table 1. Cup configuration for the simultaneous measurement of Th isotopes in MC-ICP-MS

Cup	IC#1 (SEM)	IC#5 (CDD)

Th_ISO	^{230}Th	^{232}Th

Cup	IC#1 (SEM)	L4 (Faraday Cup)
Th_ID	^{230}Th	^{232}Th

Table 2. Cup configurations for the simultaneous measurement of U isotopes in MC-ICP-MS

Cup	**IC#4**	**IC#3**	**IC#2**	**IC #1**	**L4**
U_I**SO**	^{233}U	-	^{235}U	^{234}U	^{238}U

Cup	**L1**	**IC#**1	H1	**H2**	H3
U_ID	^{233}U	^{234}U	-	-	^{238}U

Table 3. Optimized operating conditions of MC-ICP-MS and a desolvation system

	Parameter	Setting
MC-ICP-MS	RF power	1200 W
	Colling gas flow rate	15 L/min
	Auxiliary gas flow rate	0.9 L/min
	Mass resolution (ΔM/M)	400
	Number of spectra acquired	10 x 3
Desolvation system	Solution take rate	100 μL/min
	Spray chamber temp.	110 ℃
	Membrane temp.	160 ℃
	Ar flow rate	~ 4.3 L/min
	N_2 flow rate	~ 7 mL/min

3. Results and Discussion

In this study, chemical separation methods using TEVA and UTEVA resin were compared for uranium age-dating. Both methods confirmed that the recovery yield of ^{230}Th from uranium material was more than 95% and ^{232}Th impurities in the process blank were well controlled to 1~2 pg, indicating availability for determining highly accurate isotopic ratios of ^{230}Th/^{234}U and estimating uranium age-dating based on the isotopic ratios. Using the two methods, it was confirmed that the age of uranium samples showed similar values in the error range. In the future, these two methods are expected to be selectively applied to uranium age-dating according to the type of uranium material.

REFERENCES

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