

The evaluation of the influence of matrix in the analysis of ^{63}Ni recovery ratio at ICP-OES measurement

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1. Introduction

^{63}Ni is one of the radionuclides whose concentrations need to be identified by Article 8(Identification of nuclides) of the Regulations on the Delivery of Intermediate Level and Low-Level Radioactive Waste (Nuclear Safety and Security Commission Notification No. 2021-26). ^{63}Ni has low beta energy ($E_{\text{max}}=66.95$ keV), so chemical separation and purification procedure from other nuclides or impurities is essential to avoid interference in radioactivity measurements using liquid scintillation counter. After many experiments were carried out, we found that the chemical recovery showed a tendency to be overestimated even though Ni purification was the last procedure in sequential separation from one sample. Among the 120 cases, up to the top 44.8%, the chemical recovery ratio was 100~110%, and up to the top 72.8%, the chemical recovery ratio was over 95%. In this study, the influence of matrix was evaluated in the analysis of ^{63}Ni recovery ratio at ICP-OES.

2. Methods and Results

2.1 Sample preparation

3 different types of diluted solution were prepared for Ni calibration curve of ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy). The range of concentration was 0~5 ppm (0 ppm, 0.5 ppm, 1.0 ppm, 2.5 ppm, 5.0 ppm).

To make same condition with previous sequential separation procedure on concrete samples, 2 mL of 1000 $\mu\text{g/mL}$ Ni standard solution was completely dried at 80 °C and dissolved in 5 mL of 3 M HNO_3 . 10 test samples about 4 ppm were diluted by 2% HNO_3 and other 10 test samples about 4 ppm were diluted by De-ionized water.

Table 1: diluted solution for Ni calibration curve

	Diluted solution	Concentration
STD1	2% HNO_3	0~5ppm
STD2	3 M HNO_3 : 2% HNO_3 =1:100	
STD3	0.03 M HNO_3	

2.2 Reagents and equipment

1000 $\mu\text{g/mL}$ Ni standard solution was from AccuStandard[®]. 70% Nitric acid (ACS reagent grade) was purchased from Sigma-Aldrich. Ni resin which has particle size of 100-15 μm (NI-B50-A) was purchased from Eichrom. ICP-OES was SPECTRO-BLUE from SPECTRO. Automated radionuclide separation system made in house was used at radionuclide separation.



Fig.1. ICP-OES (SPECTRO BLUE)-left, Automated radionuclide separation system-right

2.3 Ni calibration curve depending on the medium

Table 2 shows the results from ICP-OES measurement of each of diluted STD1, STD2, STD3. The concentration of HNO_3 increased in the order $\text{STD1} < \text{STD3} < \text{STD2}$, but the slope of calibration curve increased $\text{STD1} < \text{STD2} < \text{STD3}$.

Table 2: Count results for calibration curve depending on the medium

	STD1		STD2		STD3	
	Conc.	cps	Conc.	cps	Conc.	cps
0.0 ppm	0.0000	3607	0.0000	4045	0.0000	4167
0.5 ppm	0.5092	97308	0.4993	100192	0.5194	107423
1.0 ppm	1.0273	186184	1.0174	191408	1.0399	202767
2.5 ppm	2.5606	462940	2.5074	475256	2.5872	509638
5.0 ppm	5.0685	936545	5.0374	958717	5.1976	1045370

2.4 Matching results with 4 ppm-test samples depending on the medium

Table 3 shows that the bias (%) between calculated concentration and measured concentration from ICP-OES of 10 test samples diluted by 2% HNO₃ and DIW. On average, the error of 2% HNO₃ was smaller than that of DIW. The combination of STD2 and ICP-OES sample diluted with 2% HNO₃ showed the smallest bias at 1.9%. And Figure 2 shows the Ni concentrations of test samples under 3 different dilution conditions and each calibration curve. The lowest bias was average 1.9% which was the combination of STD2 and 2% HNO₃ sample.

Table 3: Matching results with 4 ppm-test samples depending on the medium

	STD1		STD2		STD3	
	2 % HNO ₃	DIW	2 % HNO ₃	DIW	2 % HNO ₃	DIW
Bias (%)	6.4	10.8	0.8	0.2	12.8	11.9
	6.6	10.4	0.8	1.0	12.3	12.6
	6.3	9.2	1.3	1.4	13.4	13.4
	5.9	8.6	1.4	1.6	12.9	13.8
	6.7	7.9	1.8	2.9	13.6	14.1
	6.7	8.4	2.2	3.1	13.7	14.1
	6.8	8.1	2.2	3.2	14.0	14.3
	7.0	7.6	2.2	4.1	14.6	14.2
	7.2	7.8	3.0	5.0	14.5	14.9
	7.6	8.1	3.1	3.7	14.7	14.1
Average	6.7	8.7	1.9	2.6	13.6	13.7

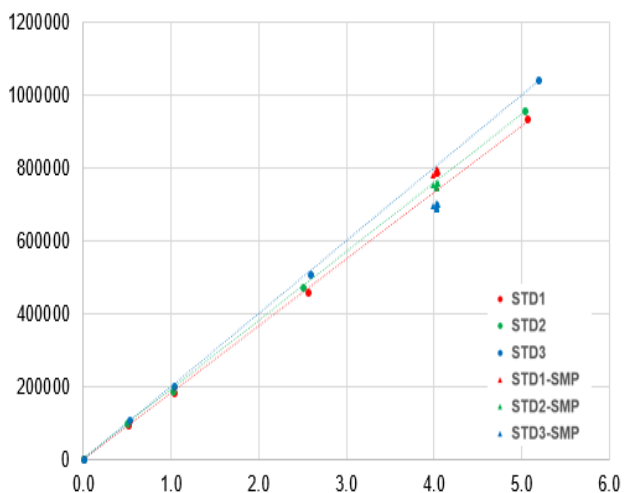


Fig. 2. Ni calibration curve depending on the medium (STD1, STD2, STD3) and matching results of 10 test samples diluted by 2% HNO₃.

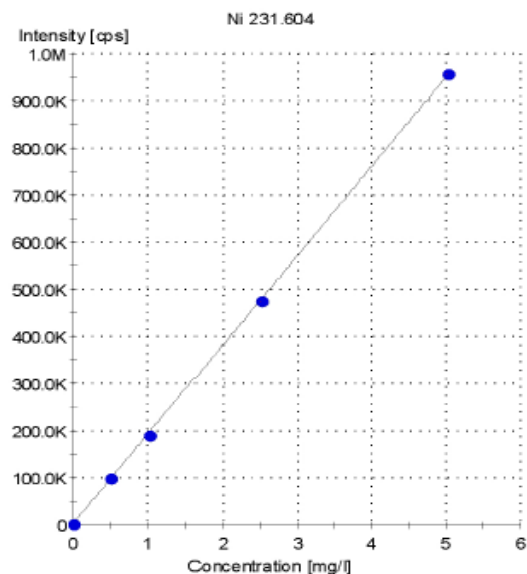


Fig. 3. Calibration curve result of STD2.

3. Conclusions

In this study, the influence of sample and standard matrix was evaluated in the analysis of ⁶³Ni recovery ratio at ICP-OES. In the calibration curve prepared with 2% HNO₃, the concentration of Ni was overestimated by 5.9~7.6%. The calibration curve produced under similar conditions to the ICP-OES sample for final concentration of the Ni purification procedure had the lowest bias at about 0.8~3.1%, and it was confirmed that the chemical recovery rate can be more appropriately evaluated in Ni analysis.

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