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Anaylsis of ^{99}Tc in radioactive waste by ICP-MS

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1. Introduction

^{99}Tc is one of 14 essential nuclides whose concentrations must be identified in radioactive waste nuclide analysis. ^{99}Tc is a long-lived nuclide ($t_{1/2}$=211,000 y) and emits beta ray, and the radioactive concentration is currently being investigated by measurement using GPC [1].

GPC is an analysis device that measures alpha or beta rays, and a process of separating ^{99}Tc is required to analyze only ^{99}Tc. However, there is a disadvantage in that accuracy is low because other beta nuclides in addition to ^{99}Tc are also measured if accurate separation is not performed [2].

In addition, in order to separate ^{99}Tc from the pretreatment liquid generated after waste pretreatment, the recovery rate of ^{99}Tc must be confirmed by adding a carrier and performing a precipitation process using TPAC (tetraphenyl arsonium chloride) [3]. At this time, there is a possibility of weight loss in the recovery process, and a lot of time is required as precipitation and drying processes are required after separation.

Therefore, in this study, we investigated whether ^{99}Tc could be analyzed and quantified using ICP-MS, which is effective for analyzing long-lived nuclides [4]. In addition, the effect of various interfering nuclides was also evaluated through ICP-MS analysis.

2. Experimental & Method

2.1. Material and chemical reagents

All chemicals used in the experiment were of analytical grade and prepared using deionized water (18.2 MΩ·cm). Re carrier (10 ppm) was used from AccuStandard. ^{99}Tc (377 Bq/mL) was used as CRM, and was used according to the concentration range available for analysis.

For seperation of ^{99}Tc, 65 wt.% Nitrate Acid (HNO_3), 48 wt.% Hydrofluoric acid(HF), 85% Phosphoric acid(H_3PO_4) and 99 wt.% Ammonium chloride(NH_4Cl) were used from Sigma Aldrich.

Each product was used after volume dilution with deionized water according to the concentration required for separation. AG MP-1M Anion Exchange Resin (100-200 mesh size, chloride from) were used as separation resin of ^{99}Tc.

In the case of separating actual radioactive waste, the carriers used were Sr, Fe, Nb, Ni, Ca at a concentration of 10 mg/mL purchased from AccuSatndard, respectively.

In addition, the elements composed of the simulated radioactive waste sample solution are 18 elements excluding carriers, and are shown in Table 1 below.

Table 1. The elements composed of the simulated radioactive waste sample solution containing carrier solution.

Element	Chemical Reagent	Element	Chemical Reagent
Al	$Al(NO_3)_3$•$9H_2O$	Sb	Standard solution
Ca	$CaCO_3$	Ba	
Cr	$Cr(NO_3)_3$•$9H_2O$	Sn	
Cu	$CuCl_2$•$2H_2O$	Ti	
K	KCl	Mo	
Li	LiCl	Zr	
Mg	$Mg(NO_3)_2$•$6H_2O$	Re	
Na	$NaNO_3$	Sr	
Zn	$ZnCl_2$	Fe	
Co	Standard solution	Nb	
Mn		Ni	
Pb		-	-

2.2. Separation of ^{99}Tc

2.2.1. Optimization of Re carrier

Re is used as a carrier for ^{99}Tc separation of anion exchange resin , and the experiment is conducted by adding 7.5 mg according to the current guideline.

In order to simultaneously analyze ^{99}Tc and Re by ICP-MS, ^{99}Tc and Re must coexist within the analyzable concentration range. Currently, since the amount of Re used for separation is greater than ^{99}Tc, it is inconvenient to analyze, respectively. Also, it can contribute to waste reduction by reducing the amount of Re.

Therefore, an experiment was conducted to optimize the minimum amount of Re required for ^{99}Tc separation by adjusting the amount of Re.

First, add 0.1 mL of ^{99}Tc (377 Bq/mL) and 0.25~20 ppb of Re, and add 0.5 M HNO_3 to make-up 8 mL.

Second, Sr, Fe, Nb, Ni, and Ca carriers are added to the prepared solution according to the maximum carrier addition amount for each nuclide to make a simulated solution.

In the final simulated solution, ^{99}Tc and Re are separated by passing solutions of 0.5 M HNO_3, 14% NH_4Cl-4% HF and 0.1 M HNO_3 through an anion exchange resin separation tube according to the separation process. ^{99}Tc eluate was eluted using 5 mL of 10 M HNO_3.

2.2.2. Effect of multi-elements

In the radioactive waste nuclide analysis, there is a simulated radioactive waste solution with interfering nuclides used to check the resolution in the presence of various elements.

