

A study for quantitative analysis of I-129 in radioactive waste using a high-temperature combustion furnace

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1. Introduction

Radioactive wastes such as concrete and soil are generated during decommissioning, and it is very important to accurately identify the concentration of nuclides such as ¹²⁹I to dispose of them and evaluate the cost of treatment [1]. ¹²⁹I is a nuclide of major interest from a disposal point of view because it has a very long half-life of 1.57×10^7 years.

To determine the radioactivity of ¹²⁹I in solid samples, the alkaline extraction and solvent concentration method have been widely used. However, the method should use many chemical reagents to change the oxidation states of iodine, and therefore, the analytical process becomes complicated [2]. Conversely, the pretreatment technique using the volatilization characteristics of iodine is a method of separate and concentrate ¹²⁹I by absorbing gaseous ¹²⁹I volatilized at a high temperature into a trap solution [3]. It can effectively remove organic matter in the sample and has the advantage of simplifying the matrix by extracting only the pure nuclides to be analyzed. Therefore, it can be measured directly without a separate purification process.

In this study, an experimental recovery evaluation of the method of extracting ¹²⁹I from a sample using a high-temperature combustion furnace was conducted. And the applicability of simultaneous analysis of gaseous nuclides such as ³H and ¹⁴C by optimizing the combustion conditions was checked. Also, the effectiveness of ¹²⁹I concentration measurement using ICP-QMS (quadrupole ICP-MS) was evaluated.

2. Methods and Results

2.1 Combustion conditions optimization

An experiment was conducted to confirm the optimal combustion conditions for extracting ¹²⁹I using Pyrolyser-6 Trio™ Furnace under 6 different combustion conditions. The method validation samples were prepared by putting about 3 g of sea sand on the sample boat, and then spiked with 0.2 g of ¹²⁹I (17.19 Bq g⁻¹). The temperature of the second zone in the furnace tube was raised to 800 °C before start sample burning, and then the sample was put in. As a trap solution, 1.0 M NaOH 20 mL was put in a bubbler and used. After combustion, 8 mL of the trap solution and 12 mL of Gold Star were added to a 20 mL plastic vial to prepare a sample for LSC measurement and then

measured for 30 minutes. To evaluate the recovery, 0.2 g of ¹²⁹I (17.19 Bq g⁻¹) was spiked into a vial same way to prepare a standard sample and measured together.

To effectively extract ¹²⁹I in the sample using the combustion furnace, it is important to inject an appropriate flow and transport it to the trap solution. When comparing the condition 1 (only air) and 2 (air and O₂ at >450 °C), it was confirmed that I₂ was more effectively oxidized to IO₃⁻ and well trapped in the form of I⁻ in Condition 2. The recoveries of the condition 3 and 4, using 7 g of Pt catalyst, were significantly lower than those of the conditions 1 and 2 which the catalyst was not used. Through the memory effect test, loss of ¹²⁹I was ascertained that ¹²⁹I remained in the catalyst. The recovery according to the amount of catalyst was compared. When the catalyst was reduced to 5 g, the recovery significantly increased about 2 times. Finally, the combustion conditions for the extract ¹²⁹I in the solid samples were optimized with condition 5 as showed in the Table I.

Table I: ¹²⁹I recovery according to combustion conditions

Condition	Catalyst	Flow	Time	Recovery (%)	
				Mean	SD
1	-	Only Air	3hr	77	10
2	-	Air → O ₂	3hr	99	10
3	7 g	Only Air	3hr	34	12
4	7 g	Air → O ₂	6hr	24	9
5	5 g	Air → O ₂	6hr	77	9
6	10 g	Air → O ₂	6hr	50	11

Using the Pyrolyser-6 Trio™ Furnace, ³H and ¹⁴C can be analyzed with a recovery of more than 95 % [4]. ³H and ¹⁴C were extracted by applying the combustion conditions optimized in this experiment. ³H and ¹⁴C were separately trapped with 0.01M HNO₃ and Carbosorb® E+, respectively. The average recovery of ³H and ¹⁴C were about 90 % and 101 %, respectively. Since both nuclides were effectively trapped, it was possible to determine the applicability of simultaneous extraction of ³H and ¹⁴C under the combustion conditions of ¹²⁹I.

