A study on ^{55}Fe, ^{63}Ni separation technique using automated radionuclide extraction system

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1. Introduction

Iron-55 and ^{59}Ni, ^{63}Ni are 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). Due to limitations of the measurement of ^{55}Fe, ^{59,63}Ni using radiometric detector, the chemical separation and purification of the radionuclide must be carried out in advance. In general, the chemical separation for radionuclides is carried out by the gravimetric method. This gravimetric method is time-consuming and labor-intensive work. So, the automated radionuclide separation system has recently received attention, and it is available in the market with the name Q-ARE® (B&B, Korea).

In this study, we presented the application of Q-ARE to simultaneously separate Fe and Ni from the sample based on ion exchange and extraction chromatography. We prepared the method standard sample containing Fe and/or Ni ion and followed Q-ARE's separation protocol to purify each ion from the sample. The performance of the separation protocol using Q-ARE is evaluated as the recovery results.

2. Method and Results

Following the pretreatment, the sample is liquified and diluted to 9 M HCl. This study begins with this solution, which is the mixture of Fe and Ni in 9 M HCl. The separation of Fe and Ni in the sample follows two steps using Q-ARE: 1) Separation from the sample using anion exchange resin (AEX), 2) Individual purification of Fe and Ni using proper resin, which was simultaneously carried out by Q-ARE. The recovery of Fe and Ni following with the protocol was estimated by the measurements of stable Fe and Ni ions using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy).

2.1 Sample preparation

For the first step using AEX, the mixture sample of Fe and Ni was prepared with 15 mg of Fe, 1 mg of Co, and 2 mg of Ni in 10 mL of 9 M HCl. For the second step, in which Fe or Ni is individually separated, 2 mg of Fe was added in 10 mL of 9 M HCl and followed Fe separation protocol. For Ni, 2 mg of Ni was added in 12 mL of 0.2 M HCl-0.1 M Ammonium citrate solution, and then its pH was adjusted to 10 by NH_4OH.

2.2 Reagents and equipment

AG® 1-X4 Resin (100-200 mesh, Cl^-, Biorad) was used as anion exchange resin. Ni resin (100-150μm, Eichrom) and pre-filter resin (100-150μm, Eichrom) coated with DIBK (diisobutyl ketone) were utilized for Ni and Fe purification, respectively.

Q-ARE is designed to operate a pre-programmed separation protocol for the radionuclide by adjusting volume and flow rate for sample or reagents. It can handle eight samples at the same time in single-mode and four samples in tandem mode. Mainly, two different separation protocols can be applied simultaneously. The detailed functional information of Q-ARE is referred from another study (Kim et al. 2020).

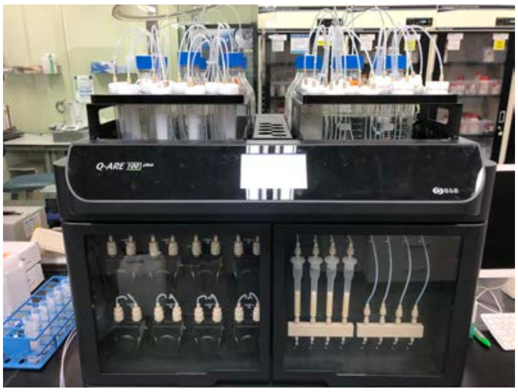

Fig. 1. Automated radionuclide extraction system (Q-ARE)

2.3 Separation of Fe, Ni using AEX

The separation protocol for Fe and Ni using AEX is presented in Table 1. We put the four mixture samples of Fe and Ni in the left section of Q-ARE having AEX and followed the protocol.

The mixture samples of Fe and Ni were passed through AEX and were collected in E2 (Elution #2). Because Ni was not retained on AEX, this solution in E2 contained Ni not Fe. Fe was strongly taken by AEX therefore the rinsing process with 9 M HCl is designed to remove Co, which interferes with the radiometric measurement of ^{55}Fe. Finally, Fe was eluted from AEX using DIW (deionzed-water). We analyzed Fe and Ni in the final elution solution (E1) and E2 solution, respectively by ICP-OES (Inductively coupled plasma-Optical emission spectroscopy). The recovery of Fe and Ni was ranged from 94 to 100%.

Table 1: Separation protocol for Fe and Ni using AEX

Process Name	Reagent	Mounted Position	Flow Rate (mL/min)	Total volume (mL)
Conditioning	9M HCl	W*	2	20
Loading	Sample	W	2	11
Loading	Sample	E2*	2	25
Rinsing	9M HCl	E2	2	10
Loading	Sample	E2	2	14
Rinsing	6M HCl	W	2	11
Elution	DIW	E1***	2	30 (LV***: 11mL)

*W: Waste, **E: Elution, ***LV: Lower volume

2.4 Separation of Fe

Diisobutyl ketone (DIBK) can uptake Fe as a form of $HFeCl_4$ at 9M HCl. Prefilter/DIBK, a homemade resin coated pre-filter (Eichrom, USA) with DIBK (ratio 2:1), was prepared every day.

We put prefilter/DIBK on the left section of Q-ARE and followed the protocol in Table 2. The rinsing process with 9 M HCl can remove all interferences for the measurement of ^{55}Fe by a liquid scintillation counter. Fe in the elution solution was analyzed by ICP-OES, and the recovery of was from 99.2%~101.3%.

Table 2: Fe separation protocol using Fe+DIBK/pre-filter

Process Name	Reagent	Mounted Position		Flow Rate (mL/min)	Total volume (mL)
Conditioning	9M HCl	W		2	20
Loading	Sample	W		1	25
Rinsing	9M HCl	W		2	12
Elution	DIW	E1		2	25 (LV 11mL)

2.5 Separation of Ni

Nickel reacts with dimethylglyoxime (DMG) and forms a a red raspberry colored $Ni(DMG)_{2(S)}$ precipitate by chelation in alkaline ammonia medium over pH 8. This reaction selectively occurs for Ni.

$$Ni^{2+}_{(aq)}+2C_4H_8N_2O_{2(aq)}\rightarrow Ni(C_4H_7N_2O_2)_{2(s)}+2H^+_{(aq)}$$

And the strong bond of Ni-DMG complex is broken at acidic condition. The protocol of Ni separation is descrbied in Table 3. The recovery of Ni using Ni resin resin was from 80.6%~90.1%.

Table 3: Ni separtion protocol using Ni resin

Process Name	Reagent	Mounted Position	Flow Rate (mL/min)	Total volume (mL)
Conditioning	0.2M AMC	W	2	20
Loading	Sample	W	1	25
Rinsing	0.2M AMC	W	2	12
Elution	3M HNO_3	E1	2	25 (LV 11mL)

3. Conclusion

In this study, we presented the separation of Fe and Ni using AEX, prefilter/DIBK and Ni resin, respectively, by the automated radionuclides separation system. Compared with the manual approach, gravimetric method (about 4 h~5 h for 4 samples), Q-ARE shows faster results (under 2 h for 4 samples) and is a more comfortable way for the analyst because the user does not add the reagent every time according to the protocol. Regarding the recovery of ions of interest, Q-ARE is comparable with the conventional method. The distinct difference between the gravimetric method and the automated separation technique is that the automatic separation way is less time-consuming and less labor-work.

REFERENCES

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