Since Mo with m/z=98 and 100 also exists in the dissolved solution, an interfering effect experiment was conducted to confirm the removal of Mo during separation and to confirm the quantitative analysis of ^{99}Tc during ICP-MS analysis.

By adding the optimum amount of Re carrier, 0.1 mL of ^{99}Tc solution, and each carrier solution (except for 0.5 M HNO_3) derived from the experiment in 2.2.1 to the solution containing each element, a simulated solution for interfering nuclide effects is prepared. The separation process was performed as in 2.2.1.

2.3. Analysis of ^{99}Tc and Re by ICP-MS

The ICP-MS was purchased from Thermo Fisher Scientific (iCAP™ 7000 series RQ ICP-MS).

For ICP-MS analysis, all eluates were prepared by diluting 20 times with 0.1 M HNO_3.

Analysis was performed after stabilization and calibration according to the Tutorial, and was analyzed in Standard(STD) mode and Kinetic Energy Discrimination(KED) mode to remove interference.

3. Results & Discussion

3.1. Optimization of Re carrier

After performing the ^{99}Tc separation experiment while varying the Re concentration from 0.25 to 20 ppb, the results of analyzing the concentrations of ^{99}Tc and Re in STD and KED mode by diluting 20 times are shown in Table 2.

Table 2. ICP-MS results of ^{99}Tc and Re in optimization of Re carrier experiment.

^{99}Tc (ppb)	Re (ppb)	STD		KED	
		Tc (ppb)	Re (ppb)	Tc (ppb)	Re (ppb)
0.5953	0.25	0.084	0.355	0.082	0.368
	0.5	0.172	0.605	0.173	0.627
	1	0.182	1.156	0.185	1.166
	2	0.216	1.871	0.213	1.922
	5	0.577	5.489	0.596	5.479
	10	0.601	10.351	0.617	10.295
	15	0.626	15.865	0.634	15.595
	20	0.642	21.510	0.642	21.242

The Re concentration was over-estimated from 0.25 to 5 ppb except for 2 ppb, and it was confirmed that ^{99}Tc was not completely captured in the resin, so that a smaller amount than the amount added was eluted.

In the case of 10 to 20 ppb Re, it was slightly over-estimated compared to the amount of both Re and ^{99}Tc, but when the recovery rate was calculated by correcting the analysis value compared to the amount of ^{99}Tc-Re, as shown in Table 3 When Re 10 ppb, the most optimal amount could be derived.

Table 3. ^{99}Tc-Re recovery rate (%) in effect of optimization of Re carrier experiment (^{99}Tc 0.5953 ppb).

Re (ppb)	STD			KED		
	^{99}Tc	Re	^{99}Tc-Re	^{99}Tc	Re	^{99}Tc-Re
5	96.93	109.78	88.29	100.12	109.58	91.36
10	100.96	103.51	97.53	103.65	102.95	100.68
15	105.16	105.77	99.42	106.50	103.97	102.44
20	108.07	107.55	100.43	107.84	106.21	101.54

When 10 ppb Re was used in the KED mode than in the STD mode, the recovery rate was 100.68%, which was a better fit.

3.2. Effect of multi-elements

After conducting a ^{99}Tc separation experiment in a simulated solution in which 18 multi-elements and 5 carriers coexist, the results of analyzing the concentrations of ^{99}Tc and Re by KED mode by diluting them 20 times are shown in Table 4.

Table 4. ICP-MS (KED mode) results of ^{99}Tc and Re in effect of multi-elements experiment.

Sample	^{99}Tc (ppb)	Re (ppb)	KED	
			^{99}Tc (ppb)	Re (ppb)
1	0.5953	10	0.71	12.01
2		10	0.65	11.09
3		10	0.68	11.63

It was confirmed through triplet experiments, and when the recovery rate was corrected, a value close to 100% was derived as an average 99.24% (Table 5).

Therefore, when using Re 10 ppb, it was confirmed that ^{99}Tc was well separated despite the presence of various elements, and it was confirmed that Tc with m/z=99 could be quantitatively analyzed with high resolution of ICP-MS.

Table 5. ^{99}Tc-Re recovery rate (%) in effect of multi-elements experiment.

Sample	KED		
	^{99}Tc	Re	^{99}Tc-Re

1	119.60	120.05	99.63
2	108.68	110.92	99.96
3	114.06	116.25	98.12

4. Conclusion

In this study, it was confirmed through various experiments whether it is possible to analysis ^{99}Tc in radioactive waste by using ICP-MS.

At this time, the amount of Re is significantly reduced compared to the existing separation method, which is economical by reducing sample usage and waste generation.

Despite the influence of various nuclides present in radioactive waste, it was found that ^{99}Tc was well separated and quantified with excellent resolution in the KED mode of ICP-MS.

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