2.2 Confirmation of catalyst necessity

When a sample containing a lot of organic matter is analyzed with a combustion furnace, a lot of

carbonaceous gas may be generated. In this case, the catalyst may serve as oxidizer to minimize contamination of the trap solution due to incomplete combustion flue gas. The different amount of catalyst was filled for each tube and dried chicken were burned. As the amount of catalyst decreased, the color of the trap solution changed to yellow. When the colored samples were measured by LSC and the SQPE values were compared. As compared with the standard solution, the SQPE values of the samples using 0 g and 3 g of the catalyst dropped significantly, and it was confirmed that there was no difference from 5 g as shown in the Figure 1. When the SQPE value decreases as resulted color quenched in sample, the counting efficiency dramatically decreases. Therefore, it was possible to confirm the necessity of a catalyst when using a combustion furnace.

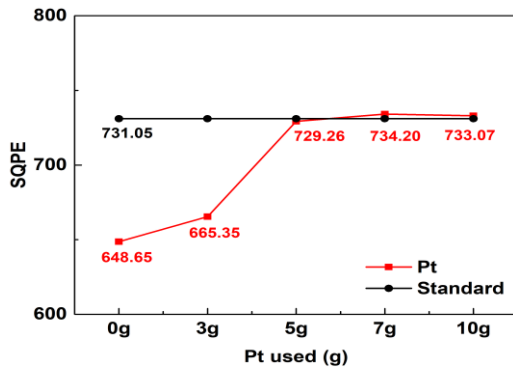


Fig. 1. Quenching effect according to the amount of catalyst

2.3 Availability of nitric acid trap solution

An experiment was conducted to confirm the applicability of 0.01M HNO₃ as a trap solution of ¹²⁹I using the combustion conditions optimized in Table 1. When the 0.01M HNO₃ 20 mL for the ¹²⁹I trap solution was used, it was found that ¹²⁹I was hardly trapped. Addition of 0.1 g of NaHSO₃ as a reducing agent to the same solution led recovery rate up to 85 %. This is because NaHSO₃ oxidizes volatilized I₂ to stable I⁻ and serves to be well trapped in the solution [3]. However, since there is a possibility that the reducing agent used in the trap solution may reduce the intensity during ICP-QMS measurement, the amount was reduced to 0.05 g. As a result, it showed a recovery of 87%. It was confirmed that 0.05 g of a reducing agent can be added to 0.01M HNO₃ as a trap solution of ¹²⁹I.

Table II: Comparison of recovery according to trap solution

Trap solution	Recovery of ¹²⁹ I (%)	
	Mean	SD
0.01M HNO ₃	4	1
0.01M HNO ₃ + NaHSO ₃ 0.1g	85	13
0.01M HNO ₃ + NaHSO ₃ 0.05g	87	14

2.4 Analyzing the ¹²⁹I using ICP-QMS

Finally, the ICP-QMS and LSC measurement for the extracting ¹²⁹I using a tube furnace was compared. 8 mL was measured by LSC, and 1 mL was diluted 10-fold with ultrapure water and measured by ICP-QMS. The analytical results for the same samples were compared in the Table III. When analyzing ¹²⁹I by ICP-QMS, ¹²⁹Xe contained as an impurity in argon gas used for plasma formation affects the background concentration. However, when the blank sample was measured in this experiment, it was at a level of 30 pg g⁻¹, which was determined to be negligible. As presented in Table III, analytical results were in a similar average recovery of about 60 %. Thus, it was confirmed that effective quantitative analysis of ¹²⁹I was possible with ICP-QMS.

Table III: Comparison of LSC and quadrupole ICP-MS in Mini-tube furnace analysis

Sample ID	Recovery of ¹²⁹ I (%)			
	LSC		ICP-QMS	
	Mean	SD	Mean	SD
Tube 1	79	17	72	10
Tube 2	35	13	35	10
Tube 3	80	13	80	10
Tube 4	45	13	51	17
Tube 5	81	11	84	7
Tube 6	40	19	45	11

3. Conclusions

The analytical method validated in this study to the analysis of ¹²⁹I in decommissioned waste could be used to quickly classify and treat large capacity radioactive waste with a simple process. In addition, it is possible to extract volatile radionuclides at the same time through a single combustion process. For ³H and ¹²⁹I collected in the same solution, the concentration measurement is different using LSC and ICP-QMS, respectively. Since they do not affect mutually measured values, accurate quantitative analysis of ¹²⁹I is possible. In actual sample analysis, 0.01M HNO₃ and Carbosorb® E+ can be used as trap solutions. ³H and ¹²⁹I can be collected in 0.01M HNO₃ and ¹⁴C in Carbosorb® E+.

Therefore, analysis of ¹²⁹I using a combustion furnace is expected to not only have excellent applicability as an efficient analysis process at the decommissioning site, but also be utilized in daily environmental radioactivity evaluation.

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